## <u>İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY</u>

## KINETIC INVESTIGATIONS IN HOMOPOLYMERIZATION AND COPOLYMERIZATION REACTIONS IN AQUEOUS MEDIA

Ph.D. Thesis by Ahmet PARIL, M.Sc.

Department :Polymer Science and TechnologyProgramme:Polymer Science and Technology

**JUNE 2008** 

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**JUNE 2008** 

# <u>İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ</u>

### SULU ORTAMDA GERÇEKLEŞTİRİLEN HOMOPOLİMERİZASYON VE KOPOLİMERİZASYON REAKSİYONLARINDA KİNETİK İNCELEMELER

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## LIST of ABREVIATIONS

ACOMP	: Automatic Continuous Online Monitoring of Polymerization
ACM	: Automatic Continuous Mixing
GPC	: Gel Permeation Chromotography
UV	: Ultraviolet Spectrophotometer
RI	: Refractive Index
LS	: Light Scattering
VB	: 4-Vinylbenzene Sulfonic Acid Sodium Salt
Aam	: Acrylamide
Aac	: Acrylic Acid
PVB	: Poly(4-Vinylbenzene Sulfonic Acid Sodyum Salt)
PAam	: Poly (Acrylamide)
PAac	: Poly (Acrylic Acid)
ACV	: 4,4'-Azobis (4-Cyanovaleric Acid)
V50	: 2,2'-Azobis (2-Amidinopropane) Dihydrochloride
NaCI	: Sodyum Chloride
NaOH	: Sodium Hydroxide
DADMAC	: Diallyldimethyl Ammonium Chloride
PLL	: Poly-L-Lysine
EVM	: Error in Variables
MRR	: Monomer Reactivity Ratio
ML	: Mayo-Lewis Equation
IS	: Ionic Strength

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## LIST of SYMBOLS

- $\xi_{M}$  : Lineer charge density parameter (Manning parameter)
- $l_B$  : Bjerrum lenth
- *b* : Average charge spacing in the fully streched configuration
- *L* : Contour length
- *N* : Number of charged groups on te polyion
- *e* : Elementary charge
- *f* : Initiator efficiency factor
- *n* : Number of moles of radicals generated per mole of initiator
- *t* : Time
- *I* : Initiator
- **R** : Radical
- *M* : Monomer
- [M] : Monomer concentration
- $[M]_{\theta}$  : Initial monomer concentration
- $k_i$  : Initiation rate constant
- $k_p$  : Propaation rate constant
- $k_{tc}$  : Rate constant for termination by combination
- $k_{td}$  : Rate constant for termination by disproportionation
- $k_t$  : Termination rate constant
- $t_{1/2}$  : Half life of the initiation
- $R_d$  : Rate of initiation decomposition
- $R_i$  : Rate of initiation
- $R_p$  : Over all rate of polymerization
- $R_t$  : Rate of termination
- $\pi$  : Degree of conversion
- *v* : Kinetic chain length
- $\overline{P}_n$  : Number average degree of polymerization
- $\overline{P}_{w}$  : Weight average degree of polymerization

 $\overline{M}_n$  : Number average molecular weight

 $\overline{M}_{w}$ : Weight average molecular weight

- $\overline{M}_z$  : Z-average molecular weight
- $x_i$  : Mole fraction of molecules with *i* monomer units in the chain
- $n_i$  : Number of molecules with *i* monomer units in the chain
- $w_i$ : Weight fraction of macromolecules with *i* degree of polymerization
- $k_{tr}$  : Chain transfer rate constant
- $R_{tr}$  : Rate of chain transfer
- *C* : Cain transfer constant

: Propagation rate constant for addition of monomer  $M_1$  to radikal  $M_1^{\bullet}$ 

 $k_{12}$ : Propagation rate constant for addition of monomer  $M_1$  to radikal  $M_2^{\bullet}$ 

<i>k</i> <sub>21</sub>	: Propagation rate constant for addition of monomer $M_2$ to radikal $M_I^{\bullet}$
<b>k</b> 22	: Propagation rate constant for addition of monomer $M_2$ to radikal $M_2$
d[M_1]	: Amount of monomer $M_i$ converted into polymer during $dt$
$d[M_2]$	: Amount of monomer $M_2$ converted into polymer during $dt$
<b>r</b> <sub>1</sub>	: Reactivity ratio of monomer $M_1$
$r_2$	: Reactivity ratio of monomer $M_2$
$f_1$	: Mole fraction of monomer $M_1$ in the monomer mixture
$f_2$	: Mole fraction of monomer $M_2$ in the monomer mixture
$F_1$	: Mole fraction of unit $M_1$ in the copolymer formed insataneously
$F_2$	: Mole fraction of unit $M_2$ in the copolymer formed insataneously
$\eta - \zeta$	: Kelen – Tüdös parameters
F - G	: Fineman-Ross parameters
α IM-1-	: Geometric average of the highest and lowest F parameters : Theoretical concentration of monomore M.
$\begin{bmatrix} IVI \end{bmatrix}$ the	• Measure of the distance of $[M_1]_{i}$ from the experimental $[M_1]_{i}$
v v	: Composition deviation in Stockmaver equation
ф,	: Molar fraction of $M_1$ monomer units in an individual chain
Bcom	: Fraction of chains terminating by combination
l	: Length of a chain
<i>l</i> *	: Number average length of live radical chains
m <sub>mon</sub>	: Molecular weight of monomer
$I_r$	: Rayleigh Ratio
$I_{\theta}$	: Intensity of incedent light
Iθ	: Intensity of the scattering light at angle $\theta$
r V	: Distance of the detector from the scatterin sample
K	: Optical constant
C No	• Solvent index of refraction
2	• Vacuum wavelength of the incident light
$N_{\Lambda}$	: Avogadro's number
$\frac{\delta n}{\delta c}$	: Differential refractive index
$A_2$	: Second virial coefficient
$q^{-}$	: Scattering wave vector
$\eta_r$	: Relative viscosity
$\eta_{sp}$	: Specific viscosity
[ŋ]	: Intrinsic viscosity
k	: Huggins constant
K - a	: Mark and Houwink paramters
$V_{RI}$	: Refractive index voltage
	: Calibration factor
$\partial V_{UV} \partial C$ T	• Transmittance
	: Cell pat legth
N(a)	: Normalization factor
$V_n(q_r)$	: Scattering voltages from the normalization solution
$V_s(q_r)$	: Scattering voltages from the solvent
$m{F}$	: Geometrical optical correction factor
Ia	: Absolute Rayleih ratio of reference scatterer

x: Conversion (Conv) $r_{VB}$ : Reactivity ratio of VB $r_{Aam}$ : Reactivity ratio of Aam $r_{Aac}$ : Reactivity ratio of Aac $M_{w,inst}$ : Insantaneous molecular weight

### KINETIC INVESTIGATIONS IN HOMOPOLYMERIZATION AND COPOLYMERIZATION REACTIONS IN AQUEOUS MEDIA

### SUMMARY

The aim in the polymer chemistry is to produce materials which has specific properties. The reactions that two different monomers undergo polymerization to give long chains are called copolymerization and the product formed is called copolymer. In this work, the kinetics of free radical homopolymerization and copolymerization reactions carried out in aqueous media were investigated. All reactions were monitored online by the Automatic Continuous Online Monitoring of Polymerization (ACOMP) system. This system supplies thousands of data points during the reaction. This application involves automatic, continuous removing a small amount of reactor solution by a pump and mixing the reactor solution at high pressure with a much larger volume of a pure solvent drawn from a solvent reservoir by another similar pump to produce a dilute reactor solution, on which, light scattering, viscosimetric, Refractive Index (RI) and Ultraviolet Spectrophotometer (UV) measurements were made. During free radical polymerization, the vinyl bond in monomer disappears, so that throughout the polymerization, the absorbance of the vinyl bond decreases. The decrease of UV absorbance is measured at the selected wavelengths at UV detector in ACOMP, which enables monomer and the polymer to be found online. In this work, the amount of monomer in the concentrations of the two comonomers in their monomeric form, as well as their concentrations incorporated into polymer, were computed from the raw UV data obtained from ACOMP by using appropriate equations.

4-Vinylbenzene sulfonic acid sodium salt (VB) – (Acrylamide) homopolymerization and copolymerization reactions with various feed ratios were performed in 0.1 M NaCl and in water for the first part of this experimental work. For the reactions performed in 0.1 M NaCl, it was seen that Aam homopolymerization was faster than VB and both homopolymerization rates were higher than copolymerization rates at any combination. In 25%VB-75% Aam and 10%VB-90% Aam reactions, Aam exhibited two phase behaviour. Its polymerization rate increases when the VB is exhausted. That is, after VB was exhausted, the remaining Aam homopolymerized rapidly. This phenomena was revealed in the light scattering raw voltages, which were seen to jump after the VB conversion phase was complete and increased during the second phase of PAam homopolymer production, as well. As known, the composition and properties of the resulting copolymer and copolymerization rate depend on the reactivity ratios of constituent monomers. The monomers take part in the polymer chain according to their reactivity ratios. Therefore, monomer reactivity ratios are very important in the copolymer production. To obtain the reactivity ratios, the data are fitted to a numerical solution of the copolymerization equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right)$$

For these monomer couple, monomer reactivity ratios (MRR) were calculated by the the Error in Variable (EVM) method, which was developed for online monitoring technique. The reactivity ratios,  $r_{Aam}=0.085\pm0.020$ ,  $r_{VB}=2.0\pm0.33$ , were found for VB-Aam copolymerization in 0.1 M NaCl. The terminal model was shown to describe the polymer composition very well. The same experimental procedure was applied to VB-Aam copolymerization carried out at 60<sup>o</sup>C in water. Unlike the reactions performed in 0.1 M NaCl solution, in this case, it was seen that VB completely depleted, further reaction was Aam homopolymerization only in the reactions with 1.5% VB, 5% VB and 10% VB. In addition, during the copolymerizations in water with from 5 to 50% VB, VB fraction in monomer mixture versus conversion each curve went through a corner at 10-30 % conversion depending on the VB content. This corner showed that the behaviour of the reaction changes ubruptly at this point. In the first phase of the reactions, the composition was seen to be almost constant. This sudden change in the reaction kinetics and the monomer reactivities was explained as probably due to reaching the c\* overlap concentration. We have obtained indirect evidence that, in water, the maximally swollen copolymer has the composition 15% VB - 85% Aam in our experimental conditions. For this system, electrostatic interactions at higher (>15% VB) and lower (<15% VB) ionic strength (IS) and the effects of ionic strength to the corner observed in the reactions were discussed, as well. It was found that higher VB fractions reduced the Debye screening length because of higher ionic strength and resulted in reduced swelling. At very low VB concentration (5%) the electrostatic interaction was less and corner occured later. As a result maximum hydrodynamic volume was obtained at 15% VB fraction in our experimental conditions. Monomer reactivity ratios (MRR) were calculated by EVM method in this system, as well. Since the reactions in water gave two distinguishable regions and the reaction part before and after the corner were evaluated separately. Therefore, The reactivity ratios were found as  $r_{Aam}=0.34\pm0.07$ ,  $r_{VB}=0.40\pm0.21$  and  $r_{Aam}=0.2\pm0.04$ ,  $r_{VB}=9.0\pm0.8$  for before and after the corner, respectively.

In the second part of this work, Acrylic acid - Acrylamide copolymerization was monitored by ACOMP and kinetic investigations were performed for this system, which is a copolyelectrolyte system. Two sets of reactions were conducted at pH 5 and pH 2. The results of the experiments performed at pH 5 showed that the reaction was not 1<sup>st</sup> order in monomer. Besides that, when a combination of cage effect and initiator concentration decrease and, in the copolymerization reactions composition drift was involved, it is seen that the equations for 1.25<sup>th</sup> order and 1.5<sup>th</sup> order kinetics both fitted the data at pH 5. In all reactions at pH 5, the Aam was depleted more rapidly regardless of the initial composition. This indicated that it was entering the copolymer at a rate greater than its fraction in the feed mixture. The results indicated that the first order kinetics failed at pH 2 as well. On the other hand both 1.25<sup>th</sup> and 1.5<sup>th</sup> order kinetics satisfactorily fitted the data. Molecular weight analysis exhibited that higher Aam content resulted in higher molecular weight. Also, the results revealed that both the molecular weight and the reaction rate was higher at pH 2 than the pH 5 for the reaction carried out at the same feed composition The reactivity ratios were found as  $r_{Aam}$ =1.88±0.17 and  $r_{Aac}$ =0.80±0.07 at pH 5 and  $r_{Aam}$ =0.16±0.04 and  $r_{Aac}=0.88\pm0.08$  at pH 2 by EVM. The reactivity calculations showed that at pH 5, acrylamide was the more active monomer and the reverse was true at pH 2. At pH 5 Aac units in the polymer chain are in sodium acrylate form due to the Na<sup>+</sup> ions screening the charges and can be considered as uncharged. At pH 2 Aac is neutral because of the very low ionization degree. This is the similarity of Aac at pH 2 and pH 5 and this is why Aac reactivity ratios at these pH's resulted in similar values. On the other hand, Aam is neutral and active monomer at pH 5. however Aam has very low reactivity as a consequence of its protonation at pH 2. Also, it was found that the electrostatic repulsion between the macro radical and the charged monomer caused the low reactivity of the Aam at pH 2. In addition, Stockmayer bivariate distribution was discussed for the experiments with 70% Aam at pH 5 and 70% Aac at pH 2.

In the last part of this work, it was examined the control of composition through pH and ionic strength during copolyelectrolyte production. For this purpose, three sets of reactions were performed at pH 3.6, which was chosen through the previous studies at pH 5 and pH 2 indicated as a candidate for the crossover point, which no composition drift was expected. The first set of experiments was performed at total monomer concentration of 0.47 mol/L. In this set concentrations of the Aac and the pH regulator (NaOH) depended on the Aac fraction in the feed mixture. The other two sets were carried out at two different constant Aac and NaOH concentrations but varying total monomer concentrations (whereas Aac and NaOH concentrations used at the set 2 are 0.1414 mol/L and 0.0275 mol/L, respectively, Aac and NaOH concentrations for the set 3 are 0.3290 mol/L and 0.0679 mol/L). Copolymer conversions, molecular weights and composition distributions were measured through ACOMP and sequence length distribution and Stockmayer bivariate distribution was discussed. The copolymerization data were analyzed by EVM and the reactivity ratios were found as  $r_{Aam}=1.66\pm0.14$  and  $r_{Aac}=2.43\pm0.19$  for set 1,  $r_{Aam}=1.66\pm0.08$  and  $r_{Aac}=2.40\pm0.17$  for set 2 and  $r_{Aam}=2.02\pm0.15$  and  $r_{Aac}=2.55\pm0.13$ for set 3. The results also clarified the effect of ionic strength, which is not surprising as the IS of the reaction medium determines to what extent the charge on the macro radical is screened. At pH 3.6 no composition drift was obtained at % 30 acrylic acid, %70 acrylamide copolymer up to % 80 conversion. It was shown that it was possible to obtained polylectrolytic copolymers having desired characteristics by choosing the pH and the IS and performing all experiments at constant ionic strength and pH was the proper experimental protocol to obtain the monomer reactivity ratios.

## SULU ORTAMDA GERÇEKLEŞTİRİLEN HOMOPOLİMERİZASYON VE KOPOLİMERİZASYON REAKSİYONLARINDA KİNETİK İNCELEMELER

## ÖZET

Polimer kimyasında amaç istenilen özelliklere sahip malzeme üretimidir. İki farklı monomerin beraberce uzun zincirler vermek üzere polimerleşmesi reaksiyonuna kopolimerizasyon ve oluşan ürüne de kopolimer adı verilir. Bu çalışmada sulu ortamda gerçekleştirilen serbest radikal homopolimerizasyon ve kopolimerizasyon reaksiyonlarının kinetik incelemeleri yapılmıştır. Tüm deneyler ACOMP (Automatic Continuous Online Monitoring of Polymerization- Polimerizasyon Reaksiyonlarının Bilgisavarla Sürekli İzlenmesi) sistemi ile reaksiyon süresince izlenmiştir. Bu sistem reaksiyon süresince binlerce verinin alınmasına imkan veren bir sistemdir. Bu uygulama bir pompa vasıtasıyla reaktörden çekilen küçük miktardaki reaksiyon çözeltisinin başka bir pompa vasıtasıyla çekilen çözücü ile yüksek basınçlı karıştırma ünitesinde karıştırılarak seyreltilmesi temeline dayanır. Bu şekilde istenilen konsantrasyona getirilen reaksiyon çözeltisi birbirlerine seri bağlı olan sırasıyla ışık saçılması dedektörü, vizkozimetre dedektörü, kırılma indisi dedektörü (RI) ve Ultraviyole Spektrofotometre (UV) dedektöründen geçer ve her bir dedektörden ölçümler an be an alınır. Serbest radikal polimerizasyonu esnasında monomerde varolan vinil bandı açılır. Bu durum polimerizasyon boyunca vinil bandı absorbansının azalmasına neden olur. UV absorbansındaki azalma daha önceden belirlenmiş dalga boylarında ölçülür ve bu sayede monomer ve polimerdeki miktarı reaksiyon boyunca sürekli izlenmiş olur. Yaptığımız çalışmada reaksiyon süresince reaktördeki monomerlerin konsantrasyonları ve polimere giren miktarları UV dedektöründen elde edilen verilerin uygun denklemeler vasıtasıyla değerlendirilmesi sonucu elde edilmistir.

Calışmanın ilk aşamasında 4-Vinilbenzen sülfonik asit sodyum tuzu (VB) -Akrilamit (Aam) homopolimerizasyon ve kopolimerizasyon reaksiyonları çözücü olarak 0.1 M NaCl ve su kullanılarak yapıldı. Tuzlu çözelti içinde yapılan reaksiyonlarda Aam homopolimerizasyonunun VB den daha hızlı olduğu ve her iki homopolimerizasyon hızının kopolimerizasyon hızlarından daha yüksek olduğu görüldü. 25%VB-75% Aam ve 10%VB-90% Aam reaksiyonlarında Akrilamidin iki farklı davranış sergilediği ve VB nin tamamen tükenmesinin ardından Akrilamidin polimerizasyon hızında artış olduğu saptandı. Böylece reaksiyonun ilk aşamasında kopolimer üretilirken VB nin tükenmesiyle akrilamidin hızlı bir şekilde homopolimerleşmeye uğradığı görüldü. Bu durum ışık saçılması sonuçlarından da açık bir şekilde tespit edidi. Işık saçılması sinyalleri VB dönüşüm aşaması tamamlandıktan sonra belirgin sıcrama gösterirken poliakrilamidin (PAam) üretildiği ikinci aşama boyunca artış gösterdi. Bilindiği gibi kopolimerleşme reaksiyonlarında elde edilecek ürünün bileşimi, özellikleri ve monomerlerin tepkimeye ne hızla girecekleri, kopolimerde yeralan monomerlerin reaktiflik oranlarına bağlıdır. Reaksiyona giren monomerler zincirde, reaksiyon hız sabitlerinin oranı olan

reaktiflik oranları uyarınca dağılırlar. Oluşan kopolimerin fiziksel özellikleri yapısında bulunan monomerlerin özelliklerini reaktiflik oranları uyarınca paylaşır. Bu nedenle kopolimer üretiminde monomer reaktiflik oranları en önemli parametrelerdir. Elde edilen verilerin kopolimer denkleminin,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right)$$

çözümlerinde değerlendirilmesi ile reaktiflik oranları bulunur. Çalışmamızda monomer reaktiflik oranları (MRR-Monomer Reaktivity Ratios) sürekli izleme metodu için hazırlanmış olan değişkenlerdeki hata (EVM-Error in Variables) metodu ile hesaplandı. 0.1 M NaCl çözeltisi içinde yapılan VB-Aam kopolimerizasyonu için monomer reaktiflik oranları  $r_{Aam}=0.085\pm0.020$ ,  $r_{VB}=2.0\pm0.33$  olarak bulundu. Terminal modelin polimer bileşimini tatmin edici bir şekilde tanımladığı ortaya koyuldu. Aynı deneysel işlem 60°C de reaktörde çözücü olarak su kullanılan VB-Aam kopolimerizasyon sistemi için de uygulandı. Tuzda gerçekleştirilen deneylerden farklı olarak suda gerçekleştirlen %1.5 VB , %5 VB ve %10 VB bileşiminde yürütülen deneylerde VB nin tamamıyla tükendiği ve bu aşamdan sonra akrilamidin homopolimerleştiği görüldü. Ayrıca, %5-%50 VB aralığında gerçekleştirilen deneyler esnasında, monomer karışımındaki VB fraksiyonunun VB içeriğine bağlı olarak %10-30 monomer dönüsümü aralığında bir dönüm noktasından gectiği görüldü. Reaksiyon davranışının bu kösede belirgin bir sekilde değiştiği gözlendi. Köşeden önce yani reaksiyonların ilk aşamalarında bileşimin hemen hemen aynı olduğu ve reaksiyon kinetiği ve monomer reaktifliklerindeki bu ani değişimin kritik konsantrayona ulasılmasından kaynaklandığı sonucuna varıldı. Aynı zamanda yaptığımız çalışmada suda gerçekleştirilen bu sistem için daha yüksek (>%15 VB) ve daha düsük (<%15 VB) iyonik siddet varlığında ortaya cıkan elektrostatik etkileşimler ve iyonik şiddetin reaksiyonlarda gözlenen köşede etkisi tartışıldı. Yüksek VB bileşimlerinde iyonik şiddetin yüksek olması nedeni ile Debye perdeleme uzunluğunun ve bobin hacminin azaldığı sonucuna varıldı. Çok düşük VB fraksiyonlarında ise elektrostatik etkileşimler daha az olduğundan köşe daha geç görüldü. Monomer reaktiflik oranları EVM yöntemi ile hesaplandı. Suda gerçekleştirlen kopolimerizasyon reaksiyonları iki farklı bölgeye sahip olduklarından reaksiyonlar köşeden önce ve köşeden sonra olmak üzere iki kısımda incelendi. Reaktiflik oranları da köşeden önce  $r_{Aam}=0.34\pm0.07$ ,  $r_{VB}=0.40\pm0.21$  ve köşeden sonra  $r_{Aam}=0.2\pm0.04, r_{VB}=9.0\pm0.8$  olarak bulundu.

Çalışmamızın ikinci bölümünde Akrilamit (Aam) - Akrilik asit (Aac) kopolimerizasyonu ACOMP ile sürekli izlendi ve bu sistem için kinetik incelemeler gerçekleştirildi. Bu çalışmada pH 5 ve pH 2 de olmak iki set reaksiyon yapıldı. pH 5 de gerçekleştirilen incelemeler sonucunda reaksiyonların monomere göre birinci mertebe kinetiğe uymadığı görüldü. Kafes etkisi, reaksiyon boyunca başlatıcı konsantrasyonundaki azalma ve kopolimerizasyon reaksiyonlarında gözlenen bileşim kayması hesaba katıldığında ise elde edilen verilerin 1.25 and 1.50. dereceye uyduğu anlaşıldı. pH 5 te gerçekleştirilen tüm reaksiyonlarda başlangıç bileşiminden bağımsız olarak Aam'in daha hızlı tükendiği belirlendi. Yapılan kinetik çalışmalar, birinci mertebe kinetiğin pH 2 de yapılan reaksiyonlar için uygun olmadığını fakat elde edilen verilerin 1.25 and 1.50. derece kinetiğine uyduğunu gösterdi. Molekül ağırlığı analizi, artan Aam bileşimi elde edilen kopolimerlerin molekül ağırlığının arttığını ortaya koydu. pH 2 ve pH 5 te gerçekleştirilmiş ve aynı başlangıç bileşimine sahip kopolimerizasyon reaksiyonları karşılaştırıldığında pH 2 de molekül ağırlığı ve

reaksiyon hızının daha yüksek olduğu belirlendi. EVM yöntemi ile pH 5 te  $r_{Aam}$ =1.88±0.17  $r_{Aac}$ =0.80±0.07 ve pH 2 de  $r_{Aam}$ =0.16±0.04  $r_{Aac}$ =0.88±0.08 olarak hesaplandı. Reaktiflik oranları Aam'in pH 5 te aktif olduğunu Aac'in ise pH 2 de aktif rol oynadığını gözler önüne serdi. pH 2 de Aac iyonlaşma derecesinin çok düşük olması nedeniyle nötral davranmaktadır. pH 5 te gerçekleştirilen reaksiyonlarda ise polimer zincirinde yeralan Aac birimlerinin sodyum akrilat formunda olması ve dolayısıyla Aac'in yüklerinin karşıt Na<sup>+</sup> iyonları tarafından perdelenmesinden dolayı Aac yüksüz olarak kabul edilebilir. Bunun sonucunda Aac'nin pH 5 ve pH 2 de benzer reaktiflik oranlarına sahip olduğu görüldü. Diğer taraftan, Aam'in pH 5 te nötral olması, aktif monomer olmasını sağlarken, pH 2 de protonlanması ve dolayısıyla yüklü monomer ile makroradikal arasında oluşan elektrostatik itme kuvvetleri nedeniyle reaktifliğinin azaldığı görüldü. Aynı zamanda bu çalışmada %70 Aam (pH 5) ve %70 Aac (pH 2) reaksiyonları için Stockmayer ikili dağılımı incelendi.

Çalışmamızın son kısmında ise, kopolielektrolit (polielekrolitik kopolimer) üretimi esnasında pH ve iyonik siddet ile bilesimin kontrolü incelendi. Bu amacla üc set reaksiyon yapıldı. Daha önce pH 5 ve pH 2 de yapılan çalışmalar ışığında bileşimin kaymadığı bir noktanın yakalanma ihtimalinin olması nedeni ile yapılan deneylerde ortamın pH 1 3.6 olarak ayarlandı. Birinci sette toplam monomer konsantrasyonu 0.47 mol/L olarak alındı. Bu setteki reaksiyonlarda Aac ve pH ayarlamak için kullanılan NaOH konsantrasyonları başlangıç bileşimindeki Aac fraksiyonuna bağlı olarak değişmektedir. Diğer iki set reaksiyonda ise sabit Aac ve NaOH konsantrasyonu kullanılırken toplam monomer konsantrasyonu setlerdeki her bir reaksiyon için farklıdır (2. Set için Aac ve NaOH konsantrasyonları sırası ile 0.1414 mol/L ve 0.0275 mol/L dir. 3. Set için ise Aac ve NaOH konsantrasyonları sırası ile 0.3290 mol/L ve 0.0679 mol/L olarak kullanılmıştır). Bu çalışmada, kopolimer dönüşümü, molekül ağırlıkları, ve komposizyon dağılımı ACOMP vasıtasıyla ölçüldü. Sekans uzunluk dağılımı ve Stocmayer iki dağılım grafikleri tartışıldı. Her üç set içinde kopolimerizasyon verisi EVM yöntemi ile değerlendirildi ve reaktiflik oranları birinci set için  $r_{Aam}=1.66\pm0.14$  ve  $r_{Aac}=2.43\pm0.19$ , ikinci set için  $r_{Aam}=1.66\pm0.08$  ve  $r_{Aac}=2.40\pm0.17$ , üçüncü set için ise  $r_{Aam}=2.02\pm0.15$  ve  $r_{Aac}$ =2.55±0.13 olarak bulundu. Çalışmanın sonuçları iyonik şiddetin etkisini açık bir şekilde ortaya koymuştur. İyonik şiddet makroradikallerin üzerindeki yüklerin ne derece perdeleneceğini belirlediğinden dolayı sonuçlar şaşırtıcı değildir. pH 3.6 da yapılan deneylerde %30 Aac-%70 Aam başlangıç bileşimine sahip reaksiyonlarda komposizyon kaymasının olmadığı görüldü. Bu çalışma sayesinde istenilen özelliklere sahip kopolimer üretiminin uygun pH ve iyonik şiddetin seçilmesi ile mümkün olduğu ve aynı zamanda monomer reaktiflik oranlarının bulunması icin en iyi yolun tüm reaksiyonları sabit iyonik şiddet ve pH da yapmak olduğu sonucuna varıldı.

#### **1. INTRODUCTION**

Macromolecules having solubility in water include polymers ranging from biopolymers which are essential to life processes, to synthetic resins of many commercial uses. Water-soluble polymers come mostly from natural sources. They include polysaccharides such as starch, tree exudate gum (arabic, karaya), seed gums (guar, carob), microbial gums (xanthan) and proteins such as albumin, gelatin. Some natural polymers are modified to have water solubility, especially cellulose ethers, (e.g., methyl-, hydroxyethyl-, hydroxypopyl-, carboxymethyl-) [1].

Polymers having ionizable groups in water, are called polyelectrolytes. They may be cationic or anionic. Polymers carrying both positive and negative groups are referred to as amphoteric polymers (polyampholytes) [2,3]. Poly(acrylic acid), poly (methacrylate acid) and poly(styrene sulfonic acid) and their salts, cellulose derivatives are synthetic polyelectrolytes, DNA, and proteins are biological polyelectrolytes [4,5].

The conformations and interactions of polyelectrolytes depend on the ionic strength of the medium [6-8]. Electrolyte concentration defines the behaviour of the polyelectrolyte [9-12]. Besides that, medium pH strongly affects the behaviour of polyelectrolytes since it is responsible for the dissociation of the ionized groups on the backbone of polyelecrolyte chain [13,14].

The monomers of polyelectrolytes are usually expensive and difficult to polymerize. For this reason, polyelectrolytes are often used in the form of copolymers with cheaper and more easily obtainable nonionic copolymers. Another reason for this usage is that the polyelectrolytic effects depend on the linear charge density of the molecule, which is limited by counterion condensation [15,16]. Since the length of a monomeric unit is about 0.25 nm, it is not effective to place the charged groups closer than a Bjerrum length (0.72 nm at room temperature); approximately two uncharged group units should be placed between two charged groups. Thus, chains

of maximum hydrodynamic volume can most economically and easily obtained by copolymerization of charged and uncharged monomers, namely copolyelectrolytes.

In addition, the composition and properties of the resulting copolymer and copolymerization rate depend on the reactivity ratios of constituent monomers. The monomers take part in the polymer chain in accordance with their reactivity ratios, which makes monomer reactivity ratios very important in the copolymer production.

The aim of this work is the kinetic investigations in polymerization reactions of 4vinyl benzene sulfonic acid sodium salt (VB)-Acrylamide (Aam) and Acrylic acid (Aac) –Acrylamide systems at various conditions. VB and Aac are charged monomers and thus, the copolymers produced from this study are polyelectrolytes, called as copolyelectrolytes. This study is also the first attempt to monitor the synthesis of polyelectrolytic copolymers.

The first section of this study includes the copolymerization of 4-vinylbenzene sulfonic acid sodium salt (VB) with Acrylamide (Aam) [17]. The reactions were carried out in water and in 0.1 M NaCl solution at 60 <sup>o</sup>C. Copolymerization reactions with salt, were studied by more recent monitoring method (ACOMP) [18-20] where a large amount of data are obtained for each experiment resulting in more accurate determination of reaction parameters and allowed to be obtained continuously during the reaction. The kinetics of the system was evaluated through the data from ACOMP. Monomer reactivity ratios (MRR) were calculated by the Error in Variables (EVM) method developed for obtaining the reactivity ratios by on-line monitoring [20,21]. It was shown that the terminal model describes the evolution of the composition with conversion for salty reactions, moderately well.

The same procedure was applied to VB-Aam copolymerization carried out in water [17,22]. Composition drift was continuously monitored and it was revealed a sudden change in reaction kinetics for the set of experiments performed in water as a salient feature. The sudden change in the reaction kinetics was investigated and the maximally swollen copolymer composition was found. Monomer reactivity ratios (MRR) were calculated seperately by EVM for two distinguishable regions seen in reaction kinetics. The results obtained from ACOMP, were compared to other experimental techniques such as GPC and sequential sampling method to exhibit the reliability of ACOMP.

In the second part of the work, Acrylic acid (Aac) – Acrylamide (Aam) copolymerization was monitored by ACOMP. Two sets of reactions were conducted at pH 5 and pH 2 [14]. Reaction kinetic such as reaction order, reactivities of the monomers was discussed for both pHs. Composition drifts were determined for all experiments at pH 5 and 2. It was seen that the reactions conducted at pH 5 and pH 2 were not 1<sup>st</sup> order in monomer and a combination of cage effect and initiator concentration decrease and, in the copolymerization reactions composition drift must have been involved. Monomer reactivity ratios were found via EVM. At pH 5, acrylamide was found to be the more active monomer and at pH 2 the reverse was true. Stockmayer [23] distribution was obtained for some reactions with various Aam and Aac fraction at two pHs.

In the third part of this study, the possibility of controlling the composition of Acrylic acid-Acrylamide copolymers by controlling the pH and the ionic strength of the reaction medium was investigated. In this work, the pH of the raction medium was adjusted to 3.6, which no composition drift was expected, as a consequence of the previous studies at pH 5 and pH 2. At pH 3.6, three sets of reactions are performed. The reactions were monitored online by the ACOMP system. Copolymerization kinetics at constant total monomer concentration and at two different constant ionic monomer concentrations were compared. The data were analyzed by EVM. The effect of polyelectrolytic interactions on the reactivity ratios were discussed in detail. The pH and composition (at 30% Acrylic acid- 70% Acrylamide )where no composition drift was obtained, were defined. The impact of pH and IS on the sequence distribution of the charged and uncharged comonomeric units on the chain and the molecular weight-composition bivariate distribution were also discussed [24].

#### **2. THEORETICAL PART**

#### 2.1. Water Soluble Polymers

Water-soluble polymers have been classified as biopolymers and synthetic polymers or non-ionic polymers and polyelectrolytes i.e. polymers with charged groups. Polyelectrolytes can be anionic or cationic, or they can be polyampholytes [25,26].

Their solution properties depend on their structural characteristics. Especially, the nature of the repeating units, polymer composition, groups on polymer backbone and their locations form the basic features of polymer structure. Homopolymers can be synthesized from a single monomer to contain the same type of structural unit in their chain. There are also polymer species with more than one type structural units. They are known as copolymers and these units are placed to give random, alternating, block or graft copolymers. Biopolymers such as proteins have multiple repeating units. Water-soluble polymers may be linear or branched. Configuration, conformation, and intermolecular interactions such as hydrogen bonding and ionic affects are secondary structures in water-soluble polymers [26].

Various functional groups can provide polymers with water solubility. The degree of solubility depends on the number, location and density of these groups on the polymer backbone. The groups imparting water solubility are given in Table 2.1.

— ОН	NH II	O II	$-PO_3^{2-}M^{2+}$
-NH <sub>2</sub>	$-NH - C - NH_2$	$-NH - C - NH_2$	−NH <sub>3</sub> X <sup>●</sup>
—соон	— NHR	$-SO_3^{\bullet}M^{\bullet}$	-NR <sub>2</sub> HX
-0-	— SH	—COO <sup>®</sup> M	$-NR_3X$

**Table 2.1** Functional Groups Imparting Water Solubility [26].

Polymers like polystyrene and polyethylene dissolving in organic solvents are well known, however polymers soluble in water also represent a major business (\$6 billion/year) [25]. They are used in numerous products varying from foodstuffs to

toiletries. Their applications include aqueous liquid separation, resource recovery, water treatment [27] and construction industry [28]. Drug reduction agents, flocculants, thickeners, and friction reduction agents are other specific examples[29-32]. Water soluble polymers, especially acrylamide copolymers, are used worldwide in large quantities for paper making, and in mining operations [33]. Poly (acrylic acid) and poly (methacrylic acid) have enormous technical importance in the production of superabsorbent hydrogels, additives in cosmetics, and membrane manufacturing [34].

Table 2.2 shows some properties and applications of water-soluble polymers. They have the abilities to modify the reology of an aqueous media and to adsorb from solutions onto particles or surfaces [25].

Products such as fluids for oil and gas production, lubricants, detergents and foodstuffs include water-soluble polymers to control viscosity.

Polymers are generally described in terms of hydrodynamic volume or the volume occupied by the solvated chain. Hydrodynamic volume and the molecular shape of polymer can be determined by light scatterring.

Polymer molecules increase viscosity because of their hydrodynamic volume. Viscosity may be further enhanced by intermolecular interactions [35,36]. Flory pioneered theoretical attempts to reconcile polymer dimensions with chemical structure. Hyrodynamic volume is also affected by repulsive or attractive ionic interaction. For charged polymers, ionic effects often control behaviour especially in aqueous solution [8, 37-39].

**Table 2.2** Illustration of Important Properties and Applications of Water-Soluble

 Polymers [25].

Solutions						
Adsorbtion				Association	Hydrody- namic volume	High M
Crystal Growth Inhibition	Water- Borne Polymers coatings, adhesives	Colloids (1nm-1 Dispersions ( >1) Stabilization paints, cosmatics, detergents, pharmaceuti cals, foods	0μm) 0 μm) Flocculation water treatment, mineral processing, paper making	Viscosity Control Oilfield fluids, lubricants, detergents, foods	Drag Reduction fire fighting	

A major focus in recent years is hydrophobically modified water-soluble polymers [40-43]. They give very high viscosities at low concentrations under suitable conditions [44].

#### 2.2. Polyelectrolytes

Charged polymers are essential to life; for example, DNA, RNA and proteins all of which are polyelectrolytes have critical importance on the function of living cells [26]. Many common synthetic polymers are also charged. Their ability to dissolve in water makes them environmentally friendly for several applications [45].

In a good solvent, like water, polyelectrolytes dissociate into macroion and many mobile low-molecular counterions. The counterions are not totally independent of the polyion. They are necessary to secure electroneutrality in polyelectrolyte solutions [46]. Therefore, a fraction of counterions tend to be concentrated in the vicinity, or at the surface of the polyion, in order to reduce the charge of the polyion. Counterion condensation theory was introduced by Fuoss in 1951 and developed by Manning [15,16]. Manning explained that, the counterion condensation occurs if the distance between charges along the chain is considerably small, compared to length scale set by the electrostatic interactions.

A linear charge density parameter also called "Manning parameter" can be expressed as;

$$\xi_M = \frac{l_B}{b} \tag{2.1}$$

where  $l_B$  is the Bjerrum length, which is 0.72 nm in water at room temperature [39], and *b* is the average charge spacing in the fully stretched configuration and can be written as;

$$b = \frac{L}{N}$$
(2.2)

where L is total contour length of the polyion and N is the total number of charged groups on the polyion. In its simplest form, the theory predicts that when the linear charge density,  $\xi_{M}$ , which represents the number of elementary charges per Bjerrum length of a long, rigid, polyelectrolyte rod exceeds one elementary charge (e) per Bjerrum length  $l_B$ , counterions will condense onto the polyelectrolyte until there is one *e* per  $l_B$ .

Electrolyte concentration (ionic strength) in the solution plays an important part in the conformations and interactions of polyelectrolytes [6-8]. At high added salt concentration, the electrostatic intra- and intermolecular interactions in polyelectrolytes are largely screened, where the polyelectrolyte behaves like a neutral polymer. However, at lower salt concentrations, long range effects can be important because of the fact that the charges along the polyelectrolyte are less screened, chain expands, followed by an increase in intermolecular interactions ( such as , radius of gyration and the second virial coefficient) [9, 10, 12, 39].

Besides the ionic strength, the behaviour of polyelectrolytes depends so strongly on the pH of the medium [13, 14], the pH determines the degree of dissociation of ionic groups along the polyelectrolyte which is the actual charge density of the polyelectrolyte. Poly (styrene sulfonic acid) sodium salt and poly(diallyl dimethyl ammonium chloride) are ionized into macroion and counterion in aqueous solution in the total pH range between 0 and 14 [34, 47]. However polymers like poly (acrylic acid) or poly (ethyleneimin) form a polyion–counterion systems only in a limited range of pH. They remain as undissociated polyacid in the acidic region or an undissociated polybase in alkaline region, respectively [34]. So, weak polyelectrolytes such as poly (acrylic acid) are in a more expanded form at higher pH because of the electrostatic effects between the charges along the chain with a high degree of ionization [13, 34].

Capillary viscometry is often used to characterize the polymer dimensions. Nonionic polymers have the reduced viscosity  $\eta_{sp}/c$  (where  $\eta_{sp}$  is the specific viscosity and c refers to the concentration) decreasing linearly with dilution [25]. For polyelectrolytes in pure water, the reduced viscosity incereases markedly at low concentrations, and may give a maximum at extremely high dilution [48,49]. The extremely high reduced viscosity of a polyelectrolyte at low concentrations in pure water can be attributed to chain extension because of the repulsion between charged groups on the polyion. However, interactions between polyions affect the viscometric behaviour, as well [48, 50]. Viscosity of polyelectrolytes depends on strongly the ionic strength of the aqueous medium. Variation of viscosity with

increasing ionic strength is mainly caused by an electrostatic shielding of the electric charges at the macroion with the latter increasingly approaching the behaviour of a normal uncharged macromolecule [7, 8, 34].

Most synthetic polymers do not dissolve in water because of the hydrophobic interaction between hydrocarbon backbone and water molecules. Introducing charged groups provides the solubility in water to these polymers. In aqueous medium, as in polyelectrolytic behaviour, these charged groups dissociate by giving counterions to the solution and a polymer with ionized charged groups is formed. They are called hydrophobically modified polyelectrolytes [51-53]. The competition between electrostatic and hydrophobic interactions determines the shape of the hydrophobic polyelectrolyte molecule. The polymer is forced to collapse to a spherical globule by the hydrophobic interactions to minimize the interactions between the charged monomers on the backbone and water molecules. However, electrostatic interactions cause polymer chain expansion in order to decrease the electrostatic repulsive effects between the charged monomer on the polymer chain.

Acrylic acid and methacrylic acid are copolymerized with many other monomers due to the fact that they have highly reactive double bonds and the miscibility with both water-soluble and oil-soluble monomers [34]. Poly (acrylic acid) and poly (methacrylic acid) has technical importance in cosmetic industry and waste water treatment [34]. Acrylic acid-acrylamide copolymers have extensive usage in industry and there are many published works about this system. Several monomer reactivity ratios derived from the copolymerization were noted in the literature [14, 54-62]. Since copolymerization depends on the degree of ionization of the monomers in acrylamide-acrylic acid copolymerization [14], acrylic acid is undissociated and thus more reactive in acidic media and less reactive in basic media because of the high degree of ionization whereas acrylamide is neutral and, thus more reactive in basic media (at pH 2) [63].

Polyelectrolytes can be obtained from neutral polymers, as well. For example, acrylamide –acrylic acid copolyelectrolytes are prepared by hydrolysing polyacrlamide [64,65]. Important application fields of copolymers of acrylic acid with acrylamide and other monomers are listed as mining, textile manufacturing, soil modification, oil recovery [66] and petroleum industry [33]. Acrylamide can be copolymerized with cationic monomers to obtain water soluble cationic

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polyelectrolytes used in the field of paper making, solid/liquid separation, clarification of industrial wastewater [67].

4-vinylbenzenesulfonic acid sodium salt (VB) is a charged monomer resulting in polyelectrolytes upon polymerization. It has a big hydrophobic, styrene group and a strongly charged hydrophilic sulfonate group in the molecular formula. The field of applications of sodium styrene sulfonate has rapidly grown in recent years and reaches from large-scale industrial uses due to its micelle forming properties in emulsions and slurries, binders, and flocculants to special purposes in biotechnology and medicine [68-71].

Poly (4-vinylbenzene sulfonic acid sodium salt) which is one of the strong anionic polyelectroytes is used as an ion-exchange resin and to treat hyperkalemia (high levels of potassium in the blood) as reducing potassium in the blood by replacing a sodium ion by a potassium ion [72]. Also, it is used in cosmetic industry to remove cationic buildup from keratin surfaces in hair [73].

#### 2.3. Polymerization

Industrially important polymerization process are step growth and addition reactions. Ionic polymerization reactions can be considered[74,75].

Step growth reactions or condensation polymerizations, are performed by reactions between monomers having poly functionality with or without elimination of a small molecule such as water at each step [76]. In step-growth polymerization reactions, it is often necessary to use multifunctional monomers to have polymers with high molar masses; this is not the case in addition reactions[76]. In addition reactions, long chain molecules which usually have simple repeat unit are formed from monomers like vinyl compounds having the structure  $CH_2$ =CHR. Addition mechanism includes the successive opening of carbon-carbon double bonds on the monomer if activated by free radical or ionic initiators. This reaction creates an active centre to propagate a kinetic chain leading to the formation of a single macromolecule. Then a termination reaction, neutralizing the active centre stops the growth of polymer chain.

#### 2.3.1. Free Radical Addition Polymerization

Free radical polymerization has commercial and scientific importance [77]. A free radical is an atomic or molecular species whose normal bonding system has been modified such that an unpaired electron remains associated with the new structure. The radical is capable of reacting with an olefinic monomer to generate a chain radical which is stable long enough to propagate a macromolecular chain under the appropriate conditions.

$$R^{\bullet} + CH_2 = CHR_1 \longrightarrow RCH_2 CHR_1^{\bullet}$$
(2.3)

Polymerization process has the following three steps:

### 2.3.1.1. Initiation

A molecule which undergoes homolytic degradation to radicalic groups, when exposed to heat, electromagnetic radiation or chemical reaction, is called an initiator. The initiator radicals produced in the first step of polymerization must retain their activities long enough to react with a monomer and generate an active centre. Organic peroxides or azo compounds form free radicals when heated. For example, benzoyl peroxide gives two phenyl radicals by removing of  $CO_2$ .



2,2'-Azobis(isobutyronitrile) (AIBN) is soluble in organic solvents and 4,4'-Azobis(4-cyanovaleric acid) (ACV) is a water-soluble free radicalic initiator. These initiators supply radicals in the following manner.

$$CH_{3} \xrightarrow{C}_{C} N = N \xrightarrow{C}_{C} CH_{3} \xrightarrow{\Delta} 2 CH_{3} \xrightarrow{C}_{C} + N_{2}$$
(AIBN) (2.5)  
$$CN \qquad CN \qquad CN \qquad CN$$



Persulfates are used to initiate polymerization [13]. In the case of persulfate initiated polymerization, there are two species which can start polymerization, sulfate radical anion by means of homolysis of the O-O bond and the hydroxyl radical through the disappearance of persulfate containing a water molecule: Radicals obtained in these two reactions initiate free radical polymerization. Since the hydroxyl radical is also an efficient initiator, the transfer of activity from the persulfate radical to it does not result in a large impact on the kinetics [19]. Persulfates are used as initiator in the polymerization carried out electrochemically at room temperature [78].

$${}^{\Theta}O \xrightarrow{0}_{O} \xrightarrow{0}_{O} O \xrightarrow{0$$

Initiator efficiency in thermal initiation: the efficiency factor (f) is defined as the probability for a radical to react with a monomer and to initiate a chain.

$$f = \frac{\text{Rate of initiation of propagating chains}}{n \text{ (Rate of initiator disappearance)}}$$
(2.9)

Here, n is the number of moles of radicals generated per mole of initiator.

Radicals thus formed react with a monomer to start the chain-reaction addition of monomer units to form the polymer.

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$
 (2.10)

 $k_i$  is the rate constant for initiation.



### 2.3.1.2. Propagation

After monomeric radical  $(RM^{\bullet})$  produced, the propagation step involves the addition of monomer units to the chain, consecutively.

$$RM^{\bullet} + M \xrightarrow{k_{p}} RM_{2}^{\bullet}$$

$$RM_{2}^{\bullet} + M \xrightarrow{k_{p}} RM_{3}^{\bullet}$$

$$RM_{3}^{\bullet} + M \xrightarrow{k_{p}} RM_{4}^{\bullet}$$

$$(2.12)$$

 $RM_n^{\bullet} + M \xrightarrow{k_p} RM_{n+1}^{\bullet}$ 

The  $k_p$  is the rate constant for propagation.  $k_p$  is generally more uncertain than  $k_d$  but ranges from  $10^3$  to  $10^5$  L/(mol.s).



#### 2.3.1.3. Termination

The chain can continue to propagate until all monomers are consumed [76]. Free radicals interact quickly to form inactive chains, since they are quite active species and the length of the chain depends on the radical concentration. Short chains form if the radical concentration is high because of the high probability of radical interactions. Radical interactions should be kept relatively small to obtain long chains. Termination of the active chains occurs by different processes: (1) the interaction between two active chain ends; (2) the reaction of an active chain end with initiator radical; (3) transfer of the active centre to another molecule such as solvent, monomer or initiator; (4) interactions with the impurities such as oxygen or inhibitors.

Termination of the growing radical chain by an interaction between two active chain ends occurs by two types of processes:

*By combination*: The two radical chains are destroyed to give one inactive chain. Termination by combination, is written as follows:

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_{tc}} P_{n+m}$$
(2.14)

where  $k_{tc}$  is the rate constant for termination by combination.



*By disproportionation:* A hydrogen atom transferred from one chain to the other, leaving two inactive chains. One of them has a saturated end, the other one has an unsaturated end.

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_{td}} P_n + P_m$$
(2.16)

here  $k_{td}$  is the rate constant for termination by disproportionation

Termination step can be written as,

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_t} dead \ polymer$$
 (2.18)

The rate constant  $k_t$  is ( $k_{tc}$ +  $k_{td}$ ) where the two mechanisms, combination and disproportionation are possible. The values of termination rate constants range from  $10^6$ - $10^8$  L/(mol.s) and are much higher than  $k_p$ . However, the growth of polymer chain can not be prevented since the concentration of the radical species in the system is very low. The rate of polymerization is proportional to  $k_t^{-1/2}$ .

### 2.3.1.4. Remarks on Free Radical Polymerization [76,79]

The features of a radical polymerization can be summarized as follows:

- 1. Only the active centre can react with monomer and monomer units can be incorporated to chain one by one in propagation step.
- 2. Monomer concentration decreases gradually throughout the polymerization reaction.
- 3. Macromolecules form immediately and molecular weight of polymer changes slightly during the reaction.
- 4. Long reaction times raises polymerization yield, but molar mass of polymer doesn't exhibit an important change.
- 5. The rate of conversion of monomer to polymer is proportional to  $[I]^{1/2}$ .
- 6. The average molecular weight of the polymer produced is inversely proportional to  $[I]^{1/2}$ .
- 7. Whereas the rate of polymerization increases and molar mass decreases by the increasing temperature.
- 8. Reaction mixture includes monomer, high polymer and a small portion of growing chain radical.

## 2.3.1.5. Kinetics of Free Radical Polymerization

*Initiation* in a free-radical polymerization consists of two two steps: a) a dissociation of the initiator to form two radical species with a decomposition rate constant  $k_d$ . The rate of dissociation of initiators (*I*) usually follows 1<sup>st</sup> order kinetics according to

$$I \xrightarrow{k_d} 2R^{\bullet}$$
 (2.19)

$$R_d = -\frac{d[I]}{dt} = k_d[I] = \frac{1}{2} \frac{d[R^{\bullet}]}{dt}$$
(2.20)

and the initiator concentration decreases with time exponentially as,

$$[I] = [I]_0 e^{-k_d t}$$
(2.21)

If the half-life of the initiator  $(t_{1/2} = \frac{\ln 2}{k_d})$  is long compared with the period of the polymerization the depletion of the initiator during the reaction can be considered as

polymerization, the depletion of the initiator during the reaction can be considered as negligible.

b) addition of a single monomer molecule to the initiating radical with a rate constant  $k_i$ , which correspond to primary radical formation.

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} or (M_1^{\bullet})$$
 (2.10)

While driving the equations some assumptions and approximations are considered. The first approximation is that since the initial decomposition is slow when compared with the rate of addition of a primary radical to a monomer and the termination reaction, the decomposition of the initiator is the rate determining step. Because initiator radicals are consumed as fast as they generated, the rate of initiation,  $R_i$ , is the same as the rate of initiator decomposition,  $R_d$ .

$$R_{i} = \frac{d\left[RM^{\bullet}\right]}{dt} = k_{i}\left[R^{\bullet}\right]\left[M\right]$$
(2.22)

$$R_i = R_d = 2 f k_d \left[ I \right] = k_i \left[ R^{\bullet} \right] \left[ M \right]$$
(2.23)

where f, is initiator efficiency. The factor 2 takes into account that two potentially effective radicals are produced in the decomposition.

*Propagation* involves the addition of monomer units to the growing radical after the initiation reactions. The propagation step is written as follows,

$$RM_n^{\bullet} + M \xrightarrow{k_p} RM_{n+1}^{\bullet}$$
(2.12)

It is assumed that the rate of bimolecular propagation is the same for each step and the rate of monomer consumption is given by:

$$R_p = -\frac{d[M]}{dt} = k_p \left[ M^{\bullet} \right] [M]$$
(2.24)

where  $\begin{bmatrix} M^{\bullet} \end{bmatrix}$  is the steady state concentration of active sites.

*Termination*, depending on  $\operatorname{only}[M^{\bullet}]$ , occurs by two primary processes: combination and disproportionation. The termination reactions can be written as,

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_{tc}} P_{n+m}$$
(2.14)

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_{td}} P_n + P_m$$
(2.16)

The termination step is given by,

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_t} dead \ polymer$$
 (2.18)

Here  $k_t$  is  $k_t = k_{tc} + k_{td}$  because, termination by combination and disproportionation are possible. The rate of termination is described as:

$$R_t = -\frac{d\left[M^{\bullet}\right]}{dt} = 2k_t \left[M^{\bullet}\right] \left[M^{\bullet}\right]$$
(2.25)

where the 2 denotes that two radicals disappear in this event. At steady state, the rate of radical production is equal to the rate of destruction, that is,  $R_i = R_t$ , assuming that radical-radical termination is the main destruction mechanism.

$$R_i = R_t = 2fk_d \left[I\right] = 2k_t \left[M^{\bullet}\right]^2$$
(2.26)

From this equation, the radical concentration is expressed in terms of measurable quantities:

$$\left[M^{\bullet}\right] = \left(\frac{fk_d\left[I\right]}{k_t}\right)^{1/2}$$
(2.27)

The overall rate of polymerization  $(R_p)$  is obtained by introducing the radical concentration into equation (2.24).

$$R_p = -\frac{d\left[M\right]}{dt} = k_p \left[M\right] \left(\frac{fk_d\left[I\right]}{k_t}\right)^{1/2}$$
(2.28)

This equation shows that the rate of polymerization depends on the monomer concentration and the square root of initiator concentration. That is, the overall rate of monomer consumption is 1<sup>st</sup> order with respect to monomer concentration and one-half order with repect to initiator concentration.

The assumptions underlying this calculation are the following:[74]

- 1.  $k_p$  is independent of the length of the chain to which the growing sites are attached.
- The concentration of the active sites is constant despite the fact that their lifetime is extremely short. This means that the concentration of the initiator stays constant or does not exhibit a significant change. This assumption is

valid if the half-life of the initiator  $(t_{1/2} = \frac{\ln 2}{k_d})$  under the experimental

conditions is long compared to the period of polymerization.

3. When this condition is not fulfilled, the depletion of initiator must be taken account. Then, the overall rate of polymerization is expressed introducing the equation (2.21) into equation (2.28).

$$R_{p} = -\frac{d[M]}{dt} = k_{p} \left(\frac{fk_{d}}{k_{t}}\right)^{1/2} [M] [I]_{0}^{1/2} e^{-\left(\frac{k_{d}t}{2}\right)}$$
(2.29)

In order to express the conversion as a function of time, equations (2.28) and (2.29) must be integrated so that,

For the system where the initiator concentration is constant during the reaction,

$$\ln \frac{[M]_0}{[M]} = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [I]^{1/2} t$$
(2.30)

If the depletion of the initiator is taken into account, the expression is given by:

$$\ln\frac{[M]_0}{[M]} = 2k_p \left(\frac{f}{k_d k_t}\right)^{1/2} [I]_0^{1/2} \left[1 - e^{-\left(\frac{k_d t}{2}\right)}\right]$$
(2.31)

The degree of conversion,  $\pi$ , is described as,

$$\pi = \frac{\left[M\right]_0 - \left[M\right]}{\left[M\right]_0}$$
(2.32)

The equations (2.30) and (2.31) are suited to express the degree of conversion versus time as:

$$\ln \frac{[M]_0}{[M]} = -\ln(1-\pi)$$
(2.33)

If cage effect [80-85] is taken into account,

$$I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (2I^{\bullet}) \tag{2.34}$$

$$(2I^{\bullet}) \xrightarrow{k_3} 2I^{\bullet}$$
 (2.35)

$$(2I^{\bullet}) + M \xrightarrow{k_4} M^{\bullet} + I^{\bullet}$$
(2.36)

 $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are the rate constants for the related equations. Then the reaction is no longer 1<sup>st</sup> order in monomer but 5/4 (1.25<sup>th</sup>) order according to Noyes, or 3/2 (1.5<sup>th</sup>) according to Hamielec. Although it is possible to fit for both initiator lifetime and reaction order from the experimental reaction rate, such a fit procedure involves too many fit parameters and is not reliable. Instead, the kinetic data was fitted to 5/4 order kinetics with initiator decay,

$$R_{p} = -\frac{d[M]}{dt} = k_{p} \left(\frac{fk_{d}}{k_{t}}\right)^{1/2} [M]^{5/4} [I]_{0}^{1/2} e^{-\left(\frac{k_{d}t}{2}\right)}$$
(2.37)

After integration, equation (2.37) yields

$$\frac{1}{M^{1/4}} = \frac{1}{M_0^{1/4}} + \frac{k_p}{2} \left(\frac{f}{k_t k_d}\right)^{1/2} \left[I\right]_0^{1/2} \left(1 - e^{-\left(\frac{k_d t}{2}\right)}\right)$$
(2.38)

and 3/2 order kinetics,

$$R_{p} = -\frac{d[M]}{dt} = k_{p} \left(\frac{fk_{d}}{k_{t}}\right)^{1/2} [M]^{3/2} [I]_{0}^{1/2} e^{-\left(\frac{k_{d}t}{2}\right)}$$
(2.39)

with fit parameters. Equation (2.39) is integrated as,

$$\frac{1}{M^{1/2}} = \frac{1}{M_0^{1/2}} + k_p \left(\frac{f}{k_t k_d}\right)^{1/2} \left[I\right]_0^{1/2} \left(1 - e^{-\left(\frac{k_d t}{2}\right)}\right)$$
(2.40)

## 2.3.2. Kinetic Chain Length and Degree of Polymerization

The kinetic chain length (v) is given by the ratio of the propagation rate to the rate of initiation. Under steady-state condition where the rate of termination is equal to initiation rate ( $R_t = R_i$ ), and the kinetic chain length is expressed as,

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p \left[M\right] \left[M^{\bullet}\right]}{2fk_d \left[I\right]} = \frac{k_p \left[M\right] \left[M^{\bullet}\right]}{2k_t \left[M^{\bullet}\right]^2}$$
(2.41)

Therefore, from  $[M^{\bullet}]$  given in equation (2.27), the kinetic chain length is given as:

$$\nu = \frac{k_p \left[M\right]}{2k_t \left[M^{\bullet}\right]} = \frac{k_p \left[M\right]}{2(fk_d k_t \left[I\right])^{1/2}} = \frac{k_p^2 \left[M\right]^2}{2k_t R_p}$$
(2.42)

for the polymerization reactions initiated by thermal decomposition of the initiator.

The average number of monomers converted to polymer per monomer radical is decreases with increasing radical concentration. If there are no transfer processes, the kinetic chain length is related to the number average degree of polymerization, ( $\overline{P}_n$ ). The degree of polymerization at any instant is defined as the ratio of the rate polymerization (the rate of monomer disappearance) to the rate where the polymer molecules are produced.

$$\overline{P}_{n} = \frac{\frac{d[M]}{dt}}{\frac{d[polymer]}{dt}}$$
(2.43)

$$R_{t} = -\frac{d\left[M^{\bullet}\right]}{dt} = 2k_{td}\left[M^{\bullet}\right]\left[M^{\bullet}\right] + 2k_{tc}\left[M^{\bullet}\right]\left[M^{\bullet}\right] = 2k_{t}\left[M^{\bullet}\right]\left[M^{\bullet}\right]$$
(2.25)

It follows then that

$$R_{t} = \frac{d\left[polymer\right]}{dt} = 2k_{td}\left[M^{\bullet}\right]^{2} + k_{tc}\left[M^{\bullet}\right]^{2}$$
(2.44)

The termination by combination results in the production of one polymer molecule, but two polymer molecules are produced if disproportionation is involved. After substituting equation (2.24) into (2.43) to obtain

$$\overline{P}_{n} = \frac{k_{p} \left[ M \right]}{\left( k_{tc} + 2k_{td} \right) \left[ M^{\bullet} \right]}$$
(2.45)

and by using  $\left[M^{\bullet}\right] = \frac{R_p}{k_p[M]}$  from equation (2.24),  $\overline{P}_n$  is written as follows;

$$\overline{P}_{n} = \frac{k_{p}^{2} [M]^{2}}{R_{p}(k_{tc} + 2k_{td})}$$
(2.46)

For the polymerization reaction initiated by thermal homolysis of an initiator, replacing  $[M^{\bullet}]$  by its value taken from equation (2.37) and using (2.45) give

$$\overline{P}_{n} = \frac{k_{p} [M] (k_{tc} + k_{td})^{1/2}}{(k_{tc} + 2k_{td}) (fk_{d} [I])^{1/2}} = \frac{k_{p} [M] (k_{tc} + k_{td})^{1/2}}{(k_{tc} + 2k_{td}) (\frac{1}{2} R_{i})^{1/2}}$$
(2.47)

If termination occurs by disproportionation, since  $k_{tc} = 0$ 

$$\overline{P}_n = V \tag{2.48}$$

In the case where termination is recombination of two growing chains, since  $k_{td} = 0$ , the number average degree of polymerization is

$$\overline{P}_n = 2\nu \tag{2.49}$$

The number average degree of polymerization changes inversely with  $R_i^{1/2}$ . The number of growth steps per radical decreases by the decreasing monomer concentration, whereby the average degree of polymerization is lowered correspondingly.

## 2.3.3. Molecular Weight of Polymers

In a polymer sample, though the composition of all molecules remains the same, the molecular weights of the individual polymer molecules can vary widely because of the random manner of chain growth. Hence, a molecular weight for a polymer is an average value. This average can be defined in several ways.

The number average degree of polymerization  $\overline{P}_n$  is described as follows,

$$\overline{P}_n = \sum_{i=1}^{\infty} i x_i$$
(2.50)

or

$$\overline{P}_n = \frac{\sum_{i=1}^{\infty} in_i}{\sum_{i=1}^{\infty} n_i}$$
(2.51)

 $n_i$  is the number and  $x_i$  the mole fraction of molecules with *i* monomer units in the chain. Providing that  $M_i$  is the molecular weight of this species, the number average molecular weight is given by;

$$\bar{M}_{n} = \frac{\sum_{i=1}^{\infty} n_{i} M_{i}}{\sum_{i=1}^{\infty} n_{i}} = \sum_{i=1}^{\infty} x_{i} M_{i}$$
(2.52)

or

$$\overline{M}_n = m_0 \sum_{i=1}^{\infty} i x_i \tag{2.53}$$

where  $m_0$  denotes the molecular weight of a repeat unit.

Thus,  $\overline{M}_n$  is defined as the total weight of polymer divided by the total number of polymer molecules in the sample. There are several methods to determine the number average molecular weight. One of these methods is end group analysis.

Other methods for  $\overline{M}_n$  use colligative properties such as boiling point elevation (ebullioscopy), melting point depression (cryoscopy) or osmotic pressure.

The weight average degree of polymerization  $\overline{P}_w$  is given as;

$$\overline{P}_{w} = \sum_{i=1}^{\infty} i w_{i} = \frac{\sum_{i=1}^{\infty} i W_{i}}{\sum_{i=1}^{\infty} W_{i}}$$
(2.54)

where  $W_i$  denotes the weight and  $w_i$  is the weight fraction of the macromolecules in the polymer sample exhibiting a polymerization degree *i*. The weight fraction  $w_i$  is expressed as;

$$w_{i} = \frac{W_{i}}{\sum_{i=1}^{\infty} W_{i}} = \frac{n_{i}M_{i}}{\sum_{i=1}^{\infty} n_{i}M_{i}} = \frac{in_{i}}{\sum_{i=1}^{\infty} in_{i}}$$
(2.55)

 $\overline{M}_w$  is obtained from light scattering measurements.

$$\bar{M}_{w} = \bar{P}_{w} m_{0} = \sum_{i=1}^{\infty} w_{i} M_{i} = \frac{\sum_{i=1}^{\infty} n_{i} M_{i}^{2}}{\sum_{i=1}^{\infty} n_{i} M_{i}}$$
(2.56)

Higher averages,  $\overline{M}_z$  , can also be defined.

$$\bar{M}_{z} = \frac{\sum_{i=1}^{\infty} n_{i} M_{i}^{3}}{\sum_{i=1}^{\infty} n_{i} M_{i}^{2}}$$
(2.57)

It is apparent from the equations (2.52), (2.56) and (2.57) that  $\overline{M}_z$ , which is measured by ultracentrifugation, is more sensitive to high molecular weight species than  $\overline{M}_w$ , and both are more sensitive to this type of species more than  $\overline{M}_n$ .

In addition to the average molecular weights, another important parameter is the distribution of the molecular weights. A convenient measure of the molecular weight distribution for a sample is called its polydispersity (or heterogenety) index and expressed by the ratio of its two moments (molecular weight averages) as follows;

$$\frac{\bar{M}_w}{\bar{M}_n}.$$

Since the number average molecular weight of a distribution counts the contribution of molecules in each class while the weight average weigths their contribution in terms of mass,  $\overline{M}_w$  of a distribution will be higher than  $\overline{M}_n$ . For the monodisperse polymers, polydispersity index is equal to one, in which case all of the molecules in a sample have the same molecular weight. If there are fluctuations in molecular weight within sample, the polydispersity index will be greater than unity for a polydisperse sample.

## 2.3.4. Chain Transfer

In free-radical polymerization, there are three steps, but this does not explain the whole reaction. In many free-radical polymerizations, the molecular weight of the polymer obtained is lower than predicted. This is because of the fact that the growth of macroradicals in these systems was terminated by transfer of an atom to the macroradical from some other species in the reaction mixture. The donor species itself becomes a radical in the process, and the kinetics of chain propagation is not terminated, if this new radical can add monomer. Although the rate of monomer consumption may not be altered by this change of radical site, the initial macroradical will have ceased to grow and its size is less than it would have been in the absence of this reaction. These reactions are called chain transfer processes [35]. The molecule, which takes part in the chain transfer reaction, is called the transfer agent. Chain transfer can occur with any molecule in the system. The following reactions specifically describe transfer to initiator, monomer, solvent and the polymer molecules:

1. Transfer to initiator, *IX*:

$$M_n^{\bullet} + IX \longrightarrow M_n X + I^{\bullet} \tag{2.58}$$

2. Transfer to monomer, *MX*:

$$M_n^{\bullet} + MX \longrightarrow M_n X + M^{\bullet} \tag{2.59}$$

3. Transfer to solvent, *SX*:

$$M_n^{\bullet} + SX \longrightarrow M_n X + S^{\bullet} \tag{2.60}$$

4. Transfer to polymer,  $M_m X$ :

$$M_n^{\bullet} + M_m X \longrightarrow M_n X + M_m^{\bullet} \tag{2.61}$$

In general;

5. Transfer to *RX*:

$$M_n^{\bullet} + IX \xrightarrow{k_{tr}} M_n X + R^{\bullet}$$
(2.62)

The transfer reactions follow  $2^{nd}$  order kinetics [86]. The rate of transfer is given as;

$$R_{tr} = k_{tr} \left[ M_n^{\bullet} \right] \left[ RX \right] = k_{tr} \left[ M^{\bullet} \right] \left[ RX \right]$$
(2.63)

assuming that the transfer rate constant  $k_{tr}$  is the same for all monomerended radicals and taking  $[M^{\bullet}]$  to be the concentration of all such species. The magnitude of  $k_{tr}$ will depend on the natures of transfer agents and the reaction temperature [87].

The new radical  $R^{\bullet}$  can reinitiate as shown below

$$M_n^{\bullet} + IX \xrightarrow{K_{lr}} M_n X + R^{\bullet}$$
(2.64)

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$
 (2.65)

where  $k_i$  is the rate constant for addition of a particular monomer M to  $R^{\bullet}$ .

$$RM^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet}$$
 (2.66)

$$RM_2^{\bullet} + M \xrightarrow{k_p} \dots \xrightarrow{k_p} RM_n^{\bullet}$$
 (2.67)

where  $k_p$  is the rate constant for propagation. All propagation steps are assumed to work with the same rate constant, because the propagation rate is independent of chain length [88].

The various relations between the rate constants  $k_{tr}$ ,  $k_i'$  and  $k_p$  and their effect to the polymerization rate and molecular weight can be summarized as follows [88]:

a) $k_p \gg k_{tr}$ , $k_i = k_p$	no change in $R_p$
b) $k_p \gg k_{tr}$ , $k_i' < k_p$	decrease in $R_p$
c) $k_p \ll k_{tr}, \ k_i \ll k_p$	large decrease in $R_p$
d) $k_p \ll k_{tr}, \ k_i = k_p$	no change in $R_p$
e) $k_p \gg k_{tr}, \ k_i > k_p$	no change in $R_p$
f) $k_p \ll k_{tr}, \ k_i > k_p$	no change in $R_p$

Chain transfer ends the physical growth of macroradicals. Equations (2.44) and (2.63) can be combined to give the formation rate of polymers;

$$\frac{d\left[polymer\right]}{dt} = 2k_{td}\left[M^{\bullet}\right]^{2} + k_{tc}\left[M^{\bullet}\right]^{2} + k_{tr}\left[M^{\bullet}\right]\left[RX\right]$$
(2.68)

If (2.68) is substituted into (2.43) and inverting the resulting expression gives;

$$\frac{1}{\overline{P}_{n}} = \frac{k_{tc} \left[ M^{\bullet} \right]}{k_{p} \left[ M \right]} + \frac{2k_{td} \left[ M^{\bullet} \right]}{k_{p} \left[ M \right]} + \frac{k_{tr} \left[ RX \right]}{k_{p} \left[ M \right]}$$
(2.69)

Then, replacing  $\left[M^{\bullet}\right]$  by its value taken from (2.24),

$$\frac{1}{\overline{P}_{n}} = \frac{k_{tc}R_{p}}{k_{p}^{2}[M]^{2}} + \frac{2k_{td}R_{p}}{k_{p}^{2}[M]^{2}} + \frac{k_{tr}[RX]}{k_{p}[M]}$$
(2.70)

The ratio  $\frac{k_{tr}}{k_p}$  depends on the transfer agent, monomer and the reaction temperature

[87]. The relation can be generalized by breaking the last term on the right-hand side equation (2.70) can be written as;

$$\frac{1}{\overline{P}_{n}} = \frac{k_{tc}R_{p}}{k_{p}^{2}[M]^{2}} + \frac{2k_{td}R_{p}}{k_{p}^{2}[M]^{2}} + \frac{k_{tr,M}[M]}{k_{p}[M]} + \frac{k_{tr,I}[I]}{k_{p}[M]} + \frac{k_{tr,S}[S]}{k_{p}[M]} + \frac{k_{tr}[Ta]}{k_{p}[M]}$$
(2.71)

Where  $k_{tr,M}$ ,  $k_{tr,I}$ ,  $k_{tr,S}$  are the rate constants for the transfer reaction to monomer (*M*), initiator (*I*), and solvent (*S*), respectively. *Ta* is the any chain transfer agent which is added deliberately for this purpose. There is a characteristic chain transfer constant (*C*) for each substance as the ratio of  $k_{tr}$  for that material with a propagating radical to  $k_p$  for that radical.

$$C = \frac{k_{tr}}{k_p}$$
(2.72)

Thus, chain transfer constants for the given species,

$$C_M = \frac{k_{tr,M}}{k_p} \quad C_I = \frac{k_{tr,I}}{k_p} \quad C_S = \frac{k_{tr,S}}{k_p}$$
 (2.73)

It follows that

$$\frac{1}{\overline{P}_{n}} = \frac{k_{tc}R_{p}}{k_{p}^{2}\left[M\right]^{2}} + \frac{2k_{td}R_{p}}{k_{p}^{2}\left[M\right]^{2}} + C_{M} + C_{I}\frac{\left[I\right]}{\left[M\right]} + C_{S}\frac{\left[S\right]}{\left[M\right]} + C\frac{\left[Ta\right]}{\left[M\right]}$$
(2.74)

### 2.4. Copolymerization

The reactions in which two different monomers undergo polymerization are called copolymerization and the resulting product is referred to as copolymer. Early work on kinetic models includes reports by Mayo and Lewis [89] and, Alfrey and Goldfinger [90] and, Simha and Branson [91].

The composition and properties of the copolymer depends on the reactivity ratios of constituent monomers. Therefore, copolymerization offers the ability to design polymers with desired properties. The overall composition is an important feature of the copolymer produced. The details of the microstructural arrangement plays an important role on the properties of the molecule. It is possible that although copolymers have the same composition, they exhibit different properties because of the differences in the microstructure. Hence, copolymers can be categorized as follows;

- (a) Random or statistical copolymers are formed when irregular propagation happens and A and B units are distributed statistically along the chain. This type of copolymers is mostly encountered.
   -AABAAAABAABBABABBB –
- (b) Alternating copolymers are formed when the monomers alternate in the chain. This type of polymers can be considered as a homopolymer having AB repeating units.
   -ABABABABABABABABABABABAB
- (c) Block copolymers, some copolymer molecules may contain a small number of blocks or sequences, each of which is homopolymeric, that are linked together. They are referred to as block copolymers. This creates a linear copolymer in the form of AA...AABB...B, i.e. an {A} {B} block or sometimes an {A} {B} {A} block copolymer. The length of the blocks can range from a few units to several thousands.
- (d) Graft copolymer or branched block copolymer is formed when homopolymer sequences B are attached as side chains to the main chain of another homopolymer (poly A).



Free radical copolymerization, like homopolymerization, includes the three basic steps of initiation, propagation, and termination. The chain transfer and inhibition are

possible. These steps are important for the determination of molecular weight and its distribution. If chains are long, only the propagation step is important for the determination of the chain composition [77].

In the simplest model known as the terminal model the composition is determined solely by the properties of the monomers and the terminal units of the radicals. Other models take into account the effect of the penultimate and pen-penultimate unit on the chain radical.

## 2.4.1. Terminal Model

In terminal model, properties of the terminal radical are responsible for the reaction rate.

Terminal model has a number of approximations [77]:

- 1) It is assumed that the copolymer composition is dictated by the relative rates of only four distinctly different propagation reactions.
- 2) The second assumption is that chains are long, hence the effect of initiation and termination steps to monomer consumption rate is negligible.
- 3) The concentrations of the propagating species achieve the steady state.

In terminal model, the four possible propagation steps with monomers  $M_1$  and  $M_2$ ,

$$M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1^{\bullet}$$
 (2.75)

$$M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_2^{\bullet} \tag{2.76}$$

$$M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_1^{\bullet} \tag{2.77}$$

$$M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2^{\bullet}$$
 (2.78)

Where  $M_1^{\bullet}$  and  $M_2^{\bullet}$  represent propagating species where terminal (last added) monomer units are  $M_1$  and  $M_2$ , respectively.  $k_{11}$ ,  $k_{12}$ ,  $k_{21}$ , and  $k_{22}$  stand for the rate constants for the addition, i.e.  $k_{ij}$  is the propagation rate constant for the addition of monomer  $M_i$  to radical  $M_j^{\bullet}$ . The rate expressions for the equations (2.75-2.78) are given as [89-91];

$$rate_1 = k_{11} \left[ M_1^{\bullet} \right] \left[ M_1 \right]$$
(2.79)

$$rate_2 = k_{12} \left[ M_1^{\bullet} \right] \left[ M_2 \right]$$
(2.80)

$$rate_3 = k_{21} \left[ M_2^{\bullet} \right] \left[ M_1 \right]$$
(2.81)

$$rate_4 = k_{22} \left[ M_2^{\bullet} \right] \left[ M_2 \right]$$
(2.82)

The consumption rates of the two monomers can be expressed as;

$$-\frac{d[M_1]}{dt} = k_{11} \Big[ M_1^{\bullet} \Big] [M_1] + k_{21} \Big[ M_2^{\bullet} \Big] [M_1]$$
(2.83)

$$-\frac{d[M_2]}{dt} = k_{22} \left[ M_2^{\bullet} \right] [M_2] + k_{12} \left[ M_1^{\bullet} \right] [M_2]$$
(2.84)

 $d[M_1]$  and  $d[M_2]$  are the amounts of monomer  $M_1$  and monomer  $M_2$  that have been converted into polymer during time interval dt. The ratio  $d[M_1]/d[M_2]$  thus gives the instantaneous composition of copolymer.

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11} \left[ M_1^{\bullet} \right] [M_1] + k_{21} \left[ M_2^{\bullet} \right] [M_1]}{k_{22} \left[ M_2^{\bullet} \right] [M_2] + k_{12} \left[ M_1^{\bullet} \right] [M_2]}$$
(2.85)

The time dependence of the concentration of the radicals  $M_1^{\bullet}$  is

$$\frac{d\left[M_{1}^{\bullet}\right]}{dt} = -k_{12}\left[M_{1}^{\bullet}\right]\left[M_{2}\right] + k_{21}\left[M_{2}^{\bullet}\right]\left[M_{1}\right]$$
(2.86)

Similarly, for  $M_2^{\bullet}$  it is,

$$\frac{d\left[M_{2}^{\bullet}\right]}{dt} = k_{12}\left[M_{1}^{\bullet}\right]\left[M_{2}\right] - k_{21}\left[M_{2}^{\bullet}\right]\left[M_{1}\right]$$
(2.87)

In free radical copolymerization, under quasi steady state conditions,  $M_1^{\bullet}$  is sufficiently small, therefore  $d[M_1^{\bullet}]/dt$  is negligible when compared to the rates of change of concentrations of the reactants. That is, it is permissible to take,  $d[M_1^{\bullet}]/dt = 0$ . So, the rate at which  $M_1^{\bullet}$  is changed into  $M_2^{\bullet}$  must equal the rate at which  $M_2^{\bullet}$  is changed into  $M_1^{\bullet}$ , or

$$k_{12} \left[ M_1^{\bullet} \right] \left[ M_2 \right] = k_{21} \left[ M_2^{\bullet} \right] \left[ M_1 \right]$$
(2.88)

Solving equation (2.88) for  $\left[M_1^{\bullet}\right] / \left[M_2^{\bullet}\right]$  gives,

$$\frac{\left\lfloor M_1^{\bullet} \right\rfloor}{\left\lfloor M_2^{\bullet} \right\rfloor} = \frac{k_{21} \left[ M_1 \right]}{k_{12} \left[ M_2 \right]}$$
(2.89)

Then, dividing the right hand side of equation (2.85) by  $[M_2^{\bullet}]$ , replacing  $[M_1^{\bullet}]/[M_2^{\bullet}]$  by its value taken from (2.89), and dividing by  $k_{21}$  in order to obtain  $\frac{d[M_1]}{d[M_2]} = \frac{[M_1][(k_{11}/k_{12})[M_1] + [M_2]]}{[M_2][(k_{22}/k_{21})[M_2] + [M_1]]}$ (2.90)

Simplifying the notion by defining the reactivity ratios

$$r_1 = \frac{k_{11}}{k_{12}}$$
  $r_2 = \frac{k_{22}}{k_{21}}$  (2.91)

With these substitutions, equation (2.90) becomes

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right) = \frac{1 + r_1 \frac{[M_1]}{[M_2]}}{1 + r_2 \frac{[M_2]}{[M_1]}}$$
(2.92)

The copolymer composition equation (2.92) is known as the Mayo-Lewis equation [89] and Alfrey and Goldfinger equation [90].

The copolymer composition equation can also be written in a different form by introducing the mole fractions of  $M_1$  and  $M_2$  monomers in the monomer mixture,

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$
(2.93)

Where  $f_1$  and  $f_2$  are the mole fraction of monomer  $M_1$  and monomer  $M_2$  in the monomer mixture. The mole fractions of units  $M_1$  and  $M_2$  in the copolymer formed instantaneously can be formulated as  $F_1$  and  $F_2$ , respectively,

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$
(2.94)

Thus,  $F_1$  is written as follow;

$$F_1 = \frac{(r_1 f_1^2 + f_1 f_2)}{(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)}$$
(2.95)

If the reactivity ratios are given, this relation enables the calculation of the instantaneous mole fraction of  $M_1$  in the copolymer when the monomer mole fractions are known.

### 2.4.2. Monomer Reactivity Ratios and Copolymer Structure

Monomer reactivity ratios  $r_1$  and  $r_2$ , are indicative of the relative rate that a polymer chain terminated by radical  $M_1^{\bullet}$  prefers the monomer  $M_1$  instead of monomer  $M_2$ , and the relative rate that a polymer chain terminated by radical  $M_2^{\bullet}$  prefers the monomer  $M_2$  instead of monomer  $M_1$ , respectively. Thus, values of  $r_1$  and  $r_2$  less than 1 indicates that the radical shows preference for reaction with the comonomer, a value of 1 means that no preference in reactivity for either comonomer, while a value more than 1 indicates that the radical has a preference for the monomer of its own type. The Mayo-Lewis equation exhibits a relation between the instantaneous copolymer and monomer composition in the system. Therefore, when the reactivity ratios are known, the copolymer equation gives the amount of each monomer incorporated into the polymer chain, and it also gives evolution of monomer composition with time or drift during the reaction. In a binary system, if one of the monomer ( $M_1$ ) is more reactive than the other ( $M_2$ ), then  $M_1$  will participate more in the copolymer, which leads the fast decrease of M1 concentration in the feed solution and composition drift occurs. Hence, the structure of the copolymer will be a function of  $r_1$  and  $r_2$ .

**a:** When the copolymer composition is the same as that of the comonomer feed where no composition drift is observed, the composition of the copolymer is constant throughout the reaction. This is known as azeotropic copolymerization. In this case  $F_1=f_1$  defining the azeotropic line. Under this conditions,

$$d[M_1]/d[M_2] = [M_1]/[M_2]$$
(2.96)

and the equation (2.92) becomes,

$$\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} = 1$$
(2.97)

Equation (2.97) can be solved for  $[M_1]/[M_2]$ . Thus, the azeotropic feed composition can be expressed as,

$$\left(\frac{[M_1]}{[M_2]}\right)_{azeotrope} = \frac{1-r_2}{1-r_1}$$
(2.98)

**b**:  $r_1r_2=1$ ; any copolymer where the product  $(r_1r_2)$  is unity, is called ideal copolymer and this case is referred to as ideal copolymerization. The relative reactivity of the monomers does not depend on the radical species. In the case of  $r_1\neq 1$  and  $F_1\neq f_1$ , there is a composition drift. If  $r_1>1$ , then  $F_1 > f_1$  and thus,  $f_1$  will decrease with conversion. In the opposite situation, that is,  $r_1<1$ , then  $F_1<f_1$  and thus,  $f_1$  will have an increase with conversion.

**c:**  $r_1 > 1$ ,  $r_2 \le 1$ ; the  $F_1 - f_1$  curve is completely above the azeotropic line,  $f_1$  decreases with conversion because of composition drift.

**d**:  $r_1 \le 1$ ,  $r_2 > 1$ ; this situation exhibits the opposite of **c**. the  $F_1$ - $f_1$  curve is completely belove the azeotropic line,  $f_1$  increases as a function of conversion because of drift.

e:  $r_1 < 1$ ,  $r_2 < 1$ ; in this type of copolymerization, both kinds of radical prefer crosspropagation to homo-propagation, i.e.  $k_{12} > k_{11}$  and  $k_{21} > k_{22}$ . The polymer has a tendency for an alternating fashion. In the case of  $r_1 = 0$  and  $r_2 = 0$ , the polymer is entirely alternating. The  $F_1$ - $f_1$  curve crosses the azeotropic line and this point is called the azeotropic composition.

**f**:  $r_1 > 1$ ,  $r_2 > 1$ ; this is the opposite of the **e** and is seldom observed for free-radical polymerization. Homo-propagation is preferred to cross-propagation by each of growing radicals, which leads to conditions of favouring long sequences of each monomer in the copolymer. In extreme cases, the formation of homopolymer is dominant. This type also crosses the azeotrope line, however, copolymer composition drifts towards the azeotropic composition with conversion.

## 2.4.3. Determination of Monomer Reactivity Ratios

Initial monomer concentration is easy to control, and the resulting copolymer composition can be determined by means of various chemical analysis techniques [54,58,92], Ultraviolet (UV) spectroscopy [14, 19, 20, 93-96], refractive index [19], Nuclear Magnetic Resonance (NMR) spectroscopy [60, 97, 98], Fourier Transform Infrared (FTIR) [99], and Infrared (IR) spectroscopy [100, 101]. Obtaining the reactivity ratios from the data is based on the solution of the copolymerization equation.

#### 2.4.3.1. The Intersections Method

This method is referred as Mayo-Lewis method [89] and used to determine the reactivity ratios. In this method, the reactivity ratios are calculated from the data fitted to the differential copolymer equation. This procedure is based on solving equation (2.92) for one of the reactivity ratios. Therefore, equation (2.92) are converted to the form of

$$r_{2} = \frac{[M_{1}]}{[M_{2}]} \left[ \frac{d[M_{2}]}{d[M_{1}]} \left( 1 + r_{1} \frac{[M_{1}]}{[M_{2}]} \right) - 1 \right]$$
(2.99)

Experimental values of  $[M_1]$ ,  $[M_2]$ ,  $d[M_1]$ ,  $d[M_2]$  respectively, are substituted into Equation (2.99), and  $r_2$  is plotted as a function of values of  $r_1$ . One straight line is obtained from each experiment in  $r_1r_2$  plane and the intersection region of the lines yielded from the experiments with different feed composition gives the best value of  $r_1$  and  $r_2$ .

## 2.4.3.2. Linear Methods

Obtaining the reactivity ratios  $r_1$  and  $r_2$  from Mayo-Lewis equation requires complex numerical and iterative techniques. For this reason linearised versions have been developed.

The Finemann-Ross (FR) method has been widely used since 1950ies [102]. Later Kelen and Tüdös have shown that the results of the FR method depend on which monomer is labelled  $M_1$  and which is labelled  $M_2$ . The method also unevenly distributes and weighs the data. They proposed a better linearised method which solves these problems [102]. The Kelen-Tüdös (KT) method is invariant under reindexing the variables, distributes the data uniformly in the (0,1) interval. It is more robust in handling the random experimental errors. These methods are applicable only at low conversion ratios and are inherently wrong at moderate to high conversions.

Kelen and Tüdös have also extended their linearised and graphical evaluation method to be applicable at moderate conversions [103]. This method is called Extented-Kelen-Tüdös (EKT) method. EKT method not only protects the advantages and simplicities of the linearization techniques but also extends the application and usage of the original KT method.

In EKT method, the reactivity ratios are calculated from the differential form of traditional copolymer equation (2.92).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right)$$
(2.92)

EKT method is based on the suggestion of Walling and Briggs that

$$\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$
(2.100)

remains almost constant during the reaction [103-104]. By substituting

$$z = \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]}$$
(2.101)

and

$$y = \frac{d[M_1]}{d[M_2]} \tag{2.102}$$

so that equation (2.92) can be solved for

$$\frac{[M_1]}{[M_2]} = \frac{\frac{d[M_1]}{d[M_2]}}{\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}} = \frac{y}{z} = \overline{x}$$
(2.103)

To express z as a function of relative molar monomer conversions, equation (2.92) is integrated, yielding;

$$z = \frac{\log(1-\zeta_1)}{\log(1-\zeta_2)}$$
(2.104)

where  $\zeta_1$ ,  $\zeta_1$  are the relative molar conversions for monomer  $M_1$  and monomer  $M_2$ , respectively. Recasting the copolymer equation gives

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{2.105}$$

or

$$\eta = r_1 \xi - \frac{r_2}{\alpha} (1 - \xi)$$
 (2.106)

where

$$\eta = \frac{G}{\alpha + F}$$
 and  $\xi = \frac{F}{\alpha + F}$  (2.107)

F and G given in equation (2.107) can be expressed as follows

$$F = \frac{\left(\frac{[M_1]}{[M_2]}\right)^2}{\frac{d[M_1]}{d[M_2]}} \quad \text{and} \quad G = \frac{\frac{[M_1]}{[M_2]}}{\frac{d[M_1]}{d[M_2]}} \left(\frac{d[M_1]}{d[M_2]} - 1\right)$$
(2.108)

In KT method,  $d[M_1]/d[M_2]$  is equated to the final copolymer composition, and the ratio  $[M_1]/[M_2]$  is taken as initial monomer composition. Therefore, while  $d[M_1]/d[M_2]$  obtained from the final polymer ratio is already a cumulative average of the polymerization process, the initial monomer molar ratio used as  $[M_1]/[M_2]$  is not the average value for the whole reaction. But, in EKT method, average values of copolymer (y) and monomer ( $\overline{x}$ ) compositions are used. For this reason, EKT method is applicable at moderate conversions. Thus,

$$F = \frac{y}{z^2}$$
  $G = \frac{y-1}{z}$  (2.109)

 $\alpha$ , which enables to distribute the data uniformly in the (0,1) interval, can be described as;

$$\alpha = \sqrt{F_m F_M} \tag{2.110}$$

where  $F_m$  and  $F_M$  are the lowest and the highest values of  $(F = y/z^2)$ .

According to Equation (2.106), when  $\xi$  values calculated from the experimental data is plotted versus  $\eta$  values, a straight line is obtained and the intercepts gives  $-r_2/\alpha$  at  $\xi=0$  and  $r_1$  at  $\xi=1$ . The EKT method used widely is the exact solution for ideal copolymerization [104].

#### 2.4.3.3. Non-Linear Methods

All copolymerization reactions show a drift in the monomer ratio as the degree of conversion increases except azeotropic conditions. Above mentioned methods become increasingly sensitive to composition drift as the reactivity ratios differ more and more. For widely differing reactivity ratios, these methods are usable only for very low conversion ratios. On the other hand, in processes where the reaction proceeds very rapidly, termination at a very low fixed conversion may not be possible. Furthermore, results obtained at the time when the polymerization is just

beginning may be misleading. Although EKT is applicable at moderate conversion, there are some deviations from this method. With these problems, it becomes impossible to calculate the reactivity ratios reliably by linear methods.

Some nonlinear methods such as the nonlinear least squares (NLS) and the error in variables method (EVM) developed later to be used at moderate conversions and have also been used at low conversion to reduce the errors. In data analysis, nonlinear fitting methods are gradually replacing the older, linearized techniques of finding the reactivity ratios. Note that even in nonlinear methods based on the solution of the Mayo-Lewis (ML) equation a degree of approximation stemming from the steady-state assumption of Mayo and Lewis is involved.

Many investigators have shown that nonlinear methods, minimizing chi square ( $\chi^2$ ) and taking error propagation and individual errors on each of the measurements into account, are superior in error handling [105-108]. They avoid much of the distortion of the error structure and have the smaller and better defined regions for a given percentage probability.

In particular EVMs [109-113] take into consideration errors in all measurements.

A recent EVM is developed especially for online method [14, 21]. To obtain the reactivity ratios, the data are fitted to a numerical solution of the copolymerization equation (2.92) of the form

$$[M_1]_{the} = f([M_2], [M_1]_0, [M_2]_0, r_1, r_2)$$
(2.111)

where  $[M_1]_{the}$  is the "theoretical" concentration of monomer  $M_1$  at the *i*<sup>th</sup> data point of the *j*<sup>th</sup> experiment, corresponding to a measured concentration of the other monomer  $[M_2]_{ij}$ , initial concentrations  $[M_1]_{0j}$  and  $[M_2]_{0j}$  and the reactivity ratios  $r_1$  and  $r_2$ .

This equation can be written as,

$$Q_{ij} = [M_1]_{ij} - f([M_2]_{ij}, [M_1]_{0j}, [M_2]_{0j}, r_1, r_2) = 0$$
(2.112)

where Q is a measure of the "distance" of the theoretical  $[M_1]_{the}$  from the experimental  $[M_1]$ . The  $\chi^2$  value corresponding to this set of parameters,  $r_1$  and  $r_2$ ,

is then obtained by summing the ratio of the square of this distance to the variation of Q at that data point,  $Var(Q_{ij})$ .

$$\chi^{2}(r_{1}, r_{2}) = \sum_{j=1}^{n(\exp)} \frac{\sum_{i=1}^{n(data)_{j}} Q_{ij}^{2}}{Var(Q_{ij})}$$
(2.113)

The sum runs over all data points in all experiments. Since, not just the best fit parameters, but the statistically acceptable part of the parameter space is important, the whole parameter space is scanned by repeating the procedure for each pair of  $r_1$  and  $r_2$  within the search zone. The  $\chi^2$  contours are plotted as functions of the reactivity ratios for each individual experiment. The contours for the combined results of all experiments are also plotted. They show the acceptable region in the  $r_1$ ,  $r_2$  parameter space.

### 2.4.4. Composition Drift

All copolymerization reactions exhibit a composition drift in the monomer ratio with conversion except azeotropic conditions. As the more reactive monomer incorporates into the copolymer faster, the feed composition drifts during the reaction. This drift is an undesirable effect and must be compensated for in-batch methods. However, in on-line methods, the composition drift is continuously monitored and it can be used to give a rough idea of the reactivity ratios before any numerical computation is performed. The composition of the material incorporating instantaneously into copolymer is found from the instantaneous monomer composition and its derivative.

Let  $f_{1,inst}$  be the instantaneous  $M_1$  fraction in the feed mixture when conversion is x, and  $F_{1,inst}$  be the  $M_1$  fraction in the amount dx that incorporates into copolymer at this instant. The amount of  $M_1$  in the feed mixture is equal to  $(1-x)f_{1,inst}$  and that of  $M_2$  is written as  $[(1-x)(1-f_{1,inst})]$ . The dx contains  $dx(F_{1,inst})$  amount of  $M_1$  and  $dx(1-F_{1,inst})$ of  $M_2$ . Therefore,

After a change for dx in the conversion, the amount of  $M_1$  and  $M_2$  are thus given by,  $[f_{1,inst}(1-x)]-[F_{1,inst}dx]$  and  $[(1-f_{1,inst})(1-x)]-[(1-F_{1,inst})dx]$ , respectively. So, the total amount of  $M_1$  and  $M_2$  monomers can be expressed as [(1-x)-dx]. The new instantaneous  $M_1$  fraction in the feed mixture  $(f_{1,inst,new})$  is described as;

$$f_{1,inst,new} = \frac{f_{1,inst}(1-x) - F_{1,inst}dx}{(1-x) - dx}$$
(2.114)

And the derivative of the instantaneous fraction with respect to conversion yields:

$$\frac{df_{1,inst}}{dx} = \frac{f_{1,inst,new} - f_{1,inst}}{dx} = \frac{1}{dx} \left[ \frac{f_{1,inst} \left( 1 - \left[ \frac{dx}{1 - x} \right] \frac{F_{1,inst}}{f_{1,inst}} \right)}{\left( 1 - \left[ \frac{dx}{1 - x} \right] \right)} - f_{1,inst} \right]$$
(2.115)

This equation (2.115) can be solved for  $\frac{df_{1,inst}}{dx}$ :

$$\frac{df_{1,inst}}{dx} = -\frac{1}{1-x}(F_{1,inst} - f_{1,inst})$$
(2.116)

Therefore, If  $F_{1,inst} \neq f_{1,inst}$ , the composition drifts. If the monomer composition is continuously monitored,  $f_{1,inst}$  and its derivative to conversion can be used to obtain the composition of the material joining the copolymer instantaneously as [14, 22, 24],

$$F_{1,inst} = f_{1,inst} - (1-x)\frac{df_{1,inst}}{dx}$$
(2.117)

## 2.4.5. Stockmayer Bivariate Distribution

In statistical copolymerization, the copolymer chain length is finite and the individual chains don't have identical chemical compositions and chain lengths. Therefore, even within the polymer chains produced in a very small time interval (instantaneously), there exists a bivariate distribution of composition and chain length [114]. Unlike the results of Simha and Branson [91], Stockmayer [23] suggested an expression called the Stockmayer bivariate distribution. He proposed that when the monomer feed composition, the mean molecular weight and composition of the fraction polymerized are known, both the composition and chain length distributions can be obtained. In his theoretical model, the weight fraction of the part, with chain length ( $\nu$ ) and composition deviation  $u = (\Phi_l - F_l)$ ,  $w(\nu, u)$  is given by

$$w(v,u)dvdu = \left[\exp(-v/l^{*})(1 - \beta_{com} + \beta_{com}v/l^{*})vdv/l^{*2}\right]$$

$$\left[\sqrt{1/2\pi F_{1}F_{2}Q}\right]\exp(-vu^{2}/2F_{1}F_{2}Q)du$$
(2.118)

where

$$Q = (1 - 4F_1F_2(1 - r_1r_2))^{1/2}$$
(2.119)

 $\Phi_l$  is the molar fraction of  $M_l$  monomer units in an individual chain and  $\beta_{com}$  is the fraction of chains terminating by combination. The variable *l* is the length of a chain in monomer units,  $l^*$  is the number-average length of live radical chains. When  $\beta_{com}$  is 0,  $l^*$  is equal to  $(M_{w,inst}/m_{mon})/2$  and when it is 1, ,  $l^*$  is  $(M_{w,inst}/m_{mon})/3$ . For general case, ,  $l^*$  can be expressed as

$$l^{*} = \frac{(4 - \beta_{com})}{(8 + \beta_{com})} \frac{M_{w,inst}}{m_{mon}}$$
(2.120)

where  $(M_{w,inst}/m_{mon})$  is the ratio of  $M_w$  of the fraction polymerized at a specific instant to the average molecular weight of the comonomers,  $m_{mon}$ .

In actual polymerization, all concentrations are functions of time or, equivalently, of the degree of conversion. For this reason, the formula of Stockmayer is valid only for the instantaneous values during a reaction. To find the bivariate distribution of the result polymer, Stockmayer's *w* function must be integrated over the conversion.

#### 2.5. Monitoring of Polymerization Reactions

Methods for determining the reaction kinetics, with few exceptions call for a set of experiments with different initial monomer compositions which are terminated at a certain moment, then the polymer is separated and its composition and coversion are obtained. In these methods each reaction yields a single data point.

Some methods make use of the data obtained during the reaction. Samples are removed either periodically as in sequential sampling methods [61, 93, 94,115] or the experiment is performed *in situ*. This methods allow multiple data points to be obtained from each experiment. On-line and *in situ* methods yield hundreds even

thousands of data points from each experiment, thus they enable the greatest possible amount of information to be extracted.

Efforts of the monitoring of polymerization reaction kinetics start with Flory [116], who investigated a glycol/dibasic acid polyesterification reaction. Flory withdrew reaction aliquots manually from the reaction vessel in every 10 minutes and calculated the molecular weight and rate constants with KOH titration. Ballard and van Lienden [117] calculated the initial polymerization rates of vinyl monomers with dilatometry by using the polymer and monomer densities.

Spectroscopic methods allow direct and easy measurements for the polymerization reactions. For example, Storey et al. [101] used *in situ* FTIR-ATR spectroscopy for the real-time monitoring of carbocationic polymerization of isobutylene. Aldridge et al. [118] examined the function of short-wavelength near infrared (SW-NIR) to monitor the percent conversion of methyl methacrylate *in situ* in a mold. NIR spectroscopy was utilized to monitor the monomer conversion on-line during the living anionic homopolymerization, of isoprene-styrene and their copolymerization [119]. Shaikh, Puskas and Kaszas presented an approach to measure the copolymerization reactivity ratios using real-time Fourier Transform Infrared (FTIR) monitoring [99]. Raman and FTIR spectroscopy was chosen a way for *in situ* monitoring for urethane formation [120]. In situ monitoring by fluorescence and UV spectrometers is proving useful measurements for monomer conversion [121].

Besides *in situ* methods, several on-line methods allow the features of the polymerization to be followed during the reaction. Raman spectroscopy was used to monitor the emulsion polymerization of vinyl acetate on-line [122]. Also, Lousberg et al [123] developed a technique for on-line determination of the conversion in a styrene bulk polymerization batch reactor using Near-Infrared spectroscopy. In some methods, a few devices such as densitometer, viscometer, and size exclusion chromatography were put on-line to a batch reactor to monitor the monomer conversion, viscosity as well as molecular weight during the reaction [124, 125].

ACOMP, standing for Automatic Continuous Online Monitoring of Polymerization Reactions, is a continuous method to provide an opportunity to monitor the monomer conversion, molecular weight, and other properties without existence of any chromatographic columns [18]. The principle of ACOMP is to remove a small amount continuously from the reactor and mix it with a much larger volume of solvent. Two individual pumps and high-pressure mixing is used in monitoring copolymerization reactions to overcome the tendency of the pump to draw more from the solvent reservoir as the viscosity of the reactor increases with conversion during the reaction [14,20]. The diluted polymer solution is then passed through a train of detectors comprising a light scattering (LS) detector, a single capillary viscometer, refractive index detector, and ultraviolet spectrophotometer (UV), respectively. Scheme and picture of ACOMP is given in Figure 2.1.





Figure 2.1 Automatic Continuous Online Monitoring of Polymerization System (ACOMP)

There are numerous applications of ACOMP. Automatic Continuous On-line Monitoring technique has been used to follow the chain transfer kinetics in free radical polymerization [126]. Absolute online monitoring technique is also applied to step-growth polymerization [127], and the chain-growth of polymerization of vinyl

pyrrolidone [18] and acrylamide in detail [19]. Then, ACOMP was extended to copolymerization of styrene-methyl methacrylate, including determination of composition, sequence length, molecular weight distribution, and subsequent determination of reactivity ratios [20]. Characterization of the nitroxide-mediated controlled radical homopolymerization [128] and copolymerization [129] are obtained by ACOMP, as well. Furthermore, polydispersity during the polymerization was monitored by ACOMP technique [130] and the online polymerization monitoring method was adapted to a homogenous continuous reactor to monitor steady-state approximation [131] and acrylamide polymerization in inverse emulsion [132]. In addition, Coupled use of *in situ* NIR and ACOMP was realized by Florenzano et al. [133]. Recently, synthesis of polyelectrolytic copolymers of acrylamide-acrylic acid at different pH and VB-Aam copolymerization system were studied by ACOMP and investigated the effect of medium pH on the reactivity ratios [14,17,22].

## 2.5.1. Light Scattering [88]

Light scattering is one of the mostly used methods to determine the weight average molecular weight for different systems [19, 20, 61, 134-136]. The light scattering by the small particles is a phenomenon we observe in the daily life, i.e, the blue colour of the sky or the varied colour of a sunset, the poor penetration of car headlights in a fog is caused by water droplets scattering the light. Therefore, the scattering of light has interested many scientists. Historically, the first scientist to discuss the scattering of the light from small molecules was Leonardo da Vinci. Nearly 350 years later, scientific investigations of light scattering was clarified by Rayleigh in 1871 who studied the light scattering by gas molecules. Later Einstein in 1910 and Smoluchowski in 1908 developed the theory to liquids and they expounded scattering in liquids by the principle of the local thermal density fluctuations in the medium. Debye in 1944 developed the basis theory for solutions and exposed the relationship between the fluctuations and osmotic pressure.

For gases, Rayleigh proposed the reduced intensity of the scattered light  $I_r$  at any angle as;

$$I_r = \frac{I_\theta}{I_0} r^2 \tag{2.121}$$

 $I_r$  is often called Rayleigh ratio. Where  $I_0$  is the intensity of incedent light,  $I_{\theta}$  is the intensity of the scattering light at angle  $\theta$ , and r is the distance of the detector from the scattering sample. This is valid for a gas, where all the particles are considered to be independent scattering centres.

When a solute is dissolved in a liquid, it is useful to define a so-called Rayleigh ratio. Because, light scattering from a solution is arised from the scattering from local density fluctuations and scattering from the solvent. Therefore, the reduced angular scattering intensity of the solute is given by;

$$I_r = I_r(solution) - I_r(solvent)$$
(2.122)

The difference in scattering between the solution and the pure solvent is  $I_r$ , and for the molecules having dimensions less than  $1/20^{\text{th}}$  of the wavelength of the light, this can be related to the concentration and the molecular weight by

$$\frac{Kc}{I_r} = \frac{1}{M_w} + 2A_2c + \dots$$
(2.123)

where c is the polymer concentration,  $\overline{M}_{w}$  is the weight average molecular weight, and  $A_{2}$  is the second virial coefficient. Higher terms become insignificant for dilute solutions. K is the optical constant, given for vertically polarized incident light by

$$K = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4}$$
(2.124)

where  $n_0$  is the solvent index of refraction,  $\lambda$  is the vacuum wavelength of the incident light,  $N_A$  is Avogadro's number, and  $(\delta n/\delta c)$  is the differential refractive index of the polymer in the pure solvent. These two equations are valid for incident light polarized in a plane perpendicular to the plane defined by the incident and scattered light beams. If the light used is unpolarized,  $I_r$  should be corrected by a factor  $(1+cos^2\theta)^{-1}$ , where  $\theta$  is the angle between the transmitted beam and the scattered beam.

In a solution with very small particles scattering as point sources, the destructive interference of the light scattered from many sources decreases the intensity of the scattered beam. When polymer dimensions are greater than  $\lambda/20$ , the interparticle

interference causes the scattered light from two or more sources to arrive considerably out of phase, and this effect on the scattered light will be a function of the scattering angle  $\theta$ :

$$\frac{Kc}{I_r} = \frac{1}{M_w} + \frac{1}{M_w} \left[ \left( \frac{16\pi^2}{3\lambda^2} \right) n_0^2 \sin^2(\theta/2) < \overline{S}^2 >_z \right] 2A_2c + \dots$$
(2.125)

where  $\langle \overline{S}^2 \rangle_z$  is the mean-square radius of gyration, which is defined as an average distance from the centre of gravity of a polymer coil to the chain end. From equation (2.125), the magnitude of the scattering wave vector q, has its usual definition:

$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right)$$
(2.126)

Therefore, Equation (2.158) becomes

$$\frac{Kc}{I_r} = \frac{1}{M_w} \left[ 1 + \frac{q^2 < \overline{S}^2 >_z}{3} \right] + 2A_2c + \dots$$
(2.127)

By treating light scattering data,  $M_w$ ,  $\langle \overline{S}^2 \rangle_z$ , and  $A_2$  can be determined by the method of Zimm [137] in which  $Kc/I_r$  is plotted versus  $kc + sin^2 (\theta/2)$ , where k is an arbitrary constant used in plotting the data. In the Zimm method, there are curves corresponding to constant concentration and to constant angles. Each plot extrapolated to zero angles gives a point on the line  $Kc/I_r = 1/M_w + 2A_2c$  and the slope of  $\theta = 0$  line is used to calculate  $A_2$  and  $M_w$ . Similarly, each data set extrapolated concentration gives a point to zero on the line  $Kc/I_r = 1/M_w + (q^2 < \overline{S}^2 >_z)/3$ . Therefore the slope of c = 0 line is used to calculate radius of gyration and  $M_w$ .

### 2.5.2. Viscosity

The determination of viscosity plays a very important role in the study of polymers [35]. By using simple viscosity measurements, a viscosity average molecular weight

can be determined for the polymer and some information can be obtained about general form or structure of macromolecules in the solution.

The viscosity of a polymer solution depends on the temperature, the nature of the solvent and polymer, polymer concentration, and the sizes of the polymer molecules. The viscosity of dilute polymer solution is higher than the viscosity of the pure solvent. The ratio of flow time of a polymer solution to that of the pure solvent is equal to the ratio of their viscosities. It is called relative viscosity and given as follows;

$$\eta_r = \frac{t}{t_0} = \frac{\eta}{\eta_0} \tag{2.128}$$

where t and  $t_0$  are the flow times for the solution and pure solvent, respectively. Similarly,  $\eta$  and  $\eta_0$  are the viscosity of solution and solvent, respectively. Since relative viscosity has a limiting value of unity, the specific viscosity is a more useful quantity and expressed as:

$$\eta_{sp} = \eta_r - 1 = \frac{(t - t_0)}{t_0} \tag{2.129}$$

Molecules even in dilute solutions can interact. Therefore, in order to measure the influence of an isolated polymer coil,  $\eta_{sp}$  can be expressed as a reduced quantity  $(\eta_{sp}/c)$  and extrapolated to c = 0 according to relation

$$\frac{\eta_{sp}}{c} = \left[\eta\right] + k' \left[\eta\right]^2 c \tag{2.130}$$

The intercept gives the intrinsic viscosity  $[\eta]$  and k is a hydrodynamic constant as well as called Huggins constant and equal to about 0.4 for neutral, random coil polymers [138]. Total solution viscosity is

$$\eta = \eta_0 \left[ 1 + [\eta] c + k' [\eta]^2 c^2 \right]$$
(2.131)

The intrinsic viscosity can be related to molecular weight by means of a relation exposed by Mark and Hauwink.

*K* and *a* values can be determined experimentally. K depends on the type of polymer, solvent and temperature whereas *a* depends on polymer-solvent interactions. Mark-Houwink constants for different polymer-solvent pairs can be found in the literature [139].

## 2.5.3. Refractive Index

The light changes its speed when it passes from one medium to another one. Unless the light comes into the medium at an angle not perpendicular to the surface, it undergoes the refraction. Therefore, the refractive index (RI) of a medium is known as its ability to refract the light. Refractive index is expressed as the ratio of the velocity of the light in vacuum to that of light in a medium.

Before calculating  $M_w$  using light scattering measurements,  $\delta n/\delta c$ , which is the differential refractive index for the polymer in the chosen solvent, must be known. It is also expressed as follows;

$$\frac{(n-n_0)}{c} = \frac{\Delta n}{c}$$
(2.133)

where, n and  $n_0$  are the refractive indices of the solution and the solvent, respectively, and c denotes the concentration of polymer solution. The aim of a differential refractometer detector is to measure the differences in refractive index (RI) between a reference solution and a sample solution. This difference in RI is known as  $\Delta n$ .

By using a refractive index detector, it is possible to calculate the concentration of the species present in the solution by the equation given below [20, 134].

$$(V_{RI}(t) - V_{RI,base})CF = \left(\frac{\delta n}{\delta c}\right)c(t)$$
(2.134)

and equation (2.134) can be solved for concentration at time t:

$$c(t) = \frac{(V_{RI}(t) - V_{RI,solv})CF}{\left(\frac{\delta n}{\delta c}\right)}$$
(2.135)

where *CF* is calibration factor of the refractometer ( $\Delta n$ /Volt), and  $V_{RI}$  (t) and  $V_{RI,solv}$  are the RI voltage observed at time *t* and the baseline voltage of the refractometer when pure solvent is flowing, respectively. If the solution has several components responsible for the refractivity, then, the refractivity of the solution is the sum of the refractivities of the components, i.e., monomer and corresponding homopolymer in a homopolymerization.

### 2.5.4. Ultraviolet (UV) Spectroscopy

The absorption intensity described by Lambert-Beer is a more convenient expression. This law exhibits a relationship between the transmittance, the sample thickness, as well as the concentration of the species absorbing. This expression is given by;

$$\log(I_0 / I) = UV = \left(\frac{\partial V_{UV}}{\partial c}\right) c b_{cell}$$
(2.136)

where  $I_0$  is the intensity of the radiation striking the sample and I is the intensity of the radiation emerging from the sample. UV is referred to absorbance, c is molar concentration of the solution, and  $b_{cell}$  is the path length through the sample.  $\left(\frac{\partial V_{UV}}{\partial c}\right)$  is defined as UV extinction coefficient and it is constant for a certain wavelength.

Also, the intensity of the absorption can be expressed as transmittance (T), defined by;

$$T = \frac{I}{I_0}$$
(2.137)

Absorbance can be expressed in term of transmittance as follows;

$$UV = -\log(I/I_0) = \log(1/T) = -\log T$$
(2.138)

Generally transmittance is expressed as percentage, then absorbance becomes

$$UV = 2 - \log T\%$$
 (2.139)

In a solution, at a specific  $\lambda$  wavelength, more than one species have the absorption, the total absorbance for the specific wavelength is the sum of the absorbance of the species. The concentrations of the two comonomers in their monomeric form as well as their concentrations incorporated into the polymer are computed by using UV data from ACOMP [14,17,22].

# 2.6. Automatic Continuous Mixing (ACM) [39]

The automatic continuous mixing (ACM) technique allows a continuous gradient of solution components to be formed along a desired path in composition space, using two or more solution reservoirs. The properties of the continuously varying solutions can be measured by an appropriate train of detectors. It is required that the mixed sample be in equilibrium or quasi-equilibrium. This latter restriction means that properties of the mixed solution at any instant do not change during the interval from mixing to measurement.

The picture of ACM is given in Figure 2.2. The ACM technique is realized using a pump with a gradient mixer attached. The sample then passes through a light scattering detector followed by a single capillary viscometer, UV-Vis detector and a refractometer.



Figure 2.2 Automatic Continuous Mixing (ACM)
The data is collected and analyzed. Values of the varying solute concentration, whether salt or polymer, can be measured during ACM experiments using the refractometer. Also, ACM allows even small changes in scattering and viscosity behavior to be monitored.

### **3. EXPERIMENTAL WORK**

### **3.1 Chemicals**

In the experiments of 4-vinylbenzenesulfonic acid sodium salt (VB) - Acrylamide (Aam) copolymerization system, VB and Aam were obtained from Fluka. Copolymerizations were initiated in aqueous solution at 60 °C, with 2,2'-Azobis(2-amidinopropane)dihydrochloride (V50) from Aldrich. They are used as received. In Acrylic acid (Aac) - Acrylamide (Aam) system, Aac and Aam were used as

received from Aldrich. In this study, the initiator was 4,4'-Azo bis (4-cyanovaleric acid) (ACV) from Aldrich.

Sodium hydroxide (NaOH) from Aldrich was used to set the pH and 0.1M Sodium Chloride (NaCl from Aldrich) solution was used as the carrier solvent. HPLC grade ethanol, methanol, aseton were received from Merck. Polydiallyldimethyl ammonium chloride used in centrifugal experiments (IEC Centra 4B model centrifuge instrument) was synthesized in our laboratory using diallyldimethyl ammonium chloride (DADMAC) received from Aldrich. Other polymer used for verification of copolymer formation in the Aac – Aam experiments was Poly-L-Lysine Hydrobromide from Sigma. Water was deionized and filtered by a 0.22  $\mu$ m filter in a Modulab UF/UV system. All monomer and polymer solutions used in the experiments as well as the other measurements were filtered by 0.22  $\mu$ m Millex- GS filter. Chemical structures and molecular weights of the materials used in this work were given in Table 3.1.

### 3.2. Instruments

• UV Spectrophotometer used for Sequential Sampling Method: An Hewlett Packard Array 8452A model spectrophotometer were used to measure the absorbance of aliquots removed from the diluted reactor solution after having passed thorough the detector train of ACOMP to compare the results of ACOMP with an off-line UV spectrophotometer performing in range from 190 to 800 nm. 1 mm path length cell was used in the measurements.

 pH meter: In Tulane University, Beckman Φ45 model pH meter was used to measure pH of the reaction medium. WTW model pH meter was used in the experiments performed in İstanbul Technical University

### • ACOMP Set in Tulane University

**1. Isocratic Pumps:** Two Agilent 1100 HPLC isocratic pumps controlled by a computer were used. Whereas one of them removed a small amount of reactor solution, the other one drew a much larger volume of a pure solvent from solvent reservoir.





 Light Scattering Detector: Light scattering measurements were made by a home-built seven-angle absolute light scattering detector. LS detector used vertically polarized diode lasers operating at a wavelength 677 nm.



Figure 3.2 Home-built seven-angle absolute light scattering detector developed by Wayne F. Reed and his group

**3. Viscometer Detector:** A single capillary viscometer (Validyne DP 15-36 differential pressure sensor) were used to measure the viscosity of the diluted reactor solution.



Figure 3.3 Validyne brand single capillary viscometer

4. UV Detector: Dual wavelength Shimadzu SPD 10AV-VP model UV spectrophotometer detector with a 0.1 mm path length cell was used to measure the absorbance during the reaction (to monitor rhe disappearance of monomer during the reaction). UV detector was operated at 206 nm and 260 nm for VB-Aam system and at 205 nm and 226 nm for Aac-Aam system.



Figure 3.4 Shimadzu SPD 10AV-VP model UV detector

**5. Refractive Index Detector:** Waters 2410 differential refractometer was used as refractive index detector.



Figure 3.5 Waters 2410 model refractive index detector

 ACM Set in Tulane University: ACM contains a Schimadzu LC-10AD VP pump with a gradient mixer attached. δn/δc values of polymers were measured by Shimadzu RID 10A differential refractometer.

### • ACOMP Set in İstanbul Technical University

- **1. Isocratic Pumps:** Two Agilent 1100 brand HPLC pumps conrolled by a computer were used during the studies in ITU.
- Light Scattering Detector: Brookhaven Instruments (BIMwA) multi angle light scattering detector were used for light scattering measurements. LS detector with seven angles used vertically polarized diode lasers of vacuum wavelength 677 nm



Figure 3.6 Brookhaven Instruments (BIMwA) light scattering detector

- **3. Viscometer Detector:** A single capillary viscometer (Validyne DP 15-36 differential pressure sensor) were used.
- **4. UV Detector:** Dual wavelength Shimadzu SPD 10AV-VP model UV spectrophotometer detector was used.
- **5. Refractive Index Detector:** Refractive index measurements were made through Shimadzu RID 10A differential refractometer.



Figure 3.7 Shimadzu RID 10A differential refractometer

Material	Molecular Weight
	(g/mole)
4-vinylbenzenesulfonic acid sodium salt (VB) $CH_2 = CH$ O = S = O	206.20
Acrylamide (Aam) $CH_2 = CH$ $CH_2 = 0$ $NH_2$	71.10
Acrylic acid (Aac) $CH_2 = CH$ $CH_2 = 0$ OH	72.06
2,2'-Azobis(2-amidinopropane)dihydrochloride (V50) $\begin{array}{c} CH_3 \\ Cl \ NH_2 \end{array} = C \xrightarrow{C} C \xrightarrow{C} C \xrightarrow{N} N = N \xrightarrow{C} C \xrightarrow{C} C \xrightarrow{NH_2} 0 \\ NH_2 \ CH_3 \\ NH_2 \ CH_3 \\ CH_3 \end{array} = N \xrightarrow{C} C \xrightarrow{R} N \xrightarrow{R} N \xrightarrow{C} C \xrightarrow{N} N \xrightarrow{R} $	271.17
4,4'-Azo bis (4-cyanovaleric acid) (ACV) $HO - C - (CH_2)_2 - C + N = N - C + (CH_2)_2 - C - OH$ $C - (CH_2)_2 - C - OH + C + (CH_2)_2 - C - OH$	280.29
Sodium hydroxide (NaOH)	40.00
Sodium Chloride (NaCl)	58.40

Table 3.1 Chemical Materials Used in VB-Aam and Aac-Aam (  $pH\ 2$  ,  $pH\ 3.6$  and  $pH\ 5)$  Copolymerization Systems

### **3.3. The ACOMP System**

Polymerization and copolymerization experiments were monitored by ACOMP (Automatic continuous on-line monitoring of polymerization reactions). In the ACOMP technique, a small amount of solution is continuously withdrawn from the reactor by an isocratic pump and mixed with a much larger volume of pure solvent drawn from a reservoir, in the mixing chamber. The diluted polymer solution is sent through a train of detectors comprising a light scattering detector, a single capillary viscometer (Validyne differential pressure sensor), an ultraviolet detector (UV, Shimadzu SPD-10AV) and a refrective index (RI) detector. During the experiments performed in Tulane, a home-built seven-angle absolute light scattering [18] intensity monitor was used as light scattering detector and Waters 2410 differential refractometer was used as refractive index detector. In the ACOMP set used in ITU, Brookhaven Instruments (BIMwA) multi angle light scattering detector and Shimadzu (RID 10A) differential refractometer were used. The pumps are used to adjust the dilution factor before the reaction. Material concentration should be kept around 1 mg/ml level in the detector solution, in order to obtain a measurable signal at the UV and RI detectors without causing them to overflow. Depending on the reaction type one or two pumps are used. During copolymerization, two individual pumps and high-pressure mixing was preferred over a single pump and low-pressure mixing to overcome the tendency of the pump to draw more from the solvent reservoir as the viscosity of the reactor increased with conversion. Still, it was necessary to terminate the reaction when the increase of viscosity of the reactor solution caused the reactor side pump to de-prime. Hence, 100% conversion was not achieved in the reactions.

### 3.3.1 Normalization and Calibration of Light Scattering Detector

### 3.3.1.1 Normalization

Each detector responds differently to the scattered light, and may detect light from the different size scattering volumes. So, when multiple angle detectors are used, they must be normalized before starting the measurements. A normalization factor, N(q), is applied to all scattering angles. Normalization is a procedure where the response of each detector is scaled to the response of a detector chosen as the reference detector (generally, reference detector is the 90<sup>0</sup> detector). For normalization, firstly, a normalization solution known as a Rayleigh scatterer is chosen. A Rayleigh scatterer is any particle or molecule which has a characteristic size much smaller than the wavelength of the light, that is,  $d(\text{diameter}) << \lambda$ . Aqueous normalization solution can include low molecular weight dextran or polyethylene oxide. The concentration of the normalization solution should be high enough to obtain a scattering signal well above the pure solvent level. After choosing the normalization solution, the definition of N(q) is given as follows;

$$N(q) = \frac{V_n(q_r) - V_s(q_r)}{V_n(q) - V_s(q)}$$
(3.1)

where  $V_n(q_r)$  and  $V_s(q_r)$  are the scattering voltages from the normalization solution and pure solvent, in which the normalization solution is prepared, at the scattering vector  $q_r$  corresponding to the reference angle  $\theta_r$ , respectively.  $V_n(q)$  and  $V_s(q)$  are the normalization and pure solvent scattering voltages at angle  $\theta$ , respectively [9].

#### 3.3.1.2 Calibration

Calibration is required to determination of the absolute Rayleigh scattering ratio of the polymer in solution obtained by subtracting the pure solvent scattering, and relating the scattering detector voltages to the known absolute Rayleigh ratio ( $I_a$ .) of a reference scatterer. Toluene generally used as a reference scatterer, has Rayleigh ratio measured as 1.069x10<sup>-5</sup> cm<sup>-1</sup> at 677 nm at 25 <sup>o</sup>C. The absolute Rayleigh scattering ratios are determined according to;

$$I(q) = \frac{V(q) - V_s(q)}{V_a(q_r) - V_d(q_r)} N(q) F I_a$$
(3.2)

where  $V_a(q_r)$  and  $V_d(q_r)$  are the scattering voltages of the calibration reference solvent and the dark voltage at the reference angle  $\theta_r$ , respectively. *F* is a geometrical optical correction factor and accounts for refractive index differences between the refractive indices of the calibration solvent and the solvent used in the preparation of the sample solutions. Therefore, it is used when the samples are not in the same solvent as the absolute calibration solvent. *F*=1 if the sample and absolute reference solvent are the same. For aqueous solution, F=0.944 when toluene is used as calibration solution [140].

Normalization and calibration procedures automatically subtract out the constant stray light arising from glaring of misaligned laser beam, optical dirtiness, etc, and being most pronounced at very low and very high scattering angles. Since absolute value of  $M_w$  depends on the calibration parameters, care should be taken in calibration process.

Once calibrated, the light scattering detector can remain calibrated for many months unless impurities, salts, or polymer are allowed to dry inside the chamber in the instrument. Therefore, calibration was performed always before starting the new series of experiments. A nominal 20 nm diameter polystyrene latex sphere in 20 mL of deionized water was chosen as the normalization solution whose stock concentration is 1% solids. All solutions were filtered by appropriate filters (0.22  $\mu$ m) after flushing the filter with 20 mL of liquid. The solutions were injected to the light scattering detector by using a syringe pump at a flow rate of 1 mL/min. Firstly, the dark voltage, which is the voltage from the detector when no light is incident on it, was measured for all detectors and, later, the pure solvent was injected to obtain its scattering voltage  $(V_s(q))$ . After that, normalization solution passed through the detector to determine the scattering voltage from the normalization solution  $V_n(q_r)$ . By using the scattering voltages arising from the normalization solution and the pure solvent, normalization coefficients (N(q)) for all angles were calculated with Equation (3.1). From Equation (3.1),  $90^{\circ}$  is the angle where the N(q) is exactly 1. Then, the system is cleaned from the normalization solution with deionized water. Before going from water to toluene, the detectors were washed by acetone, which is an intermediate solvent. Then, the system was flushed with toluene until stability was attained. The last steps were to pump acetone through the detectors to clean toluene traces and water to clean the system completely, respectively. The steps in the normalization and calibration process for the  $90^{\circ}$  detector are shown in Figure 3.8. The scattering voltages from the detectors were determined in all steps and the normalization factors were calculated for all angles given in Table 3.2.

Detector	Dark	Solvent	Sphere	Toluene	N(q)
	Voltage (V)	Voltage (V)	Voltage (V)	(V)	
39	0	3.6202	8.9861	1.8084	1.0263
56	0	0.4099	3.6990	0.72651	1.6744
73	0	0.11774	3.6461	0.80273	1.5609
90	0	0.13109	5.6383	1.2328	1.0000
107	0	0.13324	4.6635	1.0039	1.2157
124	0	0.37839	7.2276	1.5845	0.80407
141	0	0.95095	8.7334	1.8722	0.70764

 Table 3.2 Scattering voltages and normalization factors for all angles



Figure 3.8 The steps in the normalization and calibration process

Time intervals in normalization and calibration process are given below;

0-3000	sec = solvent baseline
3000-4320	sec = 20 nm polystyrene latex sphere (concentration = $c_1$ )
4320-6420	sec = 20 nm polystyrene latex sphere (concentration = $c_1/2$ )
6420-8100	sec = water baseline to rinse
8100-9720	sec = acetone as intermediate solvent
9720-12160	sec = toluene as calibration solvent
12160-16700	sec = acetone as intermediate solvent
16700-26000	sec = water to rinse

The scattering voltage of toluene, the dark voltage and the normalization coefficients (N(q)), found by means of calibration process in light scattering detector, were used to calculate the Rayleigh scattering ratios at individual angles, which enabled to calculate  $M_w$  in copolymerization reactions according to Zimm equation [137].

### 3.3.2 Calibration of Refractive Index Detector

One of the detectors in ACOMP system is refractometer (RI). The refractive index detector voltage obtained from the refractometer by,

$$(V_{RI}(t) - V_{RI,solv}) = \frac{\left(\frac{\delta n}{\delta c}\right)c(t)}{CF}$$
(3.3)

and Equation (3.3) can be solved for concentration at time t:

$$c(t) = \frac{(V_{RI}(t) - V_{RI,solv})CF}{\left(\frac{\delta n}{\delta c}\right)}$$
(3.4)

where CF is calibration factor of the refractometer ( $\Delta n/Volt$ ), and  $V_{RI}$  (t) and  $V_{RI,solv}$ are the RI voltage observed at time t and the baseline voltage of the refractometer when pure solvent is flowing, respectively.  $\delta n/\delta c$  is the differential refractive index for the polymer in the chosen solvent. The differential refractive index of a polymer / solvent pair is one of the important parameter to determine the concentration of the components and to calculate the absolute molecular weight by light scattering measurements. Before the measurements, the RI was calibrated by NaCl whose  $\delta n/\delta c$ is known to be  $0.174 \text{ (cm}^3/\text{g})$  to determine the calibration factor of the instrument. For this reason, the solutions of NaCl of different concentrations were prepared in deionized water. Firstly, deionized water as solvent was pumped through the detector by using an isocratic pump to obtain the solvent baseline. After stabilization, NaCl solutions were pumped at a flow rate of 2 ml/min for almost 20 minutes, that is, until obtaining stability, in the order from more dilute solution to more concentrated one, and the baseline of each solution was taken (Figure 3.9). The output voltages  $(V_{RI})$ measured for each solution were recorded through a computer. The concentrations of NaCl solutions and refractive index voltages  $(V_{RI,sol})$  due to these solutions, which were determined by taking the arithmetic mean of the baselines, are given in Table

3.3.  $(V_{RI,sol} - V_{RI,solv})$  vs  $c_{NaCl}$  (M) was plotted to obtain the slope referring to  $(\delta n / \delta c)_{NaCl} / CF$  as shown in Figure 3.10.

$c_{NaCl}$ (g/ml)	$V_{RI,sol}\left(\mathbf{V} ight)$	$(V_{RI,sol} - V_{RI,solv})$ (V)
0 (water)	0.0097656	0
$C_1 = 0.0050630$	1.1270	1.11720
$C_2 = 0.0030050$	0.67578	0.66601
$C_3 = 0.0020060$	0.45410	0.44433
$C_4 = 0.0015060$	0.34578	0.33601
$C_5 = 0.0005015$	0.12207	0.11230

Table 3.3 NaCl Concentrations and Refractive Index Voltages (V<sub>RI,sol</sub>)



Figure 3.9 Raw refractive index voltages obtained from RI detector for sodium chloride solutions of various concentrations ( $c_{NaCl}$ )



**Figure 3.10** The plot of  $(V_{RI,sol} - V_{RI,solv})$  vs  $c_{NaCl}$  (M) to obtain the calibration factor (CF) of RI detector

Using the slope of the line in Figure 3.10 allowed CF to be found as 7.86903  $10^{-4}$  for scale # 32 which shows the sensitivity of Waters 410 refractometer, and 3.934515x10<sup>-4</sup> for scale # 64. The output voltage of the refractometer increases with increasing sensitivity. Also, different model refractive index detector (Shimadzu RID 10A differential refractometer) has a CF of 1.148  $10^{-3}$  for range 2.

### 3.4. Homopolymerization and Copolymerization Procedures

### **3.4.1. 4-** Vinylbenzenesulfonic Acid Sodium Salt (VB)- Acrylamide System [17, 22]

### 3.4.1.1. Determination of the Wavelengths Used in the UV Measurements

UV absorption spectra of VB, Aam, their homopolymers (PVB, PAam) and the initiator (V50) are given in Figure 3.11 in g/mL concentration. Thus, 206 nm and 260 nm were selected to operate the dual wavelength UV spectrophotometer during the polymerization reactions. Only VB absorption dominates in the 260 nm signal, and 206 nm signal is dominated by monomeric Aam and VB as seen in Figure 3.11. At 206 nm the contribution of the polymeric units (PVB, PAam) is minor, PAam doesn't have any absorbance at this wavelength. None of polymeric units has absorbance at 260 nm and by adding the initiator (V50), neither of the UV signals

changes, which indicates that the absorbance of V50 can be neglected at these wavelengths. Thus 206nm (refers to  $UV_1$ ) and 260nm (refers to  $UV_2$ ) were selected in UV detector to monitor the reactions and all species absorbances included in the calculations. The decrease of 206 nm and 260 nm signals serve as visual guides to Aam and VB conversions. The actual concentrations were calculated using the procedure described below.



**Figure 3.11** Values of absorbance/concentration in g/mL between the 200–300 nm range for VB, PVB, Aam, Paam and the initiator (V50) with UV cell with 1 mm pathlength

# **3.4.1.2.** Homopolymerization and Copolymerization of 4-Vinylbenzenesulfonic Acid Sodium Salt (VB) and Acrylamide (Aam) in 0.1M NaCl Solution [17, 22]

Homopolymerizations of VB and Aam and copolymerization of VB-Aam were monitored by the continuous, absolute, on-line monitoring technique, ACOMP. The experiments were carried out in 0.1 M NaCl solution and the same solution was used as the carrier solvent. Before the reaction, the monomer solution in reactor was purged for 30 minutes with N<sub>2</sub>. The reactor was a three-necked flask. A condenser was mounted to one of the arms, and, pH probe was inserted into the reactor through another arm. The last arm was used to insert the thermometer and system tubings. The reactor was placed into a temperature controlled bath at  $60^{\circ}$ C. The reactor solution was diluted with NaCl solution up to ~0.4mg/ml in the detector train. Before the reaction, the carrier solvent was pumped through the detector train consisting of light scattering, capillary viscometer, refractometer (RI), and a dual wavelength UV spectrophotometer having 0.1 mm path length. The baseline of each instrument was obtained.

After the stabilization of solvent baselines, for homopolymerization, one of the monomers send to the detectors and monomer baseline for each detector were obtained.

In the copolymerization, monomers were added into the reactor consecutively and first monomer baseline for only one monomer, then the baseline for the monomer mixture were obtained. When the reactor temperature reached  $60^{\circ}$ C, reaction was initiated by adding the V50 in a small amount of the degassed solution, which was taken from the reactor at  $60^{\circ}$ C. The reactor was stirred during the reaction and purged by N<sub>2</sub> slowly. The initial reactor and detector concentrations of the monomers used, pH's measured at the beginning of the experiment, after adding initiator, and at the end of the reaction are given in Table 3.4. The flow rates were kept constant throughout the experiment. The diluted solution always reached the detector train at 25°C, regardless of the reactor temperature. Two UV absorption measurements at 206nm and 260nm were used in monitoring conversion of the monomer to polymer. At the end of the reaction, the contents of the reactor were added into ethanol, and the polymer was precipitated for subsequent GPC and other measurements.

Exp.	%VB	in reactor in detector		in reactor		tector	in reactor (at 60 <sup>0</sup> C)
#		c <sub>vBSANa</sub> (M)	c <sub>Aam</sub> (M)	c <sub>V50</sub> (M) x10 <sup>-3</sup>	c <sub>VBSANa</sub> (M) x10 <sup>-3</sup>	c <sub>Aam</sub> (M) x10 <sup>-3</sup>	pH <sub>initial</sub> - pH <sub>afterV50</sub> - pH <sub>final</sub>
S 1	100	0.3636	0	2	2.5451	0	9.41-8.45- 7.82
S 2	75	0.2727	0.0909	2	2.3996	0.7999	10.3-9.21- 8.93
S 3	50	0.1808	0.1818	2	1.9898	1.9690	9.34-8.57- 8.03
S 4	25	0.0909	0.2727	2	0.9088	2.7270	9.26-8.27- 8.08
S 5	10	0.03636	0.3272	2	0.3636	3.2721	8.72-7.67- 7.90
S 6	0	0	0.3636	2	0	6.5448	8.86-7.96- 8.18

**Table 3.4** VB-Aam Copolymerization Reactions Performed in 0.1 M NaCl Solution  $(T=60^{\circ}C)$ 

### **3.4.1.3** Homopolymerization and Copolymerization of 4-Vinylbenzenesulfonic Acid Sodium Salt (VB) and Acrylamide (Aam) in Water

The same procedure was applied to VB-Aam copolymerization carried out at  $60^{\circ}$ C in water [17, 22]. In the experiments, the baseline stabilization period for pure solvent, the baseline of pure monomers were taken before adding initiator to define the coefficients used to calculate the comonomer concentration and its corresponding polymer amount during the reaction. After stabilization periods of the comonomers, the reactor was placed into a constant temperature bath at  $60^{\circ}$ C. When the temperature of the reactor solution reached to  $60^{\circ}$ C, initiator (V50, 2,2'-Azobis(2-amidinopropane) dihydrochloride) was added. In all reactions, sodium chloride solution of 0.1 M concentration was used as the carrier solvent in ACOMP to prevent the system with the capillary tubes to be plugged because of the polyelectrolytic nature of the copolymer. 206 nm and 260 nm UV wavelengths were used to monitor the polymerizations. Table 3.5 shows the parameters of the copolymerization reactions of VB and Aam performed in water.

Exp.	%VB		in reactor		in reactor in detector			in reactor (at 60 <sup>0</sup> C)
#		c <sub>vBSANa</sub> (M)	c <sub>Aam</sub> (M)	c <sub>V50</sub> (M) x10 <sup>-3</sup>	C <sub>VBSANa</sub> (M) x10 <sup>-3</sup>	c <sub>Aam</sub> (M) x10 <sup>-3</sup>	pH <sub>initial</sub> - pH <sub>afterV50</sub> - pH <sub>final</sub>	
W 1	100	0.1818	0	3.8	1.8187	0	9.02-8.07- 7.86	
W 2	50	0.1818	0.1818	2.0	1.8181	1.7995	9.68- 8.50 - 7.89	
W 3	25	0.0908	0.2727	2.0	0.9088	2.7270	9.21-8.44- 7.97	
W 4	15	0.0550	0.3091	2.0	0.5505	3.0907	8.73-7.57- 7.57	
W 5	10	0.0364	0.3272	2.0	0.3655	3.2723	8.57-7.38- 7.95	
W 6	5	0.0182	0.3453	2.0	0.1822	3.4533	7.71-6.81- 8.21	
W 7	1.5	0.0055	0.3582	2.0	0.0983	6.4467	5.91-5.14- 6.61	
W 8	0	0	0.1818	2.0	0	1.8179	6.30-5.91- 6.33	

**Table 3.5** VB-Aam Copolymerization Reactions Performed in Water  $(T=60^{\circ}C)$ 

## **3.4.2.** Copolymerization of Acrylic acid (Aac) – Acrylamide (Aam) at pH 5 and pH 2 in Water [14]

Before the polymerization reaction, the carrier solvent (0.1 M NaCl) was pumped through the detector train to obtain the baseline of each instrument. After stabilization, the comonomer mixture containing the Aam and Aac at predetermined pH, was pumped at a flow rate of 0.06mL/min from the reactor and diluted in mixing chamber with a flow of 1.94mL/min of the carrier solvent. These flow rates from the reactor and the solvent reservoir were maintained throughout the entire experiment. The diluted solution always reached the detector train at 25<sup>o</sup>C, regardless of the reactor temperature.

At the beginning of the reaction, reactor was purged for 30min with  $N_2$  and then was placed into a temperature-controlled bath at 60<sup>0</sup>C. Reaction was initiated by adding the 4,4'-Azobis (4-cyanovaleric acid) (ACV) in powder form. After adding the initiator, the pH was measured. The solution was magnetically stirred during the reaction. The amounts used, pH's measured at the beginning of the experiment, after the initiator addition and at the end of reaction are given in Table 3.6. Two UV

absorption measurements at 205nm and 226nm were used in monitoring conversion of the monomer to polymer.

Exp Code	Aac %	c <sub>Aac</sub> (M)	c <sub>Aam</sub> (M)	с <sub>NaOH</sub> (M)	c <sub>ACV</sub> *10 <sup>-3</sup> (M)	PH <sub>at 60</sub> °C – pH <sub>after initiator</sub> - pH <sub>final</sub>
Ι	0		0.47164	0.0025	8.917	8.30-5.20-5.08
II	10	0.04764	0.42289	0.04682	8.921	7.56- 4.95-5.14
III	23	0.11261	0.37585	0.09369	8.919	7.80- 5.01-5.23
IV	30	0.14135	0.32929	0.14102	8.917	7.34- 4.82-5.41
V	50	0.23506	0.23523	0.23521	8.916	7.37-5.02-5.67
VI	70	0.33039	0.14181	0.32851	8.920	7.20-5.10-6.62
VII	76	0.35736	0.11291	0.35688	8.916	7.20-5.20-6.68
VIII	90	0.42455	0.04732	0.42755	8.921	7.26-5.31-7.16
IX	100	0.46536		0.46534	8.920	7.22-5.29-7.41
X	50	0.23506	0.23523		8.925	2.22-1.58-2.34
XI	70	0.32877	0.14112		9.004	2.41-1.59-2.87

**Table 3.6** Parameters of Aac-Aam Copolymerization Reactions at pH 5 and 2 (Reaction temperature is  $T=60^{\circ}$ )

# **3.4.3.** Copolymerization of Acrylic acid (Aac) and Acrylamide (Aam) at pH **3.6** in Various Ionic Strength [24]

Three sets of experiments were performed. One set at total monomer concentration of 0.47mol/L. In this set concentrations of the Aac and the pH regulator (NaOH) depended on the Aac fraction in the feed mixture. The other two sets were performed at two different constant Aac and NaOH concentrations but varying total monomer concentrations. The monomer, initiator and NaOH concentrations and the pH values, before and after initiator addition and at the end of the reaction are given in Table 3.7 for all experiments.

**Table 3.7.** Parameters of the Copolymerization Reactions for Three Sets of Aac-Aam Copolymerization at pH 3.6 (For all reactions,  $T=60^{\circ}C$  and initiator (ACV) concentration = 8.9 10<sup>-3</sup> M)

		$pH_{at 60}^{0}C -$	C <sub>Aac</sub>	<b>C</b> <sub>Aam</sub>	c <sub>NaOH</sub>
Set	%	pH <sub>after ACV</sub> -	(M)	(M)	(M)
#	Aac	pH <sub>end</sub>			
	30	3.62-3.61-	0.1414	0.3290	0.0275
		3.85			
1	50	3.72-3.69-	0.2350	0.2350	0.0456
		4.04			
	70	3.59-3.63-	0.3290	0.1411	0.0679
		4.07			
	30	3.62-3.61-	0.1414	0.3290	0.0275
		3.85			
	50	3.57-3.54-	0.1414	0.1416	0.0275
2		3.90			
	70	3.57-3.55-	0.1414	0.0606	0.0277
		3.94			
	30	3.70-3.72-	0.3290	0.7680	0.0680
		3.81			
	50	3.70-3.68-	0.3290	0.3290	0.0680
3		3.98			
	70	3.59-3.63-	0.3290	0.1411	0.0679
		4.07			

At the beginning of the reaction, reactor was purged for 30min with  $N_2$  and very slow purging continued during the reaction. The reactor was then lowered into a temperature-controlled bath at 60<sup>o</sup>C. Reaction was initiated by adding the ACV in powder form. The solution was magnetically stirred during the reaction. Monitoring procedure was similar to Aac-Aam copolymerizations performed at pH 2 and pH 5. In these experiments, two UV absorption measurements at 205nm and 226nm were used in monitoring the conversion of the monomer to polymer. The pH of the reactor solution was measured off-line, periodically.

Flow rates were arranged in such a way to keep the detector concentration 1 mg/ml. These flow rates from the reactor and the solvent reservoir were maintained throughout the entire experiment. The diluted solution always reached the detector train at  $25^{\circ}$ C, regardless of the reactor temperature. The flow rates used are shown in Table 3.8.

		Flow Rat	Flow Rate (mL/min)		Total Detector
			From		Concentration
Experiment	Aac		solvent	Dilution	
		From	reservoir	(%)	(mg/mL)
Set	%	reactor			
			(0.1 M		
No			NaCl)		
	30	0.060	1.940	3.00	1.01
	50	0.060	1.940	3.00	1.01
1	70	0.060	1.940	3.00	1.01
	30	0.060	1.940	3.00	1.01
	50	0.100	1.900	5.00	1.01
2	70	0.140	1.860	7.00	1.01
	30	0.030	1.970	1.50	1.17
	50	0.043	1.957	2.15	1.17
3	70	0.060	1.940	3.00	1.01

 Table 3.8 Pump Settings Used in Aac-Aam Copolymerization at pH 3.6

#### 4. RESULTS and DISCUSSION

4.1. 4-Vinylbenzenesulfonic Acid Sodium Salt (VB) and Acrylamide (Aam) System

### 4.1.1. Homopolymerization and Copolymerization of 4-Vinylbenzenesulfonic Acid Sodium salt (VB) and Acrylamide (Aam) in 0.1M NaCl Solution

Figure 4.1 shows the raw ACOMP data for VB homopolymerization reaction, where each step is indicated. These are the baseline stabilization period for pure solvent, the baseline of pure monomer, the point of addition of initiator, and the polymerization period. The two UV signals increase during the pure monomer suction period, while the viscosity and light scattering voltages don't change. After adding initiator, the viscosity and light scattering signals increase as the polymer concentration increases during the reaction. During free radical polymerization, the double bond of the monomer disappears since it incorportaes into polymer, which causes UV absorption in two wavelengths to decrease differentially.

The similar raw data is obtained for copolymerization process. The ACOMP data for 10%VB – 90%Aam copolymerization is given in Figure 4.2. In Figure 4.2, 0.1 M NaCl baseline as the solvent, the Aam baseline, the baseline of VB+Aam mixture obtained after adding VB to the reactor solution containing Aam, the time for initiator, and the signals of detectors after initiation of the copolymerization experiment are shown, respectively. The LS and viscosity signals increase with increasing polymer concentration as in homopolymerization. Also, the loss of the double bonds of each comonomer as it participates to the polymer chain leads to decreasing UV absorption in both bands.



**Figure 4.1** ACOMP raw data for homopolymerization of VB performed in 0.1 M NaCl



Figure 4.2 ACOMP raw data for experiment S5 with 10%VB-90%Aam copolymerization

As seen in Figure 4.2, the  $UV_{206nm}$  signal increased when Aam was added and with the subsequent addition of VB, both UV signals increased.

#### 4.1.1.1. Determination of Comonomer and Polymer Concentrations

The concentrations of the two comonomers in their monomeric form, as well as their concentrations incorporated into polymer, are computed from the raw UV data [17, 20-21]. The absorbances of the initiator at these wavelengths can be neglected in comparison with the absorbances of the monomers at the same wavelengths. Therefore the UV voltages,  $V_{UV}$  at specific wavelengths are composed of the signals from the four species:

$$V_{UV,206nm} = s \left( \frac{\partial V_{UV}}{\partial c_{VB}} c_{VB} + \frac{\partial V_{UV}}{\partial c_{PVB}} c_{PVB} + \frac{\partial V_{UV}}{\partial c_{Aam}} c_{Aam} + \frac{\partial V_{UV}}{\partial c_{PAam}} c_{PAam} \right)$$
(4.1)

$$V_{UV,260nm} = s \left( \frac{\partial V_{UV}}{\partial c_{VB}} c_{VB} + \frac{\partial V_{UV}}{\partial c_{PVB}} c_{PVB} + \frac{\partial V_{UV}}{\partial c_{Aam}} c_{Aam} + \frac{\partial V_{UV}}{\partial c_{PAam}} c_{PAam} \right)$$
(4.2)

where  $c_{VB}$  and  $c_{PVB}$  are the monomer and polymer concentrations (in monomols) in the reactor of VB, and likewise for  $c_{Aam}$  and  $c_{PAam}$ . *s* is the dilution ratio. While  $\frac{\partial V_{UV}}{\partial c_{VB}}$  and  $\frac{\partial V_{UV}}{\partial c_{PVB}}$  are the UV extinction coefficients for VB and PVB at a specific

wavelength, respectively,  $\frac{\partial V_{UV}}{\partial c_{Aam}}$  and  $\frac{\partial V_{UV}}{\partial c_{PAam}}$  are for Aam an PAam. UV absorption

coefficients for Aam and VB were determined by the UV detector response to their stepwise additions. As seen in Figure 3.11 the absorbance of PVB is very weak, PAam doesn't have any absorbance at 206 nm and none of polymeric units has absorbance at 260 nm. Besides that, VB and Aam both contribute to 206 nm signal and 260 nm signal are dominated by almost only VB absorption, which result in the linear independence of the two relations obtained by the application of the equations (4.1 and 4.2). UV absorption coefficients at 206 nm and 260 nm are given in Table 4.1 and 4.2, respectively. As in Tables 4.1 seen and 4.2,  $(\partial V_{UV} / \partial c_{Aam})_{206nm} / (\partial V_{UV} / \partial c_{Aam})_{260nm}$  and  $(\partial V_{UV} / \partial c_{VB})_{206nm} / (\partial V_{UV} / \partial c_{VB})_{260nm}$ , are not close to each other, which guarantees lineer independence of the equations.

VB %	$(\partial V_{UV} / \partial c_{VB})$	$(\partial V_{UV} / \partial c_{PVB})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{PAam})$
100	760.306	359.602	-	-
75	689.463	326.095	1140.056	0
50	696.773	329.553	1093.799	0
25	695.891	329.136	1128.822	0
10	706.980	334.380	1113.892	0
0	-	-	1123.452	0

**Table 4.1**  $(\partial V_{UV} / \partial c)$  Values as g/mL for VB, PVB, Aam, PAam at 206 nm for the Reactions Performed in 0.1 M NaCl in ACOMP (UV cell path length =0.1 mm)

**Table 4.2**  $(\partial V_{UV} / \partial c)$  Values as g/mL for VB, PVB, AAm, PAam at 260 nm for the Reactions Performed in 0.1 M NaCl in ACOMP (UV cell path length =0.1 mm)

VB %	$(\partial V_{_{UV}} / \partial c_{_{VB}})$	$(\partial V_{UV} / \partial c_{PVB})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{PAam})$
100	1413.199	2.421	_	_
75	1375.944	2.357	14.083	0
50	1384.629	2.372	22.319	0
25	1412.412	2.419	22.786	0
10	1427.834	2.446	6.482	0
0	_	_	16.869	0

UV absorption measurements are combined with the conservation equations,

$$c_{PVB} + c_{VB} = c_{VB,0} \tag{4.3}$$

where  $c_{VB,0}$  is the monomer VB concentration at the beginning of the reaction. A similar relation holds for monomer Aam.

$$c_{PAam} + c_{Aam} = c_{Aam,0} \tag{4.4}$$

Here, the density increase of the reaction medium with conversion is neglected, as this effect is very small in dilute solution polymerization.

The two monomer concentrations are obtained from the observed UV absorbances via,

$$U_{k}^{+} = UV_{ksignal} - UV_{kbaseline} - \frac{\partial V_{UVk}}{\partial c_{PVB}} c_{VB,0} - \frac{\partial V_{UVk}}{\partial c_{PAam}} c_{Aam,0}$$
(4.5)

Here  $UV_{signal}$  and  $UV_{baseline}$  are the voltages recorded during the reaction and the solvent baseline voltage, the index k is 1 for measurements at wavelength 1 and 2 otherwise.

$$c_{VB} = (\Delta U_{2Aam} U_1^+ - \Delta U_{1Aam} U_2^+) / \det$$
(4.6)

$$c_{Aam} = -(\Delta U_{2VB} U_1^{+} - \Delta U_{1VB} U_2^{+}) / \det$$
(4.7)

where,

$$\Delta U_{kVB} = \frac{\partial V_{UVk}}{\partial c_{VB}} - \frac{\partial V_{UVk}}{\partial c_{PVB}}$$
(4.8)

 $\Delta U_{\rm kAam}$  are defined similarly and the determinant det is given by,

$$\det = \Delta U_{1VB} \Delta U_{2Aam} - \Delta U_{1Aam} \Delta U_{2VB}$$
(4.9)

The analysis of the UV data according to the above scheme yields a continuous record of the monomer concentrations  $c_{VB}$  and  $c_{Aam}$ , and the concentrations of VB and Aam units in the copolymer  $c_{PVB}$  and  $c_{PAam}$ . Since  $(\partial V_{UV} / \partial c)$  found as g/mL were used, the concentrations were calculated in g/mL. Then, concentrations of all species were converted to molar concentration.

After the reactor temperature reached 60°C, the initiator was added (at 8500 sec for 10%VB and at 9800 sec for 25%VB). VB was copolymerized faster than Aam in first order fashion during the first phase of the reaction, seen by the 260 nm signal in Figure 4.3. After VB was consumed the remaining Aam homopolymerized rapidly; both phases can be seen in the 206nm signal in Figure 4.3, as well. Hence, a blend of copolymer and PAam homopolymer was produced.



**Figure 4.3** Raw ACOMP UV data at 206 and 260 nm for 10%VB/90%Aam and 25%VB/90%Aam copolymerization in 0.1 M NaCl

Monomer conversion were calculated by

$$Conv_{VB} = 1 - \frac{c_{VB,t}}{c_{VB,0}}$$
(4.10)

$$Conv_{Aam} = 1 - \frac{c_{Aam,t}}{c_{Aam,0}}$$
(4.11)

$$Conv_{Total} = 1 - \frac{c_{VB,t} + c_{Aam,t}}{c_{VB,0} + c_{Aam,0}}$$
(4.12)

Conversions of Aam, VB and for the all reactions in 0.1 M NaCl are shown in Figures 4.4 and 4.5.



**Figure 4.4** Conversion of Aam for several different starting ratios of [VB]/[Aam] in 0.1 M NaCl. Bimodality is lost between 25%VB/75%Aam and 50%VB/50%Aam



**Figure 4.5** Conversion of VB for several reactions with starting ratios of [VB]/[Aam] in 0.1 M NaCl

Figure 4.6 shows the evolution of total conversion with time. Aam homopolymerization is faster than VB and both homopolymerization rates are higher than copolymerization rates at any combination. The acceleration seen in S4 (25%VB) and S5 (10%VB) with the depletion of VB indicate that rest of the reaction is acrylamide polymerization.



Figure 4.6 Conversion versus time plots for VB-Aam copolymerization in 0.1M NaCl

### 4.1.1.2. Comparing ACOMP with Other Methods

### 4.1.1.2.1. Comparison with the Squential Sampling Method

In the sequential sampling method, the evolutions of the monomer and polymer compositions and conversion are obtained from UV measurements performed on aliquots periodically withdrawn from the reaction medium. It was used to verify the results of ACOMP. Figure 4.7 includes the conversion results obtained from ACOMP and sequential method, in which aliquots removed from the diluted reactor solution after having passed through the detector train. After further dilution, their UV spectra were measured by an off-line UV spectrophotometer, of a different model (Hewlett Packard Array 8452A) from that used in the ACOMP system. The concentration of comonomers and their conversions obtained from off-line data are compared to the ACOMP results.



Figure 4.7 The comparison results for conversion obtained from ACOMP and sequential sampling method for 50%VB-50%Aam copolymerization reaction in 0.1 M NaCl

### 4.1.1.2.2 Comparison with GPC

Gel Permeation Chromotography (GPC) is a method used to obtain not only the average molecular weight, but, the whole molecular weight distribution. However its dependence on use of columns precludes its use for online detection. As the unreacted monomers exit the column last, the bands corresponding to polymer and monomer are well separated. A GPC system can thus be used in analyzing sequentially withdrawn samples.



**Figure 4.8** UV voltages at 260 nm measured in GPC for the aliquots taken during the 25% VB-75% Aam copolymerization reaction

For GPC measurements, the solutions, if necessary, were diluted to the suitable detector concentration used in GPC. After filtration using a 0.22  $\mu$ m millipore filter, they were injected to the GPC. The conversions of the monomers were calculated by means of the areas of the individual UV peaks of remained monomer in the reactor solutions. The area calculated from the peak gives the absorbance voltage for the monomer. In GPC graph, the first peaks belong to Aam and the second ones are those of VB. As seen in UV spectra of monomers and polymers, only VB has absorbance at 260 nm. But, here UV cell with 1 cm path length was used, which enables us to observe the peaks of Aam. It is seen in the Figure 4.8 that the first sample taken from the system before adding initiator has only monomer peaks, whereas the samples taken after starting of the polymerization have individual monomer peaks and the peak of copolymer produced, which can not be seen because of the fact that they don't have any absorbances. The calculation procedure is given below.

$$Conv_{VB}$$
 at t (time) =  $1 - \frac{C_{VB,t}}{C_{VB,0}}$  (4.10)

$$Conv_{VB} = 1 - \frac{\frac{V_{UV,VB,t}}{(\partial V_{UV} / \partial c_{VB})_{260nm}}}{\frac{V_{UV,VB,0}}{(\partial V_{UV} / \partial c_{VB})_{260nm}}} = 1 - \frac{V_{UV,VB,t}(inGPC)}{V_{UV,VB,0}(inGPC)}$$
(4.13)

A similar equation can be written for Aam,

$$Conv_{Aam} = 1 - \frac{\frac{V_{UV,Aam,t}}{(\partial V_{UV} / \partial c_{Aam})_{260nm}}}{\frac{V_{UV,Aam,0}}{(\partial V_{UV} / \partial c_{AAm})_{260nm}}} = 1 - \frac{V_{UV,Aam,t}(inGPC)}{V_{UV,Aam,0}(inGPC)}$$
(4.14)

The conversion results calculated by analyzing ACOMP and GPC results for 25% VB -75% Aam experiment performed in 0.1 M NaCl is given in Figure 4.9.



**Figure 4.9** Monomer conversions obtained from GPC and ACOMP results for the copolymerization with 25%VB-75%Aam molar ratio in 0.1 NaCl

# 4.1.1.3. Determination of $\delta n/\delta c$ of copolymer by ACM (Automatic Continuous Mixing) [39]

After terminating the polymerizations, the reactor content was poured into ethanol immediately, and the polymer was precipitated. After precipitation, the polymer was dried under vacuum until it reached constant mass.

The ACM technique allows a continuous gradient of solution components to be formed using two or more solution reservoirs. The properties of the continuously varying solutions can be measured. It is required the mixed sample be in equilibrium or quasi-equilibrium, which means the properties of the mixed solution at any instant do not change during the interval from mixing to measurement.

The ACM technique was implemented using an Schimadzu LC-10AD VP model pump with a gradient mixer attached. Following the pump can be a lightscattering flow cell followed by a single capillary viscometer and a refractive index (RI) detector. The use of a programmable mixing pump in ACM enables any parametrized path to be investigated for the solutions containing a salt and a polymer. Here, we ramped polmer concentration at a constant salt concentration and the  $\delta n/\delta c$  values were found for PAam and PVB by using only RI detector to conduct molecular weight analysis.

In this procedure, the homopolymer of VB and Aam were dissolved in 10 mM NaCI which was prepared in water and then filtered with 0.22 µm filter after the sample was completely dissolved. The polymer solution and 10 mM NaCl solution used as solvent to adjust the polymer concentration during the ramp, were then primed in the lines of an Schimadzu LC-10AD VP with programmable gradient mixer, which is a programmable mixing pump to pull a constant percentage.

Before the experiments, 10 mM NaCl was pumped by a programmable mixing pump through the detector train to obtain the baseline of RI detector for 10 mM NaCl. After stabilization, the gadient of the polymer solution was began by withdrawing from reservoir of polymer solution in 10 mM NaCl and mixing it with 10 mM NaCl solution, continuously. Polymer concentration ramp were carried out from low to high solute. At the end of the gradient, the polymer solution in 10 mM NaCl at 7 mg/mL was sent to detector train without any withdrawing from the solvent reservoir to take the baseline of polymer in 10mM NaCl solution. Figures 4.10 and 4.11 shows RI signals vs time for PVB and PAam , respectively while polymer concentration increases with constant NaCl concentration.

Figures 4.10 and 4.11, where each step is indicated, exhibits RI vs time for homopolymers obtained from the experiments carried out in 0.1 M NaCl whose polymerization period was monitored through ACOMP. The first potion, up to ~ 750

s, is the baseline stabilization period of RI detector with 10mM NaCI. After solvent baseline, polymer ramp begins, where concentration regime of homopolymer increased from 0 to  $\sim$  7 mg/mL. The ramp lasted  $\sim$  1 hour. The RI signal versus time increase with increasing polymer concentration during the procedure. The final baseline is for 7 mg/mL of homopolymer in 10mM NaCI.



**Figure 4.10** Raw RI data in ACM vs time, at fixed [NaCl] = 10 mM for PVB homopolymer obtained from the experiment carried out in 0.1 M NaCl



**Figure 4.11** Raw RI data in ACM vs time, at fixed [NaCl] = 10 mM for PAam homopolymer obtained from the experiment carried out in 0.1 M NaCl

Thus,  $\delta n/\delta c$  values of homopolymers was calculated by using RI baselines of solvent and homopolymer as;

$$\left(\frac{\delta n}{\delta c}\right)_{homopolymer} = \frac{CF(V_{RI,homopolymer in 10mM NaCl} - V_{RI,10mM NaCl})}{c_{homopolymer}}$$
(4.15)

 $\delta n/\delta c$  values of homopolymers obtained from the reactions are given in Table 4.3.

**Table 4.3.**  $\delta n/\delta c$  Values of Homopolymers Obtained from ACM Studies for VB/Aam System. ACM (Experiments listed here were done in 10mM NaCl solutions)

VB% (Molar)	0	100	
$\delta n/\delta c$ (cm <sup>3</sup> /g)	0.1635	0.1705	

### 4.1.1.4. Molecular Weight Analysis in VB-Aam Copolymerization in 0.1 M NaCl

Traditional Zimm equation [137] is the starting point for light scattering measurements. Analysis of the light scattered by polymers in dilute solution has been made via zimm approximation.

$$\frac{Kc}{I(q,c)} = \frac{1}{MP(q)} + 2A_2c +$$

$$\left[ 3A_3Q(q) - 4A_2^2MP(q)(1 - P(q)) \right]c^2 + O(c^3)$$
(4.16)

Where c is the polymer concentration as  $g/cm^3$  and I(q,c) is the excess Rayleigh scattering ratio (cm-1). P(q) is the form factor, and Q(q) involves a set of Fourier transforms of the segments interactions defining  $A_2$ . The scattering vector q is defined as

$$q = (4\pi n/\lambda) \sin(\theta/2) \tag{4.17}$$

 $\theta$  is the scattering angle. Here *K* is an optical constant, given for vertically polarized light as

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4}$$
(4.18)

Equation (4.16) forms the basis of the well known Zimm plot, which, at low concentrations an for  $q^2 \langle S^2 \rangle \ll 1$  can be written, for a polydisperse polymer populationas

$$\frac{Kc}{I(q,c)} = \frac{1}{M_w} \left( 1 + \frac{q^2 \left\langle S^2 \right\rangle_z}{3} \right) + 2A_2 c$$
(4.19)

The problems of light scattering interpretation for copolymers was demonstrated long ago by Benoit and Stockmayer of unknown composition distribution [20]. They showed that it was necessary to make light scattering measurements in at least three different solvents of varying index of refraction in order to determine  $M_w$  for copolymers of unknown composition distribution. Since ACOMP allows the average composition to be directly measured, the Benoit/Stockmayer equation can be integrated with the aid of ACOMP composition data and online measurements of  $M_w$ made.

The  $\delta n/\delta c$  values were found by ACM, which was explained above in detail. For the VB-Aam copolymerization system, the  $\delta n/\delta c$  for two comonomers in polymeric form is similar to eachother. This simplifies the light scattering interpretation. Therefore, the weight average  $\delta n/\delta c$  of the two homopolymers was used as follows

$$\left(\frac{\delta n}{\delta c}\right)_{copolymer} = y \left(\frac{\delta n}{\delta c}\right)_{PAam} + (1-y) \left(\frac{\delta n}{\delta c}\right)_{PVB}$$
(4.20)

where y is the mass fraction of accumulated polymer composed of Aam monomer

$$y = \frac{c_{PAam}}{c_{PAam} + c_{PVB}}$$
(4.21)

Total polymer concentration during the reaction was calculated from raw ACOMP data as described above and  $M_w$  was calculated from these concentrations by using the  $(\delta n/\delta c)_{copolymer}$  values obtained from the weight average of  $(\delta n/\delta c)_{PVB}$  and

 $(\delta n/\delta c)_{PAam}$  during the reaction. Only the intensities measured at 90<sup>0</sup> LS detector were used to calculate the molecular weights. A very small detector concentration was selected to avoid A<sub>2</sub> and A<sub>3</sub> effects. The  $M_w$  provided by LS in ACOMP is the cumulative average of the polymer in the reactor.

Figure 4.12 shows the fractional conversion of each comonomer,  $Conv_{VB}$  and  $Conv_{Aam}$  for the copolymerization with 10%VB feed ratio in 0.1M NaCl, obtained from the dual wavelength UV data. The two phase behavior of  $Conv_{Aam}$  is striking. Its polymerization rate increases when the VB is exhausted. Figure 4.12 also shows 90<sup>0</sup> light scattering raw voltages, which are seen to jump after the VB conversion is complete and increase during the second phase of PAam homopolymer production.



**Figure 4.12** Comonomer conversions  $Conv_{VB}$ ,  $Conv_{Aam}$  and light scattering intensity obtained from 90<sup>0</sup> scattering for experiment with 10%VB-90%Aam in 0.1 M NaCI

Figure 4.13 shows the evolution of molecular weight. Unlike the 10% VB (S5) experiment, where there is an actual increase in molecular weight, coinciding with the depletion of VB monomer in the reaction mixture, in the experiments with 75%VB (S2) and 50%VB (S3) the molecular weight decreases with conversion, a consequence of the decrease of the monomer concentration, typical results for radical polymerization. Furthermore, in the 25% VB (S4) experiment no decrease was observed in the molecular weight. In these experiments where the VB is completely depleted, the Aam enters the reaction at a higher rate so that the reaction picks up
speed and the molecular weight increases. As the polymer concentrations are calculated by substracting the measured monomer concentrations from the initial concentrations, at low conversion (below 10-20%) polymer concentration and conversion have large errors. For this reason, data obtained after 20% conversion are more reliable.



Figure 4.13 The evolution of  $M_w$  with conversion for the experiments in 0.1M NaCI (All reactions were performed at the same pH)

## 4.1.1.5. Reactivity Ratios for VB-Aam Copolymerization Performed in 0.1 M NaCl Solution [22]

As the more reactive monomer incorporates into the copolymer faster, the feed composition drifts during the reaction. In online methods the composition drift is continuously monitored and it can be used to give a rough idea of the reactivity ratios before any numerical computation is performed. In all reactions performed in salt solution the VB fraction in the feed is decreasing, indicating that it is enterin the reaction at a rate higher than its fraction in the monomer mixture. This shows that  $r_{VB}>r_{Aam}$ .

Figure 4.14 shows the confidence contours for the MRR in salt solution for the individual experiments. As the ionic strength is determined mainly by the 0.1M NaCl the effect of VB concentration is less and as a result the contours intersect nearly at

the same point. The reactivity ratios,  $r_{Aam}=0.085\pm0.020$ ,  $r_{VB}=2.0\pm0.33$ , are found from the combined confidence region in Figure 4.15.



**Figure 4.14** Confidence contours for monomer reactivity ratios for all experiments in 0.1 M NaCl solution



**Figure 4.15** Combined confidence interval contours for monomer reactivity ratios in VB-Aam copolymerization in 0.1M NaCl

The instantaneous VB fraction in the remaining monomer mixture as a function of total conversion is given in Figure 4.16. Here the VB concentration versus Aam

concentration data (Figure 4.17) is fitted to a numerical solution of the copolymerization equation to calculate the terminal model MRRs, by the EVM method [20-22].



Figure 4.16 Instantaneous VB fraction versus total conversion. The data (top to bottom) are 75%, 50% 25% and 10% VB experiments



**Figure 4.17** Instantaneous VB concentration vs Instantaneous Aam concentration as Molar (M). The data (left to right) are 75%, 50% 25% and 10% VB experiments

In Figures 4.16 and 4.17, the continuous lines are the predictions of the terminal model with  $r_{Aam}$ =0.085 and  $r_{VB}$ =2.0. In all cases the model adequately describes the evolution of the composition with conversion.

# **4.1.2.** Homopolymerization and Copolymerization of 4-Vinylbenzenesulfonic Acid Sodium Salt (VB) and Acrylamide (Aam) in Water

The raw UV absorptions at 206nm and 260 nm were used to determine the comonomer and polymer concentrations in the same manner as VB-Aam system conducted in 0.1M NaCI. Table 4.4 and 4.5 gives  $(\partial V_{UV} / \partial c)$  values as g/mL obtained of monomers and polymers at 206 nm and 260 nm for the reaction performed in water, respectively.

**Table 4.4**  $(\partial V_{UV} / \partial c)$  Values as g/mL for VB, Aam, PVB, PAam at 206 nm for the reaction performed in water. (UV cell path length =0.1 mm)

VB %	$(\partial V_{UV} / \partial c_{VB})$	$(\partial V_{UV} / \partial c_{PVB})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{PAam})$
100	NA*	NA*	-	-
50	875.007	275.097	1209.859	0
25	991.725	311.792	1131.724	0
15	1193.127	375.112	1109.175	0
10	1223.738	384.736	1147.416	0
5	2022.549	635.877	1162.826	0
1.5	5153.065	1620.093	1202.669	0
0	-	_	1390.377	0

\* 220 nm at UV was used to monitor VB homopolymerization.  $(\partial V_{UV} / \partial c_{VB})_{220nm} = 337.379$  and  $(\partial V_{UV} / \partial c_{PVB})_{220nm} = 747.293$ 

VB %	$(\partial V_{UV} / \partial c_{VB})$	$(\partial V_{UV} / \partial c_{PVB})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{PAam})$
(Molar)				
100	NA	NA	-	-
50	1698.426	13.683	23.410	0
25	1639.820	13.167	18.815	0
15	1637.598	13.149	18.684	0
10	1678.719	13.479	22.484	0
5	1805.152	14.494	19.253	0
1.5	2052.023	16.477	19.123	0
0	-	-	23.086	0

**Table 4.5**  $(\partial V_{UV} / \partial c)$  Values as g/mL for VB, Aam, PVB, PAam at 260 nm for the Reaction Performed in Water.

Since  $(\partial V_{UV} / \partial c)$  found as g/mL were used, the concentrations were calculated in g/mL and then, concentrations of all species were converted to Molar.

Whereas Figure 4.18 and 4.19 gives conversion results for the salt free experiments carried out in water with various VB molar feed fractions, Figure 4.20 exhibits the overall conversion in the copolymerization reactions.



Figure 4.18 Aam conversions in the experiments performed in water



Figure 4.19 VB conversions in the experiments performed in water



Figure 4.20 Conversion versus time plots for VB-Aam copolymerization in water

In the reactions W5 (10% VB), W6 (5% VB), W7 (1.5% VB) (Table 3.5), VB is completely depleted, further reaction is Aam homopolymerization.

Measurements were made to prove two phases observed in the experiments. VB-AAm copolymers are in anionic nature due to anionic VB on the chain. Hence, reactor end solutions after termination were mixed with solution of polydadmac, which is a cationic polymer. Because of the anionic-cationic interactions between Aam-VB copolymers and polydadmac, a precipitation was formed in all reactor solutions with various VB content except for 100% Aam hopolymerization reactor solution. After that, the solutions were santrifuged and their supernatant phases were taken and injected to the GPC. Figure 4.21 shows RI signals in GPC results of the supernatants of the mixture VB-Aam copolymers with polydadmac. As seen in Figure 4.21, only 1.5 % VB, 5 % VB, 10 % VB experiments give a RI peak in the same place as polyacrylamide. This result supports two phases observed in ACOMP results and the formation of homopolyacrylamide after VB exhausted for the reactions with 1.5 % VB/ 98.5 % Aam, 5 % VB / 95 % Aam and 10 % VB / 90 % Aam.



Figure 4.21 GPC results for the supernatants of the mixture VB-Aam copolymers with polydadmac

In all copolymerization reactions carried out in 0.1 M NaCl as well as in water, it was observed that the conversion of VB was nearly 100%. However, in its homopolymerization, VB is incorporated to the chain less than it does in 90%Aam-10%VB copolymerization reaction. It appeared that Aam helps VB to polymerize. To

verify that this actually is the case, an experiment whose result is shown below was performed. Firstly, VB was polymerized in water. At about 15330 sec when the decreases of 206 and 260 nm signal stopped which serve VB conversion and VB polymerization was considered not to continued anymore, Aam was poured into the reaction mixture. As soon as Aam was put into the reactor, VB started to polymerize again. Starting of VB re-polymerization can be clearly seen from the slope observed after 16530 sec in Figure 4.22. It is noted that there is a delay time between reactor and ACOMP detectors.



Figure 4.22 Re-polymerization of VB after adding Aam

## 4.1.2.1. Composition Drift for VB-Aam Copolymerization Performed in Water

Figure 4.23 show the evolution of instantaneous VB fraction in the monomer mixture for the reactions performed in water. VB incorporates to the copolymer more than Aam does, in water as seen in the reactions carried out in 0.1 M NaCl solution. For this reason it is depleted faster. In the reactions 10% VB, 5% VB, 1.5% VB where VB is completely depleted further reaction is Aam homopolymerization.



Figure 4.23 Instantaneous VB fraction versus total conversion for reactions performed in water

During the copolymerizations in water with 5 to 50% VB, VB fraction in monomer mixture versus conversion each curve went through a corner at 10-30 % conversion depending on the VB content as seen in Figure 4.23 and its inset. This corner indicates that the behaviour of the reaction changes ubruptly at this point. This sudden change in the reaction kinetics and the monomer reactivities is probably due to reaching the c\* overlap concentration. Beyond this point the whole reaction vessel is within the coils of the polymers already formed so that the electrostatic repulsion

between the macro radical and the charged VB monomer is suppressed. The reactivity of VB increases substentially.

The corner occurred approximately at 11% conversion in the 15% VB experiment. In experiments both at lower and higher VB concentrations it occurred at higher conversions as seen in Figure 4.24. Coil volume of a polymer depends on its molecular weight and persistence length (PL). As the molecular weights of these copolymers are similar up to 30% conversion, as seen in the light scattering data in Figure 4.25, this effect probably originates from differences in PL. PL is a function of Debye screening length and the strength of electrostatic interactions. Here the Figure 4.24 indicates that the PL is maximum at 15% VB fraction. At higher IS the reduction of the Debye screening length with increasing IS is the dominant effect. Further increase in VB fraction reduces the coil volume. At very low VB concentration (5%) the electrostatic interaction is less and corner occurs later. As a result maximum hydrodynamic volume is obtained at 15% VB fraction in our experimental conditions. After the end of the copolymerization phase, the reaction rate suddenly increases, and reaches the Aam homopolymerization rate.



**Figure 4.24** The evolution of conversion at overlap concentration versus VB fraction in feed for reactions carried out in water



Figure 4.25 Raw Light Scattering  $(90^{\circ})$  data for the experiments carried out in water

## 4.1.2.2. Reactivity Ratios for VB-Aam Copolymerization Performed in Water

Monomer reactivity ratios (MRR) were calculated by the EVM method [20, 21] as made in those performed in 0.1M NaCl

The reactions in water gave two distinguishable regions and the reaction part before and after the corner were evaluated separately. In the first phase of the reactions, the composition is almost constant.

The valleys in Figures 4.26 and 4.27 show the results before the "corner". As shown in Figure 4.26, 1, 2 and 3  $\sigma$  confidence regions for the individual experiments do not intersect at exactly the same point. This is because one of the experimental conditions, namely the ionic strength which depends on the VB concentration is not the same in each experiment, in fact, it changes with conversion, during the experiment itself. For this reason the combined confidence region given in Figure 4.27 represents the cumulative average over the conditions valid during the early parts of the experiment series. The reactivity ratios are found as  $r_{Aam}=0.34\pm0.07$ ,  $r_{VB}=0.40\pm0.21$ .



**Figure 4.26** The 1 2 and 3 sigma confidence contours for the MRR for individual experiments performed in water (Early part of the reaction)



Figure 4.27 The confidence contours for the combined results of experiments performed in water (Early part of the reaction)

After the corner, the nature of the reaction changes and the VB fraction starts to drop rapidly with further conversion resulting in a sudden increase in VB reactivity. The reactivity ratios calculated using the data after the corner (shown in Figures 4.28 and 4.29) gave  $r_{Aam}=0.2\pm0.04$ ,  $r_{VB}=9.0\pm0.8$ .



**Figure 4.28** The 1 2 and 3 sigma confidence contours for the MRR for individual experiments performed in water (Late part of the reaction)



Figure 4.29 The confidence contours for the combined results of experiments performed in water (Late part of the reaction)

## 4.2. Copolymerization of Acrylic acid and Acrylamide at pH 5 and pH 2 [14]

Acrylic acid / acrylamide copolymerization is an extensively studied topic. Due to increasing usage of acrylic acid acrylamide homo and copolymers in industry a reliable set of reactivity ratios are still necessary. Cabaness [54-56] worked at 60°C with sequential sampling with conversions less than 10% and pH ranged from 2 to 6. In the work of Hamielec's group [57] pH was not considered. He also reevaluated the Cabaness data. Ponratnam has performed experiments at 30°C with conversions ranging from 5% to 60% and pH ranging from 2 to 9. Composition drift was taken into account in data evaluation [58]. These studies were all performed by batch techniques where data is obtained only after the reaction was terminated at some point. Kurenkov discussed the effect of nature of solvent, medium pH, polarity and dielectric constant on acrylic acid / acrylamide copolymerization [59].

The most recent and detailed study was performed by Wandrey et al. [61-62], where sequential sampling method was applied and pH was ranged from 2 to 12 at 40°C. The basic method of Kelen and Tüdös [103] was applied in this study. A detailed discussion of the calculation methods is also included.

Monitoring the evolution of copolymerization up to high conversion was not considered in any of the above studies. Supplying thousands of data points will bring high resolution to the reaction kinetics of copolymerization. That's why acrylamide acrylic acid copolymerization was monitored by ACOMP [14]. Considering the importance of pH in polyelectrolyte systems and pKa value of acrylic acid one above (pH=5) and one below (pH=2) pH was chosen as a working pH.

Figure 4.30 shows the raw ACOMP data for the 30% Aam / 70% Aac reaction at pH 5, where each step is indicated. These are, the baseline stabilization period, the baseline of pure monomer, the point of initiator addition, and the polymerization period. The two UV signals increase during the pure monomer suction period, whereas the LS and viscosity do not change. During polymerization, the loss of the double bonds of each comonomer as it incorporates into polymer leads to (differentially) decreasing UV absorption in both bands, while the viscosity and LS signals increase with increasing polymer concentration.



Figure 4.30 ACOMP data for reaction VI with 70% Aac and 30% Aam, at pH 5

#### 4.2.1. Determination of Comonomer and Polymer Concentrations

Raw UV data were used to calculate the concentrations of the two comonomers in their monomeric form and their concentrations incorporated into polymer during the reaction. The initiator (ACV) doesn't absorb light at selected wavelengths (205 and

226 nm) in comparison with the absorbances of the monomers at the same wavelengths. Therefore the UV voltages,  $V_{UV}$  at specific wavelengths are composed of the signals from the four species:

$$V_{UV,205nm} = s \left( \frac{\partial V_{UV}}{\partial c_{Aam}} c_{Aam} + \frac{\partial V_{UV}}{\partial c_{PAam}} c_{PAam} + \frac{\partial V_{UV}}{\partial c_{Aac}} c_{Aac} + \frac{\partial V_{UV}}{\partial c_{PAac}} c_{PAac} \right)$$
(4.22)

$$V_{UV,226nm} = s \left( \frac{\partial V_{UV}}{\partial c_{Aam}} c_{Aam} + \frac{\partial V_{UV}}{\partial c_{PAam}} c_{PAam} + \frac{\partial V_{UV}}{\partial c_{Aac}} c_{Aac} + \frac{\partial V_{UV}}{\partial c_{PAac}} c_{PAac} \right)$$
(4.23)

where  $c_{Aam}$  and  $c_{PAam}$  are the monomer and polymer concentrations (in monomols) in the reactor of Aam, and likewise for  $c_{Aac}$  and  $c_{PAac}$ . The dilution ratio is s=0.06/2.00. As given above the ratio of the absorption coefficients of Aam and Aac is 1.62 at 205nm namely wavelength 1 and 10.01 at 226nm, wavelength 2. Also, neither PAam nor PAac have absorbance at these wavelengths. The non-equality of these ratios results in the linear independence of the two relations obtained by the application of the equations (4.22) and (4.23) to measurements at these wavelengths. Absorption coefficients for Aam and Aac monomer are given in Table 4.6.

UV absorption measurements are combined with the conservation equations,

$$c_{PAam} + c_{Aam} = c_{Aam,0} \tag{4.24}$$

where  $c_{Aam,0}$  is the monomer Aam concentration at the beginning of the reaction. A similar relation holds for monomer Aac.

$$c_{PAac} + c_{Aac} = c_{Aac,0} \tag{4.25}$$

In these copolymerization system ,the increase of the density of the reaction medium with conversion is neglected, as this effect is very small in dilute solution polymerization, as well.

The two monomer concentrations are obtained from the observed UV absorbances via,

$$U_{k}^{+} = UV_{k signal} - UV_{k baseline} - \frac{\partial V_{UVk}}{\partial c_{PAam}} c_{Aam,0} - \frac{\partial V_{UVk}}{\partial c_{PAac}} c_{Aac,0}$$
(4.26)

Here  $UV_{signal}$  and  $UV_{baseline}$  are the voltages recorded during data gathering and the baseline voltage when pure solvent is passing through the detectors and the index *k* is 1 for measurements at wavelength 1 and 2 otherwise.

$$c_{Aam} = (\Delta U_{2Aac} U_1^+ - \Delta U_{1Aac} U_2^+) / \det$$
(4.27)

$$c_{Aac} = -(\Delta U_{2Aam} U_1^+ - \Delta U_{1Aam} U_2^+) / \det$$
(4.28)

where,

$$\Delta U_{kAam} = \frac{\partial V_{UVk}}{\partial c_{Aam}} - \frac{\partial V_{UVk}}{\partial c_{PAam}}$$
(4.29)

 $\Delta U_{\rm \tiny kAac}$  are defined similarly and the determinant det is given by,

$$\det = \Delta U_{1Aam} \Delta U_{2Aac} - \Delta U_{1Aac} \Delta U_{2Aam}$$
(4.30)

pН	Aac %	205 nm		226 nm	
		$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{Aac})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{Aac})$
5	0	669.470	-	326.315	-
	10	665.678	405.578	332.444	32.776
	23	652.587	397.602	341.940	33.712
	30	653.474	398.142	353.746	34.876
	50	628.876	383.156	396.903	39.131
	70	606.705	369.967	459.968	45.349
	76	617.586	376.277	524.101	51.672
	90	562.245	342.559	675.526	66.602
	100	-	344.636	-	102.093
2	50	685.986	417.951	396.903	33.088
	70	963.187	586.841	684.012	67.438

**Table 4.6**  $(\partial V_{UV} / \partial c)$  values as g/mL obtained for Aam and Aac at 205 and 226 nm

The analysis of the UV data according to the above scheme yields a continuous record of the monomer concentrations  $c_{Aam}$  and  $c_{Aac}$ , and the concentrations of Aam and Aac units in the copolymer  $c_{PAam}$  and  $c_{PAac}$ .

After determination of the concentration of all species in the reactor, the monomer conversions were calculated in the same manner given in equation (4.10), (4.11) and (4.12). Conversions of Aac and Aam for the reactions at pH 5 are shown in Figures 4.31 and 4.32 respectively. Figure 4.33 shows total monomer conversion for the experiments performed at pH 5.



Figure 4.31 Conversion of Aac for several reactions at pH 5



Figure 4.32 Conversion of Aam for several reactions at pH 5



Figure 4.33 Total conversion versus time plots for Aam-Aac copolymerization at pH5

## 4.2.2. Verification of Copolymerization

To verify the copolymerization, following tests were done: a polycation poly-Llysine (PLL) ( $M_w = 140,000$ ) was mixed with several copolymers in water, as well as homopolymer of acrylamide and homopolymer of acrylic acid and the mixture of homopolymers. The solutions were then centrifuged at 10,000 rpm for one hour, and the supernatant removed by pipette from the undisturbed solutions. This liquid was then injected into GPC. Those samples consisting of acrylamide homopolymer, or acrylamide and acrylic acid homopolymers yielded GPC elution traces due to the presence of neutral polyacrylamide, which as expected didn't interact with PLL. In contrast, all supernatant solutions containing copolymer or pure acrylic acid yielded no GPC elution traces. That is, the PLL interacted with these polyanions, leading to complete precipitation, with no detectable residual homopolymer. The results are shown in Figure 4.34.





#### 4.2.3. Reaction Kinetics for Aam-Aac Copolymerization at pH 5 and 2

The reaction rate depends on the initiator and comonomer concentrations and the propagation, termination and initiator decomposition rate constants. The initiator concentration and the reaction temperature are the same in all reactions. The termination step is believed to be diffusion controlled, thus, with the initiation and the termination rates in all reactions being roughly the same, it is possible to treat the reaction with 1<sup>st</sup> order kinetics and define an effective 1<sup>st</sup> order rate constant as,

$$-\frac{dc_{Total\ monomer}}{dt} = k_{eff}c_{Total\ monomer}$$
(4.31)

where  $c_{Total monomer}$  is the total monomer concentration.

Plots of the logarithm of monomer concentration versus time, given in Figure 4.35, indicate that this simple scheme fails to account for the kinetics of these reactions. The reactions show a marked slowing down as compared to 1<sup>st</sup> order kinetics. The "slowing down" of the polymerization reaction can be due to a combination of a) decrease of the initiator concentration as the reaction times are comparable to initiator life-times at the reaction temperatures or due to composition drift, whereby the rapid depletion of the highly reactive species leaves the reaction medium rich in the less reactive species, b) higher order effects. It is unlikely that a single cause is the reason and probably all three factors have a role. Since a parameter search for the best fit reaction-order, initiator-decay-half-life and the composition-drift would involve too many fitting parameters, we instead compared our results with reaction order as would be expected in cage effect and with an initiator decay time.



**Figure 4.35** Plots of the logarithm of monomer concentration versus time at pH 5 If the depletion of the initiator during the reaction is taken into account, the initiator concentration decreases with time as,

$$[I_2] = [I_2]_0 \exp(-k_d t)$$
(4.32)

where  $k_d$  is the decomposition rate constant of the initiator. If the reaction is 1<sup>st</sup> order in monomer, the monomer concentration decreases according to,

$$ln\left(\frac{c_{Total \ monomer,0}}{c_{Total \ monomer}}\right) = k_{eff}\left(1 - exp(-k_dt/2)\right)$$
(4.33)



**Figure 4.36** The fits showing initiator decay obtained from Aam and Aac homopolymerizations at pH 5

The fits shown in Figure 4.36 indicate that initiator decomposition is still inadequate by itself to account for the reaction kinetics. Furthermore the best-fit values for the initiator decay for Aam and Aac homopolymerizations differ by more than a factor of 3. This difference cannot be explained unless the monomers take part in the initiation process.

At pH5 the reaction system contained the monomer mixture including acrylamide and acrylic acid in sodium acrylate form and initiator ACV. As shown in Figure 4.37, the pH of reaction medium increased during the reaction. The changes were small in acrylamide rich mixtures becoming more significant with increasing Aac. Final pH in the Aac homopolymerization was close to 7.



Figure 4.37 The change at the pH of reaction medium during the reactions performed at pH5

In the reaction medium acrylic acid is in the salt form and 98% ionized but dissolved ACV itself will tend to share the same positive Na<sup>+</sup> ions. As a result negatively charged Aac and ACV ions repel each other, causing the Aam to initiate the reaction at a faster rate. Due to the ionic nature of the ACV, its decomposition rate will also depend on the amount of acidic comonomer at the reaction medium. If they play such a role through cage effect, [80-85]

$$I_2 \underset{k_2}{\overset{k_1}{\longleftrightarrow}} (2I^{\bullet}) \tag{4.34}$$

$$(2I^{\bullet}) \xrightarrow{k_3} 2I^{\bullet} \tag{4.35}$$

$$(2I^{\bullet}) + M \xrightarrow{\kappa_4} M^{\bullet} + I^{\bullet}$$
(4.36)

Then the reaction is no longer first order in monomer but 5/4 (1.25<sup>th</sup>) order according to Noyes, or 3/2 (1.50<sup>th</sup>) according to Hamielec.

When the initiator is ionized the cation can also disrupt a cage via,

$$(2I^{\bullet^-}) + Na^+ \xrightarrow{k_5} 2I^{\bullet^-} + Na^+$$
(4.37)

Although it is possible to fit for both initiator life-time and reaction order from the curve of the reaction rate, such a fit procedure involves too many fit parameters and is thus not reliable. Instead, the kinetic data was fitted to 1.50<sup>th</sup> order kinetics with initiator decay,

$$\frac{1}{c_{Total \ monomer}^{1/2}} = \frac{1}{c_{Total \ monomer,0}^{1/2}} + k_{eff} \ (1 - exp(-k_d t/2))$$
(4.38)

and 1.25<sup>th</sup> order kinetics,

$$\frac{1}{c_{Total \ monomer}^{1/4}} = \frac{1}{c_{Total \ monomer,0}^{1/4}} + k_{eff} \ (1 - exp(-k_d t/2))$$
(4.39)

with  $k_d$  and  $k_{eff}$  as fit parameters.

Figure 4.38 and 4.39 show that equations for 1.25<sup>th</sup> order and 1.50<sup>th</sup> order kinetics both fit the data. The initiator decay rate constant is greater for Aam homopolymerization than for Aac homopolymerization, indicating that the neutral Aam monomer is more active in initiating the primary radical.



Figure 4.38 Initiator decay rate fits for 1.25<sup>th</sup> (5/4) order kinetics at pH 5



Figure 4.39 Initiator decay rate fits for 1.50<sup>th</sup> (3/2) order kinetics at pH 5

Figure 4.40 shows the apparent initiator decay rate constant as a function of the Aac content for the experiments performed at pH 5. The higher apparent decay rates seen for copolymerization environments is probably due to the composition drift and penultimate effects which are not taken into account in these fits.



Figure 4.40 The apparent initiator decay rate constants as a function of the Aac content in feed at pH 5

The conclusion is that the reaction is not 1<sup>st</sup> order in monomer. A combination of cage effect and initiator concentration decrease and, in the copolymerization reactions composition drift is involved. In all reactions at pH 5, the Aam is depleted more rapidly regardless of the initial composition. This indicates that it is entering the copolymer at a rate greater than its fraction in the feed mixture.

Evolution of comonomer conversions  $Conv_{Aac}$ ,  $Conv_{Aam}$  for experiments with 50% Aac and 70% Aac at pH 2 are given in Figure 4.41. Figure 4.42 shows total conversion results for the experiments performed at pH 2, as well.



Figure 4.41 Monomer conversion in the experiments performed at pH2



Figure 4.42 Total conversion versus time for Aam-Aac copolymerization at pH 2

As seen in Figure 4.43, where plots of the logarithm of monomer concentration versus time for the reaction carried out at pH 2, the results show that the first order kinetics fail at pH 2 as well, on the other hand both  $1.25^{\text{th}}$  and  $1.50^{\text{th}}$  order kinetics satisfactorily fitted the data.  $1.25^{\text{th}}$  ve  $1.50^{\text{th}}$  order fits are given in Figure 4.44 and 4.45.



Figure 4.43 Plots of the logarithm of monomer concentration versus time at pH 2



Figure 4.44 Initiator decay rate fits for 1.25<sup>th</sup> (5/4) order kinetics at pH 2



**Figure 4.45** Initiator decay rate fits for 1.50<sup>th</sup> (3/2) order kinetics at pH 2

## 4.2.4. Composition Drift for Aam-Aac Copolymerization at pH 5 and 2

$$F_{Aam} = f_{Aam} - (1 - x) \frac{df_{Aam}}{dx}$$
(4.40)

where x refers to conversion (*Conv*). The  $f_{Aam}$  versus conversion data in reaction IV with 70% initial Aam content at pH 5 are given in Figure 4.46. The dots are the

experimental  $f_{Aam}$  data and the  $F_{Aam}$  contours are obtained by applying the equation (4.40) to the best fit curve to the experimental data and then using the Stockmayer distribution function to flesh it out. The Aam fraction is greater in polymer than in monomer, indicating that it is entering the reaction at a rate higher than its fraction in the monomer mixture. As a result the Aam fraction is decreasing both in monomer mixture and in the instantaneous copolymer formed. This graph shows the amount of polymer produced at a given point in the reaction. The molecular weight is integrated over the fact that Aam fraction is drifting down at this initial composition shows that  $r_{Aam} > r_{Aac}$  at pH 5.



**Figure 4.46** The compositional drift during the reaction at pH 5 with 70% initial Aam content

At pH 2 the Aac is the more active monomer and it is depleted faster. Composition drift during the reaction with 70% Aac content at pH 2 is given in Figure 4.47. The Aac content of the unreacted monomer mixture is decreasing throughout the reaction, indicating that the Aac is entering the reaction at a faster rate. This is due to the ionic nature of Aam which is protonated at pH 2 [63]. As a result the Aac fraction is higher in the polymer than it is in the reaction mixture. The broadening of contours indicating the composition distribution of copolymer depends on the length of the chain formed.



**Figure 4.47** The compositional drift during the reaction at pH 2 with 70% initial Aac content

## 4.2.5. Reactivity Ratios for Aam-Aac Copolymerization at pH 5 and 2

Figures 4.48 and 4.49 show superposition of  $\chi^2$  contours for the individual experiments at pH 5 and the combined results of all experiments at this pH. The valleys in Figure 4.48 show the 1, 2 and 3  $\sigma$  confidence regions for the individual experiments. Note that they do not intersect at exactly the same point. This is because one of the experimental conditions, namely the ionic strength which depends on the Aac concentration is not the same in each experiment, in fact, it changes with conversion, during the experiment itself. For this reason the combined confidence region given in Figure 4.49 represents the cumulative average over the conditions valid during the whole experiment series.



**Figure 4.48** The reactivity contour maps for the individual experiments conducted at pH 5



Figure 4.49 The reactivity contour maps for combined results at pH 5

Figures 4.50 and 4.51 show the reactivity contour maps for the individual experiments conducted at pH 2 and their combined results, respectively. Again the contours in Figure 4.50 represent the average of the conditions during individual experiments and the Figure 4.51 the cumulative average over both experiments.



Figure 4.50 The reactivity contour maps for the individual experiments conducted at pH 2



Figure 4.51 The reactivity contour maps for combined results at pH 2

The reactivity ratios at pH 5 are found as  $r_{Aam}=1.88\pm0.17$  and  $r_{Aac}=0.80\pm0.07$  from Figure 4.49 and the reactivity ratios are found as  $r_{Aam}=0.16\pm0.04$  and  $r_{Aac}=0.88\pm0.08$  at pH 2 from Figure 4.51.

The dramatic shift in the reactivity ratios with pH had been noted in the literature as shown in Table 4.7. On the other hand numerical values obtained by various authors show considerable scatter. Factors that can contribute to this scatter include differences in reaction conditions including temperature and conversion as well as differences in data analysis techniques. Also, as seen from the Table 4.7, the reactivity of acrylamide decreases and the reactivity of acrylic acid increases with decreasing pH.

PH	r <sub>Aam</sub>	r <sub>Aac</sub>	Reaction	Ref
			Conv %	
6.25	$1.32 \pm 0.12$	$0.35 \pm 0.03$	<10	[54]
6	$0.85 \pm 0.62$	$0.33 \pm 0.20$	34-77	[58]
5.3	1.83	0.51	30-40	[61]
2.17	$0.48 \pm 0.06$	$1.73 \pm 0.21$	<10	[54]
2	$0.25 \pm 0.36$	$0.92 \pm 0.82$	28-70	[58]
1.8	0.54	1.48	30-40	[61]
2	0.16±0.04	0.88±0.08	80-90	[14]-This work
5-6	1.88±0.17	0.80±0.07	80-90	[14]-This work

Table 4.7 pH Dependence of Reactivity Ratios for Aac and Aam

The strong pH dependence of the Aam reactivity is not surprising as ionic strength of the reaction medium determines to what extent the charge on the macro radical is screened.

We would expect the change in the Aac reactivity to be larger too. Previous literature results show a greater increase in  $r_{Aac}$  with decreasing pH. However in our experiments the increase was much more limited. Even so, as the reactivity of Aam decreases almost to zero at pH 2 the Aac enters the reaction at a much faster rate.

The Henderson-Hasselbach equation with pKa taken as 4.26 [62] for Aac, predicts more than 99% ionization at pH 5. At this pH The acid units in the chain are effectively screened by the Na<sup>+</sup> ions which were added to the system to set the pH at the beginning of the reaction. Therefore sodium acrylate units can be considered as uncharged. At pH 2, the ionization degree for Aac is very low, only 0.05%. The proton is tightly bonded to the acid group and Aac groups can be considered as

neutral at pH 2. This is the similarity of Aac at pH 2 and pH 5 and their reactivity ratios at these pH's resulted in similar values.

On the other hand Aam is neutral at pH 5 but it is known to be protonated at pH 2 [63]. The difference in the reactivities of this monomer at this pH is no doubt a consequence of the protonation of the Aam at pH 2. The electrostatic repulsion between the macro radical and the charged monomer is likely to be the cause of the low reactivity of the Aam at pH 2.

## 4.2.6. Molecular Weight Analysis in Aac-Aam Copolymerization at pH 5 and 2

The evolution of the  $M_w$  for various reactions conducted at pH 5 is shown in Figure 4.52.  $M_w$  decreases as conversion proceeds. The figure shows the  $M_w$  of cumulative polymer production up to the measurement time.  $M_w$  of the instantaneous polymer produced decreases roughly twice as rapidly. As the monomer is depleted in the reaction mixture, the late production polymers can form only shorter chains. The figure also shows that higher Aam content leads to higher molecular weight. A result consistent with the much higher reactivity of the Aam at this pH.



**Figure 4.52** The evolution of the  $M_w$  for various reactions conducted at pH 5.  $[(\delta n/\delta c)_{PAac}=0.15 \text{ and } (\delta n/\delta c)_{PAam}=0.19 \text{ were used in the calculations}]$ 

As the polymer concentrations are calculated by substracting the measured monomer concentrations from the initial concentrations, at low conversion (below 10-20%)

polymer concentration and conversion have large errors. For this reason, data obtained after 20% conversion are more reliable.

Figure 4.53 shows the  $M_w$ s at 50% and 75% conversion versus initial Aac content for these reactions. Since the reactions are terminated at different conversion points comparison of results at fixed conversion is more meaningful than the final  $M_w$ . The decrease of the molecular weight with increasing Aac content and hence with decreasing reaction rate originates from the propagation step. Suppressing the propagation while initiation and termination rates are unchanged results in both lower reaction rates and lower molecular weights.



Figure 4.53  $M_w$ s at 50% and 75% conversion versus initial Aac content for reactions at pH 5

Figure 4.54 also shows the cumulative weight average mass  $M_{w}$ , which reduces with conversion, for the reactions performed at pH 2.



Figure 4.54 The evolution of the  $M_w$  for various reactions conducted at pH 2

Both the molecular weight and the reaction rate is higher at pH 2 than the pH 5 at the same feed composition. Similar behaviour have been observed in pure acrylic acid homopolymerization where the reactions conducted at pH 2 resulted in higher reaction rates and molecular weights 8-10 times those resulting in pH 5 reactions [13].

In this work at pH2 and 5 assuming the rate is proportional to  $k_p \sqrt{k_d f}$  and the molecular weight is proportional to  $k_p \sqrt{k_d f}$ . From these we can obtain,

$$\left(\frac{k_{p5}}{k_{p2}}\right)^2 = \frac{M_{w5}}{M_{w2}} \frac{R_{p5}}{R_{p2}} , \qquad (4.41)$$

$$\frac{k_{p5}}{k_{p2}} = \sqrt{\frac{M_{w5}}{M_{w2}} \frac{R_{p5}}{R_{p2}}}$$
(4.42)

and,
$$\frac{k_{15}f_5}{k_{12}f_2} = \frac{\frac{R_{p5}}{R_{p2}}}{\frac{M_{w5}}{M_{w2}}},$$
(4.43)

Figure 4.55 exhibits the molecular weights for the experiments with 70% Aac initial content at pH 2 and 5. Since the reaction rate is higher at pH 2 by a factor of 3/2 and the molecular weight by a factor of 5/2., we can conclude that the propagation rate constant is higher at pH 2 by a factor of about 2 and the initiation efficiency is lower by a factor of about 2.



**Figure 4.55** The molecular weights for the experiments with 70% Aac initial content at pH 2 and 5. Inset shows the decreasing of monomer concentration monitored by ACOMP during the experiment for the same experiments

# 4.2.7. Stockmayer Bivariate Distribution in Aac-Aam Copolymerization at pH 5 and pH 2

Stockmayer formula is valid for the material produced at a certain average molecular weight and composition. However, in our case, composition of copolymer drifts as well as the molecular weight changes throughout the reaction. Hence, Stockmayer distrubition function was integrated over the whole conversion range. These graphics give the amount of polymer produced at a given molecular weight and composition. The initial production is mostly composed of active monomers and form long chains while late production is mostly composed of the remaining unreactive monomer and form short chains due to monomer depletion.

Figure 4.56, shows the bivariate distribution for reaction IV with 70% initial Aam content at pH 5 in three dimensional plot. Note that the high molecular weight material produced early in the reaction has high Aam content while the low molecular weight material including the late production polymer has higher Aac content. Unlike the PS, PMMA study [20] where the same technique was used the effect of the composition drift is clearly visible in this reaction. Figure 4.57 shows the same plot in two-dimensional form.

It is seen very well the composition drift for this reaction. As seen in Stockmayer bivariate plot of the cumulative copolymer, shorter chains have a wide compositional distribution (50-85% Aam). Their distribution peaks around 75% Aam content. This shows that this group contains both early and late production material. By the means of this result, the most produced material in the reaction vessel was seen to have a composition of 25%Aac-75% Aam with a polymerization degree of 1200. Since Aam is active monomer at pH 5, it is depleted faster. It incorporates to polymer chain less toward the end of the reaction due to the its decreasing concentration in monomer mixture. This results in decreasing of its fraction in polymer. This is seen as a shoulder in the late part of reaction in Stockmayer distribution plot.



**Figure 4.56** Stockmayer bivariate distribution for reaction with 70% Aam initial content at pH 5 in three dimensional form



**Figure 4.57** Stockmayer bivariate distribution for reaction with 70% Aam initial content at pH 5 in two dimensional form

Figures 4.58 and 4.59 show the Stockmayer bivariate distribution for the pH 2 experiment with 70% Aac. As the composition is drifting toward lower Aac content early production high  $M_w$  polymer is seen as a plateau extending towards high  $M_w$  side at higher than average Aac fraction of about 80%.



**Figure 4.58** Stockmayer bivariate distribution for reaction with 70% Aac initial content at pH 2 in three dimensional form



**Figure 4.59** Stockmayer bivariate distribution for reaction with 70% Aac initial content at pH 2 in two dimensional form

## **4.3.** Control of Composition Through pH and Ionic Strength During Copolyelectrolyte Production. Copolymerization of Acrylic acid (Aac) and Acrylamide (Aam) at pH 3.6 in Various Ionic Strength [24]

Large differences in the reactivity ratios, result in composition drift during copolymerization as the conversion increases. Early production material is rich in the more active monomer. As it is depleted, the late production chains become poorer in the active one. When the effect of composition drift is severe, chain properties of polymers produced at the beginning of the reaction are different from those produced late in the reaction. Finally homopolymer chains of less active monomer are effects produced. These result in inhomogenities in the microstructure properties. In the case of copolymers designed with specific properties it is important to have well distributed functional groups throughout each chain. In research the composition drift is usually avoided by working at low conversion (less than % 5-10), but this measure is out of question in industry.

Microstructure properties are especially important in the coatings and adhesives industry. Stockmayer [23] had first calculated the compositional heterogeneity and derived an equation for copolymer composition as a function of chain length, his work involves the distribution for material produced under fixed reaction conditions and does not include the effect of changing reactor conditions due to composition drift.

Living polymerization, anionic, group transfer or coordination polymerization reduce heterogeneity. Initiators used for these methods are called iniferters (*initiator*, trans*fer*, *ter*minator) or initers (*initiator*, *ter*minator) however these specialized methods are expensive and are not applied in the industry except for research purposes [141-143]. In nonionic systems, changing the feeding system or changing physical properties of the medium are some of the ways to change reactivity ratios. For example choosing highly water soluble less active monomer and less soluble more active monomer [144] and controlling the addition rate in emulsion systems is another way to obtain homogenous composition [145].

On the other hand in ionic systems the composition drift can be more severe and its undesirable effects are more significant. It is desirable to place the charged units at approximately one Bjerrum length apart. The Bjerrum length is 0.72Å at room

temperature in water. A monomer unit is typically about 0.25Å. Therefore approximately two uncharged units must be placed between two charged groups. If the charged units are placed more densely, counterion condensation occurs and no extra hydrodynamic volume is gained. On the other hand decreasing the charged group density below the Bjerrum limit results in is low hydrodynamic volume as the chain does not swell to its maximal volume. The composition drift results in some chains having a concentration of charged units much higher than the critical concentration while other chains have a much lower than critical concentration.

In copolyelectrolytes, such as the acrylamide acrylic acid system [14, 54-62], monomer reactivity ratios are closely related with the pH of the medium. The IS affects the electrostatic repulsion between the macro radical and the ionic monomer by altering the screening length. It is also expected to be a factor in reaction kinetics and the reactivity ratios. There have been suggestions that the ionic strength (IS) as well as the pH influences the reactivity ratios but there is not a systematic study on this effect.

In this part of the studies, the possibility of controlling the composition of Acrylic acid/Acrylamide copolymers by controlling the pH and the ionic strength of the reaction medium is investigated.

Our previous work at pH 2 and 5 has suggested that the cross over point, where the reactivities of the two monomers are equal, is expected to be about pH 3.6 for reactions performed without added salt.

Here the effects of the IS on the reactivity ratios of AAm and Aac are investigated. The working pH was chosen as 3.6. It is also aimed to determine under which conditions no composition drift occurs.

Three sets of experiments were performed. One set at total monomer concentration of 0.47mol/L. In this set concentrations of the Aac and the pH regulator (NaOH) depended on the Aac fraction in the feed mixture. The other two sets were performed at two different constant Aac and NaOH concentrations but varying total monomer concentrations.

Figure 4.60 shows the raw ACOMP data for a typical reaction (50%Aac-50%Aam in set 1), where each step is indicated. These are, the solvent (0.1 M NaCl) baseline

stabilization period, the baseline of monomers, the point of initiator addition, and the polymerization period.

Firstly 0.1 M NaCl as carrier solvent was pumped through to the detector train using only solvent pump. After stabilization was obtained for all detectors, reactor solution containing Aac at pH 2 was passed through the system, which took 40 min. Then, NaOH was added to the reactor solution to adjust pH to 3.6 and next was to take the baseline of reactor solution at pH 3.6 (3666 - 6690 sec). To complete monomer baseline step, Aam was added to the reactor. The pH of the solution didn't change after adding Aam since it is a neutral monomer. Mixture of two comonomers was pumped to detectors by diluting to predetermined concentration (6690-11964 sec). At around 12000 sec, ACV (4,4'-Azo bis (4-cyanovaleric acid)) was added. pH was also stable at 3.6 after initiator. UV absorption measurements at 205nm and 226nm were used in monitoring the conversion of the monomer to polymer. The two UV signals increase during the pure monomer suction period, whereas the LS does not change. During polymerization, the loss of the double bonds of each comonomer as it incorporates into polymer leads to (differentially) decreasing UV absorption in both bands, while the LS signals increase with increasing polymer concentration. At the beginning of the reaction, reactor was purged for 30min with N<sub>2</sub> and very slow purging continued during the reaction. The reactor was then lowered into a temperature-controlled bath at  $60^{\circ}$ C. Reaction was initiated by adding the ACV in powder form. The solution was magnetically stirred during the reaction.



**Figure 4.60** Raw ACOMP data for a copolymerization reaction (50%Aac-50%Aam in set 1 at pH 3.6), where each step is indicated

The monomer and polymer concentrations at any given moment are found through ACOMP data, using two UV absorption signals at 205nm and 226nm. The UV absorption coefficients for Aac and Aam were determined from the UV detector response to their stepwise additions, and used subsequently to compute the concentration of each comonomer during the reaction by solving the two simultaneous equations from the dual wavelength UV data. The absorption coefficients ( $\partial V_{UV} / \partial c$ ) are given in Table 4.8. These two signals in addition to the two conservation equations (ie, the total amide concentration in monomer and polymer is equal to the initial concentration) provide the linear independence of four equations, which are sold to obtain the concentrations of the four species (Aac, Aam, PAac, and PAam) as functions of time, as described in Aam-Aac system at pH 2 and pH 5 [14].

Set #	Aac %	205 nm		226 nm	
		$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{Aac})$	$(\partial V_{UV} / \partial c_{Aam})$	$(\partial V_{UV} / \partial c_{Aac})$
	70	5.244	3.021	635.289	84.114
	50	5.308	3.105	632.572	85.591
1	30	5.212	3.109	622.692	83.772
	10	5.088	2.539	608.715	82.812
2	70	5.317	2.979	638.772	81.285
	50	5.251	3.003	632.320	83.576
	30	5.212	3.109	622.692	83.772
	70	5.244	3.021	635.289	84.114
3	50	5.015	3.029	622.351	85.128
	30	4.949	3.099	602.722	85.032

**Table 4.8**  $(\partial V_{UV} / \partial c)$  values as g/mL obtained from UV detector response of Aam and Aac at 205 and 226 nm

The Aac, Aam and total conversion versus time plots for the set 1 were given in Figures 4.61, 4.62, 4.63, respectively.



Figure 4.61 Evolution of Aac conversion for the set 1 at pH 3.6



Figure 4.62 Evolution of Aam conversion for the set 1 at pH 3.6



Figure 4.63 Time – total conversion plots for the set 1 at pH 3.6

In the  $1^{st}$  set of experiments, conducted at constant total initial monomer concentration, the reaction rate is seen to decrease with increasing Aac content from 10% Aac to 50% Aac. Indicating that the Aam is the faster monomer at these conditions. Probably the electrostatic repulsion between charged macroradicals and charged monomers has a role here. The reaction at 70% Aac is as fast as the fastest

of the group. This reaction is conducted at a very high IS so that the electrostatic repulsion is suppressed.

Figures 4.64, 4.65, 4.66 show the fractional conversion of each comonomer  $Conv_{Aac}$ ,  $Conv_{Aam}$  and evolution of total conversion,  $Conv_{Total}$  for the set 2 copolymerization experiments, obtained from the dual wavelength UV data.



Figure 4.64 Evolution of Aac conversion for the set 2 at pH 3.6



Figure 4.65 Evolution of Aam conversion for the set 2 at pH 3.6



Figure 4.66 Time – total conversion plots for the set 2 at pH 3.6

The  $2^{nd}$  set of experiments are conducted at constant and low IS (equal to the 30% Aac experiment above), this set confirms the trend seen in the  $1^{st}$  set, that is the reaction rate decreases with increasing Aac fraction. The  $3^{rd}$  set conducted at very high IS (equal to the 70% Aac experiment in the first set) shows almost complete independence of the reaction rate from Aac fraction. Here the screening is so effective that the electrostatic effects vanish. Whereas Figures 4.67 and 4.68 gives conversion results for Aac and Aam, Figure 4.69 exhibits the overall conversion in the copolymerization reactions for the set 3.



Figure 4.67 Evolution of Aac conversion for the set 3 at pH 3.6



Figure 4.68 Evolution of Aam conversion for the set 3 at pH 3.6



Figure 4.69 Evolution of total conversion for the set 3 at pH 3.6

### 4.3.1. Reactivity Ratios for Aac-Aam Copolymerization at pH 3.6

The contour maps for the combined results of experiments of each set gives the acceptable part of the  $r_{Aac}$ ,  $r_{Aam}$  parameter space valid for the conditions of that set. Figures 4.70, 4.71, 4.72 shows the confidence contours for the MRR (Monomer Reactivity Ratios) for the individual experiments of the set 1, set 2, set 3, respectively.



**Figure 4.70** The 1 2 and 3 sigma confidence contours for the MRR for individual experiments in the set 1 at pH 3.6



**Figure 4.71** The 1 2 and 3 sigma confidence contours for the MRR for individual experiments in the set 2 at pH 3.6



**Figure 4.72** The 1 2 and 3 sigma confidence contours for the MRR for individual experiments in the set 3 at pH 3.6

The combined confidence intervals for the experiments at 30, 50 and 70% Aac content are shown in Figure 4.73 for all 3 sets. They show the acceptable regions in the  $r_{Aac}$ ,  $r_{Aam}$  parameter space for the applicable experimental conditions.



Figure 4.73 The reactivity contour maps for combined results at pH 3.6

Here, for the reactivity ratios of Aac and Aam at the nominal pH value 3.6 in water without salt, the IS of the medium is determined by the concentrations of Aac and the NaOH added to set the pH. Thus, without additional salt the ionic strength is sensitive to Aac concentration but not on the Aam concentration.

Reactivity ratios calculated for each set including the previous results are given in Table 4.9 Note that at pH 3.6 the reactivity ratios of Aam and Aac are much closer to each other than the experiments at pH 2 and 5.

Experiment		<i>r<sub>Aac</sub></i>	<i>r<sub>Aam</sub></i>	$r_{Aac}/r_{Aam}$	$r_{Aam}/r_{Aac}$
PH=2		0.88	0.16	5.5	0.1818
PH=3.6	Set 1	2.43	1.66	1.46	0.68
PH=3.6	Set 2	2.40	1.66	1.44	0.69
PH=3.6	Set 3	2.55	2.02	1.26	0.79
pH 5	5	0.8	1.88	0.42	2.35

**Table 4.9** Aac, Aam Reactivity Ratios Calculated for the Set 1, Set 2, Set 3 and theExperiments Conducted at pH 2 and 5

The regions for sets 2 and 3 conducted at the same pH 3.6 but different acrylic acid contents (0.1414 M, and 0.329 M respectively) do not overlap. This indicates that the reactivity ratios depend on the IS as well as the pH. The experiment set 1 is performed at constant total initial monomer concentration but each experiment is done at a different IS. The confidence region partially overlaps with the result of set 2. However as the results depend on the IS, working at constant monomer concentration but varying IS does not represent valid experimental planning in the case of ionic monomers.

#### 4.3.2. Composition Drift for Aam-Aac Copolymerization at pH 3.6

The composition of the material incorporating instantaneously into copolymer was found from the instantaneous monomer composition and its derivative.

In ACOMP method the feed composition is continuously monitored and its evolution can be used to give a rough idea of the reactivity ratios before any numerical computation is performed. Figures 4.74, 4.75 and 4.76 show the evolution of the feed composition as a function of conversion for experiments in sets 1, 2, and 3 respectively. The composition of the polymer produced instantaneously can be obtained from these data using the equation (4.40), where x is conversion (*Conv*).

$$F_{Aam} = f_{Aam} - (1-x)\frac{df_{Aam}}{dx}$$
(4.40)

To prevent noise amplification by the derivative term in the equation, it is more fruitful to fit for the monomer composition evolution and apply the above formula to the best-fit curve. Here our purpose is to obtain the conditions that produce no drift. The experiment at 30% Aac (at set 1 and set 2) achieves this goal. There is no drift in the monomer composition and hence the polymer composition in that experiment up to 80% conversion. As seen in Figure 4.76 the composition in the 30% Aac experiment (at set 3) performed at a higher IS but identical initial monomer composition, drifts somewhat, The Aac fraction in the monomer mixture increasing from 29% to 35% by 80% conversion; again demonstrating that the IS as well as the pH is effective in determining the copolymer composition.



**Figure 4.74** Aac fraction versus conversion (composition drift) for the set 1 at pH 3.6



**Figure 4.75** Aac fraction versus conversion (composition drift) for the set 2 at pH 3.6



**Figure 4.76** Aac fraction versus conversion (composition drift) for the set 3 at pH 3.6

#### 4.3.3. Molecular Weight Analysis in Aac-Aam Copolymerization at pH 3.6

The evolutions of molecular weights for the experiments of all sets are given in Figure 4.77.

 $M_w(t)$  the molecular weight of the material produced up to time t and  $M_{w,inst}(t)$  the molecular weight of the material produced instantaneously at time t are related by,

$$M_{w,inst}(t) = M_w + x \frac{dM_w}{dx}$$
(4.44)

where x is the conversion at that time. This relation and equation (4.40) give the average composition and  $M_w$  at any point in the reaction.

As the polymer concentrations are calculated by substracting the measured monomer concentrations from the initial concentrations, at low conversion (below 10-20%) polymer concentration and conversion have large errors. For this reason, data obtained after 20% conversion are more reliable.



Figure 4.77 Molecular weights for the reactions at all sets performed at pH 3.6

# 4.3.4. Stockmayer Bivariate Distribution in Aac-Aam Copolymerization at pH 3.6

As the Stockmayer formula applies to reaction conditions at a single time, it is integrated over conversion to obtain the composition-molecular weight bivariate distribution. Figures 4.78 and 4.79 show the bivariate distribution for the experiment with 70% Aac (at the set 1 and the set 3) which has moderate amount of composition drift. The figure represents the overall distribution of the polymeric material synthesized. As the monomer rich environment early in the reaction results in longer polymers and lower molecular weight material are produced in the poorer environment in the later stages of the reaction, composition drift during the reaction results in broadening and loss of symmetry for the peak in the bivariate distribution. The bend in the peak at lower molecular weight is a result of this effect.



**Figure 4.78** Stockmayer bivariate distribution for reaction with 70% Aac at pH 3.6 (at the set1 and the set 3) as mesh plot



**Figure 4.79** Stockmayer bivariate distribution for reaction with 70% Aac at pH 3.6 (at the set1 and the set 3) as contour plot

The bivariate distribution for the experiment with 30% Aac (at the set 1 and the set 2) is shown in Figures 4.80 and 4.81. Here the peak is narrow and symmetric, a direct result of the no-drift reaction.



**Figure 4.80** Stockmayer bivariate distribution for reaction with 30% Aac at pH 3.6 (at the set 1 and the set 2) as mesh plot



**Figure 4.81** Stockmayer bivariate distribution for reaction with 30% Aac at pH 3.6 (at the set 1 and the set 2) as contour plot

Integration of the bivariate distribution over molecular weight gives the cumulative composition distribution. Figure 4.82 shows the cumulative distribution (continuous lines) as well as the composition distribution of material polymerized at early in the reaction, at 50% conversion and at the end of the reaction (dashed lines). For the reaction with 70% Aac (at the set1 and the set 3) (right hand side) composition extends from 65 to 80% Aac. The reaction with 30% Aac (at the set 1 and the set 2) (left hand side) has no composition drift. For this reason the gaussian distributions are all centered at 30% Aac, and distribution was only between 27 to 33% Aac. The cumulative curve is also almost gaussian in shape and shows no broadening. The reaction with 70% Aac (at the set1 and the set 3) has only moderate composition drift. Despite this, one can clearly see that the material polymerized early, at mid reaction and late in the reaction are centered at clearly distinct compositions (76%, 74% and 63% Aac). In fact material produced early and late in the reaction have non-overlapping distributions. As a result the cumulative distribution is broad and asymmetric. The effect of the composition drift is clearly visible.



**Figure 4.82** The composition distributions for the reactions with 70% Aac (at the set1 and the set 3) (right) and with 30% Aac (at the set 1 and the set 2) (left) at pH 3.6. Dashed lines show the distributions of early production, mid reaction and late reaction polymers. The continuous lines show cumulative composition distributions

The Henderson-Hasselbach equation with pKa taken as 4.26 [62] for Aac, predicts 19-20% ionization at pH 3.6. Thus even in reactions with high Aac fraction counterion condensation is not expected at reaction conditions.

The acid units in the chain are partly screened by the Na<sup>+</sup> ions, originating from the NaOH which was added to the system to set the pH at the beginning of the reaction as well as monomer ions. As the screening depends on the IS it is not surprising that the reactivity ratios and the copolymer compositions also depend on it.

#### **5. CONCLUSIONS**

In this work, the kinetics of free radical homopolymerization and copolymerization reactions carried out in aqueous media were investigated.

The first section of this study includes the copolymerization of 4-vinylbenzene sulfonic acid sodium salt (VB) with Acrylamide (Aam). The reactions were carried out in 0.1 M NaCl solution and in water. Copolymerization reactions with salt were studied by ACOMP (Automatic Continuous Online Monitoring Polymerization), where a large amount of data are obtained for each experiment resulting in more accurate determination of reaction parameters. This application involves automatic, continuous removing a small amount of reactor solution by a pump and mixing the reactor material at high pressure with a much larger volume of a pure solvent drawn from a solvent reservoir by another similar pump to produce a dilute reactor solution, on which, light scattering, viscosimetric, UV and RI measurements was made. The kinetics of the system was evaluated through the data from ACOMP. Monomer reactivity ratios (MRR) were calculated by the Error in Variables (EVM) method developed for obtaining the reactivity ratios by on-line monitoring. The same procedure was applied to VB-Aam copolymerization carried out at 60°C in water with no added salt in reactor. Composition drift was continuously monitored and it revealed a sudden change in reaction kinetics for the set of experiments performed in water. MRR were calculated separately by EVM.

In the second section of the work, Acrylic acid - Acrylamide copolymerization was monitored by ACOMP, as well. Two sets of reactions were conducted at pH 5 and pH 2. Reaction kinetic such as reaction order and the reactivities of the monomers was discussed for both pHs. Composition drifts were determined for all experiments at pH 5 and 2. Monomer reactivity ratios were found via EVM. Stockmayer distribution was obtained for some reactions with various Aam and Aac fraction at two pHs.

In the third part of this study, the possibility of controlling the composition of Acrylic acid-Acrylamide copolymers by controlling the pH and the ionic strength of the reaction medium was investigated. In this work, the pH of the raction medium was adjusted to 3.6, where no composition drift was expected. At pH 3.6, three sets of reactions are performed. The reactions were monitored online by the ACOMP system. Copolymerization kinetics at constant total monomer concentration and at two different constant ionic monomer concentrations were compared. The data were analyzed by EVM. The effect of polyelectrolytic interactions on the reactivity ratios were discussed in detail. The pH and composition where no composition drift was obtained, were defined. The impact of pH and IS on the sequence distribution of the charged and uncharged comonomeric units on the chain and the molecular weight-composition bivariate distribution were also discussed.

#### **VB-AAm Copolymerization in 0.1 M NaCl Solution**

- ACOMP has been used to monitor the synthesis of polyelectrolytic copolymers of 4-Vinylbenzenesulfonic acid sodium salt (VB) and Acrylamide (Aam).
- For the reactions conducted in 0.1 M NaCl, it was seen that Aam homopolymerization was faster than VB and both homopolymerization rates are higher than copolymerization rates at any combination. In 25%VB-75% Aam and 10%VB-90% Aam reactions, Aam exhibited two different rate behaviour. Its polymerization rate increased when the VB was depleted. The acceleration observed in these reactions with the depletion of VB indicated that rest of the reaction was homopolymerization of Aam.
- Not all starting ratios of [VB]/[Aam] led to blends of copolyelectrolyte and neutral homopolymer, polyacrylamide. For 10 % VB/90% Aam, 25% VB/75% Aam, the two phase conversion of Aam results, whereas in the other two cases 50% VB/50% Aam and 75% VB/25% Aam, there is only a single phase of conversion for Aam. In addition, VB has a single phase of conversion in each experiment, However, in 50% VB/50% Aam and 75% VB/25% Aam and 75% VB/25% Aam it is not exhausted, and continues to co-convert with Aam throughout the reaction. That is, no blend is produced.
- Sequential Sampling Method and GPC (Gel Permition Chromotography), results verified the ACOMP results.

- The evolution of molecular weight throughout the reaction was calculated from the light. The light scattering raw voltages were seen to jump after the VB conversion phase was complete and increased during the second phase of production of PAam. In experiments where the VB is completely exhausted (10% VB and 25% VB), the Aam enters the reaction at a higher rate so that the reaction picks up speed and the molecular weight increases. No such effect was seen in the 50% VB , 75% VB reactions which were copollymerizations throuhout.
- Continuous online monitoring of the copolymerization reactions is a very powerful technique for investigating reaction kinetics. The online data can be used to obtain the reactivity ratios. It also provides an insight to understand the changes in the reaction kinetics due to the changing conditions that occur during the reaction as well. The reactivity ratios,  $r_{Aam} = 0.085 \pm 0.020$ ,  $r_{VB}=2.0\pm0.33$ , for VB-Aam were found copolymerization in 0.1 M NaCl. According to the reactivity results, Although Aam polymerizes much faster than VB, the latter was the more active monomer. The terminal model was shown to give a good description of the polymer composition with the predictions of the model with  $r_{Aam}$ =0.085 and  $r_{VB}$ =2.0.

#### **VB-AAm Copolymerization in Water**

- The two rate regimes of Aam conversion was also found in the cases of 1.5% VB/98.5% Aam, 5% VB/95% Aam, and 10% VB/90%Aam copolymerization reactions carried out in water with no added salt in the reactor. In water, Aam homopolymerization is faster than VB and both homopolymerization rates are higher than copolymerization rates at any combination. VB homopolymerization rate is higher in salt solution than in water. These results are also verified by GPC.
- The salient feature of the set of experiments conducted in water was a sudden change in reaction kinetics, which appeared as a corner in the composition versus conversion data. The corners were seen at 10-30 % conversion depending on the VB during the copolymerizations in water with 5 to 50% VB. The behaviour of the reaction changed ubruptly at this

point. The sudden change in the reaction kinetics in water is probably due to reaching the c\* (overlap) concentration so that further reaction takes place within the coils so that the electrostatic repulsion between the macro radical and the charged VB monomer is suppressed. The reactivity of VB increases substentially.

- The corner occurred approximately at 11% conversion in the 15% VB experiment. In experiments both at lower and higher VB concentrations it occurred at higher conversions. Coil volume of a polymer depends on its molecular weight and persistence length (PL). The light scattering data for the reaction conducted in water indicated that the molecular weights of these copolymers were similar up to 30% conversion. Also, it is known that PL is a function of Debye screening length and the strength of electrostatic interactions. We have obtained indirect evidence that, in water, the maximally swollen copolymer has the composition 15% VB 85% Aam. Higher VB fractions reduce the Debye screening length because of higher ionic strength and result in reduced swelling. At very low VB concentration (5%) the electrostatic interaction is less and corner occurs later. As a result maximum hydrodynamic volume is obtained at 15% VB fraction in our experimental conditions.
- Monomer reactivity ratios (MRR) were calculated by the EVM and since the reactions in water gave two distinguishable regions, the reaction part before and after the corner were evaluated separately. The reactivity ratios were found as r<sub>Aam</sub>=0.34±0.07, r<sub>VB</sub>=0.40±0.21 and r<sub>Aam</sub>=0.2±0.04, r<sub>VB</sub>=9.0±0.8 for before and after the corner, respectively. In the first phase of the reactions, the composition was seen to be almost constant. After the corner, VB fraction started to drop rapidly with further conversion, which resulted in a sudden increase in VB reactivity.
- It was noted that pH is not the sole factor determining the monomer reactivity ratios, but ionic strength has a role as well.

#### Aac-Aam Copolymerization at pH 5 and 2 in Water

- ACOMP has been used for the first time to monitor the synthesis of polyelectrolytic copolymers of Acrylic acid (Aac) and Aam.
- Kinetic investigations were done in this system. The results revealed that the reactions at PH 5 showed a marked slowing down as compared to 1<sup>st</sup> order kinetics. This slowing down can be caused by a combination of three effects. One of them is decrease of the initiator. The other one is composition drift observed in case of copolymerization, whereby the reacton medium becomes richer in the less active monomer as a consequence of the rapid depletion of more active monomer . the last one is reaction with higher order. Since considering all of these effects involve too many parameters, in our work, we instead compared our results with reaction order as would be expected in cage effect and with an initiator decay time. It is seen that the first order kinetics do not satisfy the data even when the initiator depletion is taken into account. Cage effect kinetics, of 1.25<sup>th</sup> order according to Noyes and 1.50<sup>th</sup> order according to Hamielec are both compatible with our data.
- At pH 2 Aac was seen to be more active monomer ( $r_{Aam}=0.16\pm0.04$  and  $r_{Aac}=0.88\pm0.08$ ) and at pH 5 Aam was more active ( $r_{Aam}=1.88\pm0.17$  and  $r_{Aac}=0.80\pm0.07$ )
- It is seen in the literature that the numerical values for the reactivities differ. Differences in the reactor temperature, use of linear or non-linear analysis methods and using low conversion versus high conversion results are some of the factors contributing to the spread in the results. Since the behavior of polyelectrolytes depend so strongly on the reaction medium, changes in the properties of the medium, such as its pH, ionic strength and viscosity, during the reaction also effect the results. While low conversion work is purer because of the intrinsic value of the results, high conversion work is more relevant to practical applications. Online data acquisition techniques, which give hundreds or even thousands of points throughout an experiment provide much better statistics. They are also useful to determine whether the measured parameters remain constant during the reaction. That is, if low conversion results lead to different values than high conversion results, one

would conclude that the measured parameters are not constant but evolve during the reaction. For these reasons online methods give much more information from each reaction. According to reactivity ratios, at pH 5, acrylamide is the more active monomer and Aam content correlates with the reaction rate and at pH 2 the reverse is true. The strong pH dependence of the Aam reactivity is not surprising as ionic strength of the reaction medium determines to what extent the charge on the macro radical is screened. We would expect the change in the Aac reactivity to be larger too. Previous literature results show a greater increase in r<sub>Aac</sub> with decreasing pH. However in our experiments the increase was much more limited. Even so, as the reactivity of Aam decreases almost to zero at pH 2 the Aac enters the reaction at a much faster rate. At pH 5 Aac units in the polymer chain are in sodium acrylate form due to the Na<sup>+</sup> ions screening the charges and can be considered as uncharged. At pH 2 Aac is neutral because of the very low ionization degree. This is the similarity of Aac at pH 2 and pH 5 and this is why Aac reactivity ratios at these pH's resulted in similar values. On the other hand, Aam is neutral and active monomer at pH 5. however Aam has very low reactivity as a consequence of its protonation at pH 2. Also, it was found that the electrostatic repulsion between the macro radical and the charged monomer caused the low reactivity of the Aam at pH 2.

- In the molecular weight  $(M_w)$  analysis at pH 5,  $M_w$  decreased as conversion proceeded. It was seen also the instantaneous  $M_w$  of polymer decreased roughly twice as rapidly. The analysis also showed that higher Aam content led to higher molecular weight as a result of much higher reactivity of the Aam at this pH. The decrease of the molecular weight with increasing Aac content and hence with decreasing reaction rate also corroborates that this effect originates from the propagation step. Suppressing the propagation while initiation and termination rates are unchanged results in both lower reaction rates and lower molecular weights.
- Also, the results indicated that both the molecular weight and the reaction rate was higher at pH 2 than the pH 5 for the reaction carried out at the same feed composition. This arises from the propagation step, not initiation. If initiation step were responsible, then the increase in reaction rate would result in the

decrease in molecular weight. Because, more chain radicals would occur and they could terminate one another faster, which would decrease the molecular weight.

• The effects of both the composition drift and decreasing monomer concentration were seen in Stockmayer bivariate distributions.

### Aac- Aam Copolymerization at pH 3.6 in Various Ionic Strength

- In this work, the pH was chosen through the previous studies indicated as a candidate for the crossover point, which no composition drift was expected. At this pH 3.6 three sets of reactions are performed. The reactions were monitored online by the Automatic Continuous Online Monitoring of Polymerization (ACOMP) system. Copolymerization kinetics at constant total monomer concentration and at two different constant ionic monomer concentrations were compared.
- The 1<sup>st</sup> set of experiments were performed at constant total initial monomer concentration (total monomer concentration of 0.47mol/L). The reaction rate decreased with increasing Aac content from 10% Aac to 50% Aac, which indicated that the faster monomer was the Aam at these conditions. Probably the electrostatic repulsion between charged macroradicals and charged monomers has a role here. The reaction with 70% Aac is carried out at a very high IS so that the electrostatic repulsion is suppressed. This reaction was seen to be as fast as the fastest of the group.
- The 2<sup>nd</sup> set of experiments were carried out at constant and low IS (equal to the 30% Aac experiment in the first set  $c_{Aac}$ =0.1414 mol/L and  $c_{NaOH}$ =0.0275 mol/L). It was found that the reaction rate decreased with increasing Aac fraction, as well.
- The  $3^{rd}$  set were conducted at constant and very high IS (equal to the 70% Aac experiment in the first set  $c_{Aac}$ =0.3290 mol/L and  $c_{NaOH}$ =0.0680 mol/L) exhibited almost complete independence of the reaction rate from Aac fraction. In these experiments, it was understood that the screening was so effective that the electrostatic effects vanished.

- The 3 sets show that except for the experiments conducted at the highest IS the Aam is the faster monomer. This is despite the reactivity ratio of Aac being higher than that of Aam.
- The reactivity ratios were found from the combined confidence regions as r<sub>Aam</sub>=1.66±0.14 and r<sub>Aac</sub>=2.43±0.19 for set 1, r<sub>Aam</sub>=1.66±0.08 and r<sub>Aac</sub>=2.40±0.17 for set 2 and r<sub>Aam</sub>=2.02±0.15 and r<sub>Aac</sub>=2.55±0.13 for set 3. The results indicate that the reactivity ratios depend on the IS as well as the pH.
- In this study, our purpose is to obtain the conditions producing no drift. The experiment at 30% Aac -70% Aam (at Set 1 and Set2) achieved this goal. no drift was observed in the monomer composition and hence the polymer composition in these experiments up to 80% conversion. The composition in the 30% Aac experiment of Set 3 at a higher IS but identical initial monomer composition, drifted somewhat. The Aac fraction in the monomer mixture was increased from 29% to 35% by 80% conversion, which again demonstrats that the IS as well as the pH is effective in determining the copolymer composition.
- Stockmayer formula was applied to reaction with 70% Aac (at the Set 1 and the Set 3) which exhibited moderate amount of composition drift. It was integrated over the whole conversion range. The plot represents the overall distribution of the polymeric material synthesized. Composition drift throughout the reaction results in broadening and loss of symmetry for the peak in the bivariate distribution. Because, the monomer rich environment early in the reaction results in longer polymers and lower molecular weight material are produced in the poorer environment in the later stages of the reaction. The bend in the peak at lower molecular weight is a result of this effect. The bivariate distribution for the experiment with 30% Aac (at the Set 1 and the Set 2) was shown that the peak was narrow and symmetric, a direct consequence of the no-drift reaction.
- Integration of the bivariate distribution over molecular weight gives the cumulative composition distribution. The cumulative distribution as well as the composition distribution of material polymerized were investigated at

early in the reaction, at 50% conversion and at the end of the reaction. For the reaction with 70% Aac at the Set 1 and the Set 3 composition was seen to extend from 65 to 80% Aac. Since the reaction with 30% Aac at the Set 1 and the Set 2 has no composition drift, the gaussian distributions are all centered at 30% Aac, and distribution was seen only between 27 to 33% Aac. In addition, the cumulative curve was also almost gaussian in shape and showed no broadening. In our study, moderate composition drift was observed in the reaction with 70% Aac at the Set1 and the Set 3). For this experiment, the material produced early, at mid reaction and late in the reaction are centered at 76%, 74% and 63% Aac which are clearly distinct compositions, respectively and distibutions of the material produced early and late in the reaction don't overlap, which causes the cumulative distribution is broad and asymmetric.

- Unlike non-ionic systems, in copolyelectrolytes the reactivity ratios depend on the production conditions and solvent dielectric nature. The strong pH dependence of the Aam/Aac reactivities was known. These results also clarify the effect of IS. They are not surprising as the IS of the reaction medium determines to what extent the charge on the macro radical is screened.
- The ability to change the reactivity ratios by varying the pH and the IS of the medium can be used to avoid the composition drift and manufacture copolymers with narrow composition distributions.
- The practical significance of these results is in the ability to obtain different copolymer composition from the same couple of monomers by performing the reactions at different pH and ionic strength. Especially for a nonionic monomer and free acidic or basic comonomer the production conditions define the composition. Choosing the pH and the IS so that the azeotropic point is close to the desired copolymer composition is a powerful tool in forming polyelectrolytic copolymers of desired characteristics.
- Once the material is produced, its ionic character can be changed depending on the medium pH. This gives the chemist a powerful tool in controlling the copolymer composition.

- We believe that the ability to form copolymers with uniform composition distributions and with charged elements separated by one Bjerrum length within statistical fluctuations and the ability to monitor that this is the case is a significant advance made possible by modern online monitoring techniques.
- The results show that the reactivity ratios depend on the IS as well as the pH. This indicates that a proper experimental protocol for finding these ratios necessitates constant IS and pH for all experiments. Secondly as the reactivity ratios depend on the environment a iven set of ratios is valid only in the environmentit is obtained, and the reactivity ratios quoted without pH and IS are meaningless for the case of chared monomers.
- Finally, it is possible to form coplyelectrolytes with uniform compositions without any composition drift.

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He has 6 publications in SCI indexed journals.

- Copolymerization Reactivity Ratios Analysis of Sequentially Sampled Data by Error in Variables Method
  Ahmet Paril, Ahmet Giz, Huceste Çatalgil-Giz
  Journal of Applied Polymer Science, 95, 2005, 393-399
- 2- Reactivity Ratios of Acrylamide-Vinyl Pyrrolidone Copolymerization System Obtained by Sequential Sampling Ali Akyüz, Ahmet Paril, Ahmet Giz *Journal of Applied Polymer Science*, 100, 2006, 3822-3827
- Swelling Studies in Electrochemically Prepared Acrylamide/N,N<sup>r</sup> Methylene Bisacrylamide Gels
  Gülcemal Yildiz, Ahmet Paril, Ahmet Giz, Huceste Çatalgil-Giz Journal of Applied Polymer Science, 101, 2006, 1398-1401
- 4- Effect of Medium pH on the Reactivity Ratios in Acrylamide Acrylic Acid Copolymerization
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- 5- Online Monitoring of the Evolution of Polyelectrolyte Characteristics during Postpolymerization Modification Processes
  Ahmet Paril, Alina M. Alb, Wayne F. Reed
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- Reactivity Ratios and Implicit Penultimate Effect in Copolymerization of 4-Vinylbenzenesulfonic Acid Sodium Salt and Acrylamide
  Ahmet Paril, Didem Sünbül, Alina M. Alb, Huceste Çatalgil-Giz, Ahmet T. Giz, submitted.
- 8- Composition control through pH and ionic strength during copolyelectrolyte Production
  Ahmet Paril, Ahmet T. Giz, Wayne F. Reed, Huceste Çatalgil-Giz, in preparation.