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**POLİMERİK SİSTEMLERİN FAZ GEÇİŞLERİNİN
TEORİK VE DENEYSEL OLARAK İNCELENMESİ**

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LIST OF SYMBOLS

a_1	: Activity of solvent
a_i	: Activity of component i
B, C	: Parameters occurring in thermodynamic relations for dilute polymer solutions
c	: Concentration
d	: Density of solvent
D	: Final equilibrium diameter of the gel
D_0	: Initial diameter of the gel
f	: Average number of ionic units between successive junctions in a network chain
f_{el}	: Elastic force associated with a given deformation
ΔG_i	: Gibbs free energy change of component i
ΔG_m	: Gibbs free energy change of mixing
ΔG_{el}	: Gibbs free energy change of elastic deformation
$\overline{\Delta G}_i$	: Partial molar free energy of dilution
ΔH	: Enthalpy change
ΔH_m	: Heat of mixing
$\overline{\Delta H}_i$	: Partial molar heat of dilution
i	: Number of electronic charges per polymer unit in a polyelectrolyte
k	: Boltzmann's constant
k_H	: Huggins interaction coefficient
l	: Bond length

- M : Molecular weight of polymer
- M_n, M_w, M_v : number, weight and viscosity average molecular weights, respectively
- M_c : Average molecular weight between successive junctions in a network chain
- n, n_0 : Refractive index of solution and pure solvent
- n_1 : Mole fraction of solvent molecules in a solution
- n_2 : Mole fraction of polymer network in a solution
- n_3 : Mole fraction of linear polymer in a solution
- n_i : Mole fraction of component i in a solution
- N_A : Avogadro's number
- N^* : The number of Kuhn segments in a polymer chain
- N : The number of segments in a network chain
- N_1, N_2 : Mole fractions of molecules 1 and 2 in a solution
- P : Pressure
- P_1 : Partial pressure of solvent in a solution
- P_1^0 : Partial pressure of pure solvent
- p : The number of units in a Kuhn segment
- q_v : Swelling ratio by volume
- q_w : Swelling ratio by weight
- q_m : Equilibrium swelling ratio with pure solvent, i.e. maximum swelling
- $r, \langle r^2 \rangle^{1/2}, \langle r_0^2 \rangle^{1/2}$: distance between the ends of a polymer chain, its root-mean-square averaged over all configurations, and the same for unperturbed molecules
- R : The gas constant
- $\langle S^2 \rangle^{1/2}$: radius of gyration or the root-mean-square distance of the elements of the chain from its center of gravity

ΔS	: Entropy change
ΔS_m	: Entropy change for mixing
ΔS_{el}	: Entropy change for elastic deformation
ΔS_1	: Partial molar entropy of dilution
T	: Absolute temperature (K)
T_c	: Critical temperature
T_{tr}	: Transition temperature
V^*, V_0^*	: Volume of solution phase and its initial value
V	: Volume of the polymer network at equilibrium degree of swelling
V_0	: Volume of the network in the state of formation
V_h	: Hydrodynamic volume
v_1	: Molar volume of solvent
Δw_{ij}	: Interaction free energy change associated with the formation of a contact between a pair of segments of molecules i and j
x	: Number of structural units in the given polymer molecule or its number of segments
y	: Number of segments in a linear polymer chain
z	: Lattice coordination number of cells
α	: Factor expressing the linear deformation of a polymer molecule owing to solvent-polymer interaction
α_s	: Factor expressing the linear deformation of a network structure by isotropic swelling
$\alpha_x, \alpha_y, \alpha_z$	: Linear deformation factor with reference to x, y and z coordinates
ϵ	: Dielectric constant
η^*	: Protein separation efficiency
η, η_0	: Viscosity of the solution and the viscosity of the pure solvent

η_{red}	: Reduced viscosity
η_{sp}	: Specific viscosity
$[\eta]$	: Intrinsic viscosity
θ	: Theta temperature
κ_1	: Parameter expressing the energy divided by kT , of interaction between a solvent molecule and polymer
μ	: Number of junctions
μ_1, μ_2, μ_3	: Chemical potential of solvent, polymer network and polymer, respectively
μ_1^0 , ect.	: Chemical potentials in standart states
$(\mu_1 - \mu_1^0)_E$	: Excess (i.e, non ideal) chemical potential of the solvent
μ_i	: Chemical potential of component i
ν	: Number of network chains
ν_e	: Effective number of chains in a real network
ν_i	: Number of ways of arranging the i-th polymer molecule on a lattice to which i-1 polymer molecules have been added previously
ν_1	: Volume fraction of solvent
ν_2	: Volume fraction of polymer network
ν_3	: Volume fraction of linear polymer
ν_2'	: Volume fraction of polymer network in the less swollen phase
ν_2''	: Volume fraction of polymer network in the more highly swollen phase
ν_{2m}	: Volume fraction of polymer network at equilibrium degree of swelling
ν_2^0	: Volume fraction of polymer network after preparation
ξ	: Cycle rank
π	: Osmotic pressure
ρ	: Density of polymer

τ^*	: Time of hydrolysis
τ	: Reduced temperature
ϕ^*	: Average functionality
ϕ	: Volume fraction of linear polymer outside the gel phase
ϕ_2	: Volume fraction of spheres
Φ	: Parameter relating the intrinsic viscosity to the molecular dimension $\langle r^2 \rangle^{1/2}$
χ_1	: Parameter expressing the first neighbor interaction free energy, divided by kT , for solvent with polymer
χ_{ij}	: Corresponding parameter for the interaction of component i with j in a polycomponent system
ψ_1	: Parameter characterizing the entropy of dilution of polymer with solvent
Ω	: The total number of configurations

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SUMMARY

The conformations of a single polymer chain in solution have been the subject of extensive studies. At high temperatures and in good solvents, a polymer chain has an extended coil configuration, while at low temperatures and in poor solvents it is in a collapsed globule state. Similarly collapse of gels is observed upon changing temperature or solvent composition.

For the observation of phase transition, first, a polyacrylamide gel was immersed in a linear polymer solution. The swelling behavior of non-ionic polyacrylamide gel in poly(ethylene glycol), oligo ethylene glycol and polyacrylamide solutions were investigated. The effects of hydrolysis and the proportion of ionizable groups of the gel, and the effects of the molecular weight and the concentration of linear polymer solution outside of the gel phase on the gel swelling were examined. Second, temperature sensitive poly(N-isopropyl acrylamide) gels were prepared. They were used in the separation processes of dilute protein solutions. The effects of synthesis conditions on the structure and protein separation efficiency were investigated. Finally, the coil-globule transition of linear poly(methyl methacrylate) in *tert*-butyl alcohol+water mixture was examined.

It was found that, non-ionic polyacrylamide gels immersed in aqueous solutions of poly(ethylene glycol) exhibited a continuous volume change upon continuous increase of the poly(ethylene glycol) concentration in the external solution. The volume change became discontinuous when ionizable groups were incorporated into the network. On the other hand, addition of small amount of ethylene glycol oligomers in water led to the contraction of both linear and cross-linked ionic polyacrylamide chains because of their screening effects. It was also observed that, the classical Flory-Huggins theory correctly predicted the swelling behavior of non-ionic polyacrylamide gels in polyacrylamide solutions. However, in the case of ionic polyacrylamide gels deviations from predictions of Flory-Huggins theory were observed.

The protein separation efficiency values of 100% were reached after coating the poly(N-isopropyl acrylamide) gel bead surfaces with protein. Finally, viscosimetric measurements of poly(methyl methacrylate) in its θ -solvent showed that a smooth and continuous contraction was observed below θ temperature.

ÖZET

POLİMERİK SİSTEMLERİN FAZ GEÇİŞLERİNİN TEORİK VE DENEYSEL OLARAK İNCELENMESİ

Tek bir polimer zincirinin çözelti içindeki konformasyonu hakkında 1950 yılından günümüze kadar birçok çalışma yapılmıştır. Yüksek sıcaklıklarda ve iyi çözücüler içinde polimer zinciri uzamış zincir konformasyonu halindeyken, düşük sıcaklıklarda ve kötü çözücüler içinde büzülmüş kürecik halini alır. Bir polimer zincirindeki bu konformasyon değişimine “coil-globule” geçişi denir. Benzer olarak, polimerik jeller de sıcaklık ve çözücü kompozisyonu gibi dış etkilere bağlı olarak faz geçişi gösterirler.

Jeller hem katı hem de sıvı özellikleri bir arada taşıyan maddelerdir. Çapraz bağlanmış polimer zincirleri, jellerin temel yapısı olan içiçe örülmüş ağ yapıyı oluştururlar. Aynı öneme sahip çözücü (su) ise bu ağ yapıyı doldurur. Jelin özellikleri bu iki bileşiğin arasındaki etkileşime bağlıdır. Sıvı polimerik ağ yapıyı şişirerek büzülmüş bir kütle haline dönüşmesini engellerken, ağ yapıda sıvıyı içersinde hapsederek akıp gitmesini önler.

Suda şişen hidrojeller kimyasal yapılarına, kullanılan çözücüye, sıcaklık, asit oranı (pH) veya elektrik alan gibi dış uyarımlara bağlı olarak şişip büzülebilirler. Hidrojellerin hacimlerinin küçük dış uyarımlar karşısında yüzlerce kat artıp, azalabilmesi onların teknolojide kullanılabilir malzemeler olmalarını sağlamaktadır. Yüksek su emme kapasitelerinden dolayı süper-absorban jellerin yanı sıra, vücudun herhangi bir bölgesine ani veya derece derece ilaç salınımını sağlayan, sıcaklığa veya pH'a duyarlı polimerik jeller geliştirilmiştir. Ayrıca hidrojellerin biyotıp uygulamalarından biri de yapay doku olarak ve tıbbi protezlerde kullanılabilir olmalarıdır. Elektrik alan etkisi ile şişip, büzülebilen jeller elektrik devre anahtarlarında, sensörlerde ve yapay kaslarda (robotlar için) kullanılmak üzere geliştirilmektedir.

Dış uyarımlar karşısında jellerin şişmiş halden büzülmüş hale geçişi tıpkı bir polimer zincirinin çözücüyle arasındaki etkileşime göre genişleyip, büzülmesine benzer. Jellerin faz geçişleri veya jellerin kritik davranışları adı altında yapılan bütün teorik ve deneysel çalışmalarda, jeller makroskopik tek bir polimer molekülü olarak düşünülmüş ve hacımsal değişimlerinin sebebi incelenmiştir.

Jelin bir çözücü ortamından diğerine aktarıldığında, ısıtıldığında veya soğutulduğunda, hacmindeki bu ani değişikliğin sebebi polimer ağ yapı üzerine uygulanan üç kuvvet ile açıklanabilir: Kauçuk elastisitesi, polimer-polimer etkileşimi ve hidrojen-iyonu basıncı. Jel üzerine etkiyen osmotik basınç bu üç bileşenin toplamıdır. Kauçuk elastisitesi, ağ yapı içindeki polimer zincirlerinin gerilmeye veya sıkışmaya karşı dirençlerinden ortaya çıkar. Şişmiş bir jelde, tüm polimer zincirleri gerilmiş durumdadır ve kauçuk elastisitesi jelin büzülmesi yönündedir.

Tersine b z lm    jel ise kau uk elastisitesinin etkisiyle geni lemeye  alı ır. Bu durumda polimer zinciri  zerine etkiyen y nlenmi  kuvvet, t m jel  zerinde bir basıncı olu turur. E er basıncı pozitif ise jel    meye, basıncı negatif ise b z lmeye e ilimlidir. Kau uk elastisitesinin b y kl    sıcaklı a ba lıdır. Jel  zerine etkiyen ikinci kuvvet, polimer-polimer etkile imi, polimer zincirleri ile    c n n etkile imine ba lıdır. E er polimer kendisi i in k t  bir    c  i inde ise polimer zincirleri birbirlerini  ekerler ve negatif bir basıncı olu turarak jelin b z lmesini sa larlar. Jel  zerinde olu an kuvvet sıcaklıktan ba ımsızdır ve    c  konsantrasyonu artık a artar. Osmotik basıncı etkileyen son bile en hidrojen-iyonu basıncıdır. Polimer a  yapı i ine iyonik gruplar eklendi inde ortamda H⁺ iyonu konsantrasyonu artar ve bu iyonlar birbirlerini iterek, jelin    mesine sebep olurlar. Polimer a  yapıya ba lı olan zıt y kl  iyonlar y k merkezlerini n t rlerler ve b ylece jelin par alanmasını   nlerler. Hidrojen iyonu basıncı sıcaklı a ve iyon sayısına ba lıdır.

Bir polimer a  yapının    mesi termodinamik olarak en az    serbest enerji de i imi terimleri ile kontrol edilebilir. Sistemin serbest enerji de i imi,

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \quad (i)$$

 eklinde yazılabilir. ΔG_m , karı ımın serbest enerji de i imi, ΔG_{el} , elastik deformasyon serbest enerji de i imi ve ΔG_i , elektrostatik etkile imlerin yol a tı ı serbest enerji de i imidir.

Flory-Huggins teorisine g re,

$$\Delta G_m = RT \left[\sum_i n_i \ln v_i + \sum_{i < j} \chi_{ij} n_i v_j \right] \quad (ii)$$

 eklinde yazılır. Bu denklemde n_i mol sayısı, v_i hacim fraksiyonu, χ_{ij} i ve j maddeleri arasındaki etkile im parametresi, R gaz sabiti ve T sıcaklıktır.

Elastik deformasyon serbest enerji de i imi,

$$\Delta G_{el} = 3 / 2 (RT / N v_1) \left[(v_2^0 / v_{2m})^{2/3} - 1 - \ln (v_2^0 / v_{2m})^{1/3} \right] \quad (iii)$$

 eklinde dir. N bir polimer a  yapı zincirindeki ortalama segmentlerin sayısı, v_1 molar hacim, v_{2m}    me dengesine ula mı  polimer a  yapının hacim fraksiyonudur.

 yonik gruplar ta ıyan jellerde, elektrostatik etkile imlerin yol a tı ı serbest enerji de i imi  u  ekilde yazılabilir:

$$\Delta G_i = RT (f / N) (v_2 / v_1) n_1 \ln (f v_2 / N) \quad (iv)$$

Bu denklemde f, polimer a  yapı zincirindeki ortalama iyonik  nite sayısıdır.

Bir jelin polimer çözeltisi içinde şişme dengesine ulaşması jel içindeki çözücü ve lineer polimer aktivitesinin dış çözeltidekiler ile denge halinde olmasına bağlıdır. Eğer $i = 1, 2, 3$ sırasıyla, çözücü, polimer ağ yapı ve lineer polimeri belirliyorsak, şişme dengesinde herbir bileşenin polimer ağ yapı (jel) içinde ve jelin dışındaki çözeltide kimyasal potansiyelleri eşittir. Denge durumu şu şekilde yazılır:

$$\Delta\mu_1^{\text{jel}} - \Delta\mu_1^{\text{öz}} = 0 \quad (\text{v})$$

$$\Delta\mu_3^{\text{jel}} - \Delta\mu_3^{\text{öz}} = 0 \quad (\text{vi})$$

$$\pi = - \left(\frac{\mu_1^{\text{jel}} - \mu_1^{\text{öz}}}{v_1} \right) = 0 \quad (\text{vii})$$

Denge durumuna erişilene kadar jelin içi ile dışındaki çözelti ortamı arasında çözücü alışverişi olur. Denge durumunda jel üzerine etkiyen kuvvetler dengelenir. Bu durumda osmotik basınç sıfırdır.

İyonik jellerde ani faz geçişinin olduğu kritik çözelti konsantrasyonu polimer ağ yapının şişmiş ve büzülmüş durumdaki kimyasal potansiyellerinin eşitliğinden hesaplanabilir.

$$\Delta\mu_2^{\text{jel-1}} = \Delta\mu_2^{\text{jel-2}} \quad (\text{viii})$$

Bu denklemde jel-1 ve jel-2 sırasıyla şişmiş ve büzülmüş jel hallerini belirler.

Bu tezde, polimerik jellerin lineer polimer çözeltileri içindeki faz geçişleri hem teorik hem de deneysel olarak incelendi. Poliakrilamid ve poli(akrilamid-ko-akrilik asit) jellerinin lineer poli(etilen glikol) (PEG), oligo etilen glikol ve lineer poliakrilamid çözeltileri içindeki şişme davranışları deneysel olarak gözlemlendi. Bu gözlemler, Flory-Huggins teorisinden yararlanılarak yapılan hesaplar ile desteklendi. Ayrıca sıcaklığa duyarlı poli(N-izopropil akrilamid) jellerinin protein çözeltileri içindeki şişme ve seçici absorpsiyon özelliklerinden yararlanılarak, bu jellerin penisilin G asilaz enziminin saflaştırılmasında kullanılmak üzere uygulamaya yönelik çalışmalar yapıldı. Son olarak bir lineer polimer zincirinin uzamış zincir konformasyonundan, büzülmüş kürecik haline geçişi incelendi.

Poliakrilamid jelleri serbest radikal polimerizasyon ile sentezlendi ve çapraz bağlayıcı olarak N,N'-metilenbis(akrilamid) kullanıldı. Ayrıca iyonik poliakrilamid jelleri akrilamid monomeri ile akrilik asit monomerinin kopolimerizasyonu ile hazırlandı. Jeller değişik konsantrasyonlarda hazırlanan lineer poli(etilen glikol) çözeltileri içinde şişme dengesine ulaşana kadar bekletildi. Dış çözeltideki polimer konsantrasyonu arttıkça, iyonik olmayan poliakrilamid jellerinin hacminin sürekli olarak azaldığı gözlemlendi. Diğer yandan iyonik jeller, belli bir lineer polimer konsantrasyonunda ani olarak hacim değişikliği gösterdiler. Jelin içerdiği iyonik grup

yüzdesi arttıkça veya lineer polimerin molekül ağırlığı azaldıkça, ani faz geçişinin gözlemlendiği kritik polimer konsantrasyonunun arttığı tespit edildi.

Lineer polimerin jel içindeki dağılımını tespit edebilmek için refraktometre ölçümlerine dayanan deneyler yapıldı. Yapılan deneyler lineer poli(etilen glikol)'ün hem poliakrilamid hem de poli(akrilamid-ko-akrilik asit) jelleri içine girebildiğini göstermiştir. Lineer polimerin molekül ağırlığı arttıkça, jelin içine girebilen polimer miktarının azaldığı ve iyonik jellerde belirli bir kritik polimer konsantrasyonunda polimerin jel içinden ani olarak ayrıldığı gözlemlendi. Ayrıca molekül ağırlığı 6000' den büyük olan lineer polimerin jel içine giremediği saptandı.

Oligo etilen glikol çözeltileri içinde, iyonik poliakrilamid jelleri beklenilenin tersine hacim azalması gösterdi. Bu konuyu derinlemesine incelemek için, iyonik grup yüzdesi aynı olan lineer poli(akrilamid-ko-akrilik asit) ve poli(akrilamid-ko-akrilik asit) jelleri kullanılarak karşılaştırmalı deneyler yapıldı. Lineer poli(akrilamid-ko-akrilik asit)'in % 10'luk sulu tetraetilen glikol çözeltisi içindeki viskozitesi, polimerin bu çözelti içinde polielektrolit davranışı göstermediğini ortaya çıkarttı. Benzer şekilde, poli(akrilamid-ko-akrilik asit) jelinin % 10'luk sulu tetraetilen glikol çözeltisi içindeki şişme deneyleri, iyonik olmayan poliakrilamid jeli gibi davrandığını gösterdi. Bu sonuç oligo etilen glikolün, polimer zinciri üzerindeki iyonik gruplar üzerine perdeleme etkisi yaptığı ve böylece iyonik jelin beklenenden daha az şişebildiği şeklinde açıklanabilir.

Hidroliz olmuş poliakrilamid jellerinin de PEG 300 çözeltileri içinde ani faz geçişi göstermesi, jellerdeki bu hacim değişikliğinin akrilik asit üniteleri ile poli(etilen glikol) arasındaki kompleks oluşumu ile değil, osmotik büzülme yoluyla olduğunu bir kez daha kanıtlamıştır. Kompleks oluşumu sadece dissosiyasyon olmamış haldeki karboksilli asitler ile gerçekleştirebildiğinden, hidroliz edilmiş, içinde karboksilat anyonları içeren poliakrilamid jellerinin de ani faz geçişi göstermesi bu teoriyi çürütmüştür.

Poliakrilamid jellerinin lineer poliakrilamid çözeltileri içindeki deneylerle belirlenen şişme davranışı, Flory-Huggins teorisiyle hesaplanan sonuçlar ile tamamen uyum içerisindedir. Diğer yandan poli(akrilamid-ko-akrilik asit) jelleri için elde edilen deney sonuçları teoriden sapmalar göstermektedir. Bu durum jelin içinde bulunduğu ortamın dielektrik sabitinin düşmesi ile açıklanabilir.

$$\varepsilon = \varepsilon_{su} - (\varepsilon_{su} - \varepsilon_{PAAm}) v_3 \quad (ix)$$

Bu denklemde ε , ε_{su} , ε_{PAAm} , sırasıyla ortamın, suyun ve polimerin dielektrik sabitleridir. v_3 lineer polimerin jel içindeki hacim fraksiyonudur. Jelin bulunduğu sulu çözeltide lineer poliakrilamid konsantrasyonu arttıkça, ortamın dielektrik sabiti azalır ($\varepsilon_{su} = 80$, $\varepsilon_{PAAm} = 1$). Teorik çalışmalar ortamın dielektrik sabitinin azalması ile iyon çifti (iyonomer) oluşma olasılığının arttığını göstermektedir. Bu durumda, çözeltinin dielektrik sabitinin düşmesinin iyonomer oluşumunu arttırdığı ve ağ yapısı üzerindeki serbest iyonik grupların azalması ile jelin daha az şiştiği ve böylece Flory-Huggins teorisi ile tespit edilen şişme davranışından saptığı söylenebilir.

Sıcaklığa duyarlı olarak şişip, büzülebilen poli(N-izopropil akrilamid) jelleri çözelti polimerizasyonu ve invers süspansiyon polimerizasyonu teknikleri ile sentezlendi. Sentez yönteminin, jelin yapısına ve dolayısıyla jelin seyreltik enzim çözeltilerini konsantre edebilme etkinliğine etkileri incelendi. Çözelti polimerizasyonu

ile elde edilen silindir şeklindeki jellerin 1 gramı 20 ml suyu 10 dakikada absorplayabilirken, süspansiyon polimerizasyonu ile elde edilen boncuk halindeki jellerin 1 gramının aynı miktar suyu 3 dakikada emebildiği tespit edildi. Ayrıca boncuk jellerin, çözelti polimerizasyonu ile elde edilen jellere göre daha çok su emme kapasitelerinin olması bu jellerin etkin bir saflaştırma işleminde kullanılabileceğini göstermiştir. Daha öncede belirtildiği gibi büyük molekül ağırlıklı polimerlerin jel içine girememesi ve poli(N-izopropil akrilamid) jelinin düşük kritik çözelti sıcaklığı (LCST) göstermesi bu jelin, yüksek sıcaklıklarda bozunan, seyreltik enzim çözeltilerinin konsantre edilebilmesi için uygun bir kullanım alanı yaratmaktadır. Yüzeyleri protein ile kaplanan 0.8-2.8 mm çapındaki boncuklar kullanılarak, seyreltik enzim çözeltilerinin konsantre edilmesinde % 100 verim sağlanmıştır.

Son olarak lineer poli(metil metakrilat)' ın uzamış zincir konformasyonundan, büzülmüş kürecik haline geçişi *ter*-bütil alkol + su sistemi içinde çalışıldı. Molekül ağırlığı 2.55×10^6 ve 4.73×10^6 olan iki polimer örneğinin *ter*-bütil alkol + su karışımı içindeki viskoziteleri 14-70 °C sıcaklık aralığında ölçüldü. Bu polimerler metanol + toluen çöktürücü-çözücü sistemi kullanılarak yapılan fraksiyonlandırma işlemi ile elde edildi. Polimer örneklerinin molekül ağırlığı dağılımı jel geçirgenlik kromatografisi ölçümleri ile sırasıyla, 1.35 ve 1.29 olarak belirlendi. Yapılan viskozite deneyleri, teorik hesaplar ile desteklendi. Viskozite genleşme faktörünün, α_n^3 , θ koşullarındaki boyutlarına göre % 86-87 oranında büzüldüğü saptandı. Bu sonuç polimer zincirinin uzamış zincir halinden, büzülmüş kürecik haline geçtiğini göstermektedir.

CHAPTER 1

INTRODUCTION

Gels are interesting objects which have both liquid-like and solid-like properties. The liquid-like properties result from the fact that the major constituent of gels is usually a liquid, e.g. water. On the other hand, a gel can retain its shape since it has a shear modulus which becomes apparent when the gel is deformed. The modulus is due to the cross-linking of the polymers in the form of a network. These aspects of a gel represent the solid nature of gels. In addition to these liquid- and solid-like aspects, a gel can change its state drastically, similar to the way a gas changes its volume more than a thousand fold. Figure 1.1 shows schematically the two states of gels; the collapsed and swollen states.

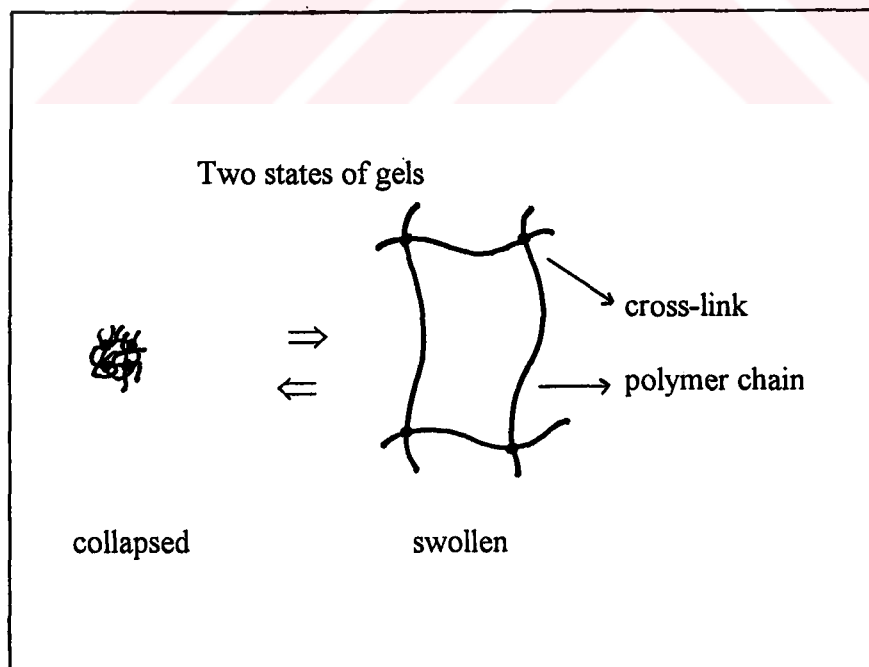


Figure 1.1. Schematic representation of gels in collapsed and swollen states.

A gel can be viewed as a container of solvent made of a three dimensional mesh. In dried state, a gel is a solid material. However, it swells until it reaches the swelling equilibrium when a solvent is added. The solvent molecules are kept in the three dimensional mesh[1,2].

Another interesting aspect of gels is that a gel can be " a single polymer molecule". The term "single polymer molecule" means that all the monomer units in a one piece of gel are connected to each other and form one big molecule on a macroscopic scale. Because of this nature, a gel is a macroscopic representation of single polymer chain behavior.

Extensive progress has been made in the technological applications of gels[3]. Disposable diapers and sanitary napkins use gels as super water absorbents. Gel sheets have been developed to keep fish and meat fresh. Gels are indispensable materials as a molecular sieve for molecular separation; such as gel permeation chromatography and electrophoresis. Temperature and/or pH sensitive gels have been developed as drug delivery systems in the human body, where the gel releases a drug gradually or suddenly at a particular location in the body in response to the change of temperature or pH around the gel. Many kinds of external stimuli, such as temperature, pH, photons, ions, electric field, etc. can control the volume of the gel. Particularly, in the case of volume phase transition, an enormous change in volume can be induced by an infinitesimal change of one of these stimuli and this is of great importance in its application, as a sensor, switching device and so on.

The fundamental studies of gels can be classified into at least three stages:

Theoretical Prediction. The study of the volume-phase transition was initiated by the theoretical prediction of Dusek and Patterson in 1968[4]. They suggested the possibility of a discontinuous volume change of a gel based on the analogy of the coil-globule transition of polymers in a solution which was predicted by Ptitsyn et.al. [5]. In a sense, the phase transition of gels is a macroscopic manifestation of a coil-globule transition.

Critical Behavior of Gels. In 1977, the critical phenomena were discovered in the light scattered from an acrylamide gel in water[6]. As the temperature was lowered, both the scattered intensity and the fluctuation time of the scattered light increased and appeared to diverge at -17°C . The phenomenon was explained as the critical density fluctuations of polymer networks although the polymers were cross-linked[7].

Volume-Phase Transition of Gels. The volume-phase transition was experimentally discovered for a partially ionized acrylamide gel in a mixture of acetone and water by Tanaka in 1978[7]. Such a volume-phase transition was found to be generated not only by changing the composition of the solvent, but also by temperature, ionic and pH changes, irradiation by light, electric fields and so on[8-13].

The object of this study is to investigate the phase transitions of various gels in linear polymer solutions both theoretically and experimentally. Then an application method for the temperature sensitive poly(N-isopropyl acrylamide) gel was examined. Finally, the coil-globule transition of a linear chain was studied to understand the underlying theory for the volume-phase transition of a gel.

CHAPTER 2

GENERAL THERMODYNAMIC RELATIONS

2.1. Thermodynamics of Polymer Solutions and Gels

Polymers, by virtue of their high molecular weight, are soluble only in selected solvents. Although the basic principles of physical chemistry are applicable to all molecules, the size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. In macromolecule solutions, only at extreme dilutions the ideality can be achieved. At concentrations exceeding a few percent, deviation from ideality usually become so great that the ideal law is of little value as a basis for rationality correlating the thermodynamic properties of polymer solutions. Some other relationship is therefore needed[1,14-15]

2.1.1. Thermodynamics of Simple Liquid Mixtures

For a system at equilibrium, the chemical potential, μ_i , of component i is related to its activity,

$$\mu_i - \mu_i^0 = RT \ln a_i \quad (2.1)$$

where μ_i^0 is the chemical potential of component i in its standard state and $\mu_i - \mu_i^0$ is the partial molar Gibbs free energy change, $\overline{\Delta G_i} = \left(\frac{\partial \Delta G_i}{\partial n_i} \right)_{P,T,n_j}$, for the formation of the system.

Ideal solutions are defined as those in which the activity a_i of each component should equal to its mole fraction n_i . In a binary solutions consisting of solvent and a polymer having molecular weight a thousand times or more that of the solvent, only a

very small percentage by weight of the solvent is sufficient to bring its mole fraction n_1 very close to unity. Hence according to Raoult's law (with $a_1 = P_1 / P_1^0$) the partial pressure P_1 of the solvent in the solution should be very nearly equal to that of the pure solvent P_1^0 over the greater portion of the composition range.

In ideal solutions, the molecules of solvent and polymer are identical size and for which the energies of like and unlike molecular interactions are equal. The latter condition leads to athermal mixing (i.e., $\Delta H_m = 0$), which also means that there are no changes in the rotational, vibrational and translational entropies of the components upon mixing. Thus ΔS_m depends only upon the combinatorial (or configurational) entropy change, ΔS_m^{comb} , which is positive because the number of distinguishable spatial arrangements of the molecules increases when they are mixed.

The evaluation of configurational entropy is usually performed by placing the n_1 and n_2 (1 and 2 denotes two spherical molecules that are identical size and intermolecular force) molecules on a lattice of $(n_1 + n_2)$ sites (Figure 2.1a). The number of distinguishable arrangements is

$$\Omega = (n_1 + n_2) ! / n_1 ! n_2 ! \quad (2.2)$$

from which it can be obtained

$$\Delta S_m = k \ln \Omega = - k (n_1 \ln N_1 + n_2 \ln N_2) \quad (2.3)$$

where N_1 and N_2 are mole fractions of molecules 1 and 2, respectively.

The conditions for ideal mixing imply that the heat of mixing is zero. Then, since $\Delta G = \Delta H - T \Delta S$, the free energy of mixing is given by,

$$\Delta G_m = kT (n_1 \ln N_1 + n_2 \ln N_2) \quad (2.4)$$

This important equation provides the fundamental basis from which standard thermodynamic relationships for ideal solutions can be derived[14,16].

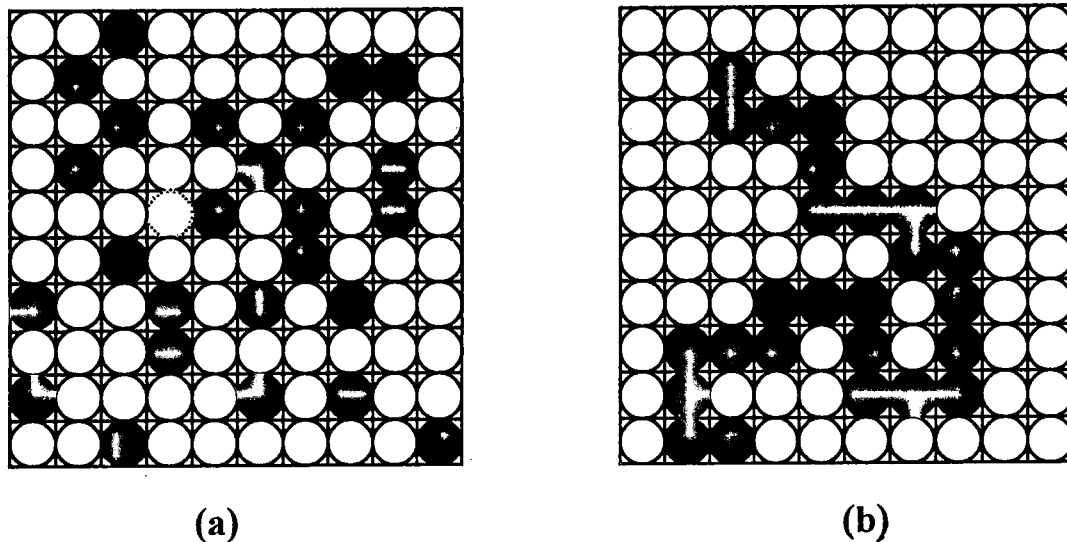


Figure 2.1. (a) Representation of two dimensional Flory-Huggins lattice containing solvent molecules (o) and a low-molecular-weight solute (•).
 (b) Lattice model for a polymer chain in solution. Symbols represents solvent molecules (o) and polymer-chain segments (•).

2.1.2. Entropy of Mixing in Polymer Solutions

Deviation from ideality in binary mixtures of the same size and shape may arise mainly from the non-athermal mixing conditions. ($\Delta H_m \neq 0$) However, the polymer solutions show deviations from ideal solution behavior, even when $\Delta H_m = 0$. These are the natural result of the large difference in molecular size between the two components. When one component of the solution is a macromolecule the connectivity of the chain segments imposes a special restriction on the arrangement of the two components in space. Paul Flory and Maurice Huggins independently derived expressions on this basis for the total number of configurations of a liquid mixture formed from n_1 solvent and n_2 polymeric solute molecules. They estimated the number of distinguishable ways in which n_1 solvent molecules and n_2 macromolecular chains could be placed on a lattice (Figure 2.1b).

Each polymer chain is represented by x segments, with the molar volume of the segment equal to that of the solvent molecule v_1 . There are a total of $(n_1 + xn_2) = n_0$ lattice sites. The n_2 polymer molecules are added one by one to the lattice before adding the solvent molecules. The individual numbers of possible placements are calculated for each segment of the chain, and by multiplying these numbers together, v , the total number of possible conformations of the polymer molecule in the lattice is obtained.

$$v_{i+1} = \{ (n_0 - x_i) ! / [n_0 - x(i+1)] ! \} [(z - 1) / n_0]^{x-1} \quad (2.5)$$

where z is the coordination number of the lattice.

The total number of distinguishable spatial arrangements of the mixture is given by

$$\Omega_{12} = \frac{1}{n_2!} \sum_{i=1}^{n_2-1} v_{i+1} \quad (2.6)$$

The number of Ω_2 by which chains can be placed on xn_2 sites is obtained by setting $n_1=0$ in Equation (2.6).

The configurational entropy of mixing is

$$\Delta S_m = k \ln (\Omega / \Omega_2) = -k (n_1 \ln v_1 + n_2 \ln v_2) \quad (2.7)$$

where k is Boltzmann's constant and v_1 and v_2 are volume fractions of solvent and the polymer defined as

$$v_1 = \frac{n_1}{n_1 + xn_2}, \quad v_2 = \frac{xn_2}{n_1 + xn_2} \quad (2.8)$$

Comparison of Equation (2.7) with Equation (2.3) reveals an interesting analogy to the ideal entropy of mixing; mole fractions occurring in the ideal expression are replaced with volume fractions in the formula for mixing of molecules dissimilar size.

The ideal mixing "law" can be derived only for the case in which solvent and solute molecular volumes are equal. When this is true, the volume fractions and mole fractions are identical and Equations (2.7) and (2.3) are then equivalent[1,14].

2.1.3. Heat and Free Energy of Mixing

Intermolecular interactions are large in the liquid state owing to the close proximity of the molecules. Since the pure solvent and pure liquid polymer are taken as reference states for the treatment of the solution, it is interested only in the difference between the total interaction energy in the solution as compared with that of the pure liquid components. In particular, it is needed to express the dependence of this difference, that is heat of mixing, on the concentration. The calculations are simplified by restriction to first neighbour interactions on the basis that the forces between uncharged molecules are known to decrease rapidly with their distance of separations. Therefore, the heat of mixing can be considered to originate in the replacement of some of the contacts between like species in the pure liquids with contacts between unlike species in the solution.

Three types of contact need to be considered, conveniently represented by the self-explanatory symbols, [1,1], [2,2] and [1,2]. For every two solvent-segment contacts one solvent-solvent and one segment-segment contact of the pure components are lost. Thus the change in the internal energy for the formation of an unlike molecular pair (solvent-polymer or 1-2) contacts given by the mean field expression as,

$$\Delta w_{12} = w_{12} - (1/2) (w_{11} + w_{22}) \quad (2.9)$$

where w_{ij} is the energy of i-j contacts.

The expression that Flory and Huggins gave for the enthalpy of mixing is

$$\Delta H_m = z n_1 x_1 v_2 \Delta w_{12} \quad (2.10)$$

where z is the lattice coordination number or number of cells that are first neighbours to a given cell, x_1 represents the number of "segment" in a solvent molecule for consideration of the most general case. Since z and Δw_{12} have the character of empirical parameters, it is convenient to define a single energy parameter called Flory interaction parameter, χ_1 , given as,

$$\chi_1 = zx_1\Delta w_{12} / kT \quad (2.11)$$

The interaction parameter is a dimensionless quantity that characterizes the interaction energy per solvent molecule (having x_1 segments) divided by kT . As Equation (2.11) indicates, χ_1 is inversely related to temperature but is independent of concentration.

The expression for the enthalpy of mixing then be written by combining Equations (2.10) and (2.11) as

$$\Delta H_m = kT \chi_1 n_1 v_2 \quad (2.12)$$

The quantity $kT\chi_1$ represent merely the difference in energy of a solvent molecule immersed in the pure polymer ($v_2 \cong 1$) compared with one surrounded by molecules of its own kind, i.e., in the pure solvent.

Well known Flory-Huggins expression for the Gibbs free energy of mixing is simply obtained by combining Equations (2.7) and (2.12). That is

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.13)$$

$$\Delta G_m = kT([n_1 \ln v_1 + n_2 \ln v_2] + \chi_1 n_1 v_2) \quad (2.14)$$

Using the Flory-Huggins equation it is possible to account for the equilibrium thermodynamic properties of polymer solutions, particularly phase-separation and fractionation behavior, melting point depression in crystalline polymers and swelling of networks[1,16,17].

2.1.4. Partial Molar Quantities and Chemical Potential

For multicomponent systems such as polymer solutions, it is important to know how thermodynamic parameters vary when a small amount of one component is added to the system whilst maintaining the pressure, temperature and amounts of all other components of the system constant. This requires the use of partial molar quantities.

The most commonly encountered one in the thermodynamics of polymer solutions are partial molar Gibbs free energies, $\overline{G}_i$. These quantities are called chemical potentials, μ_i , which therefore are defined by

$$\overline{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} \quad (2.15)$$

The chemical potential μ_1 of the solvent in the solution relative to its chemical potential μ_1^0 in the pure liquid is obtained by differentiating the free energy of mixing ΔG_m with respect to the number of n_1 of the solvent molecules. Differentiation of Equation (2.14) for ΔG_m with respect to n_1 to obtain chemical potential per mole gives

$$\mu_1 - \mu_1^0 = RT [\ln (1 - v_2) + (1 - 1/x) v_2 + \chi_1 v_2^2] \quad (2.16)$$

Differentiation of Equation (2.14) with respect to n_2 yields for the chemical potential of the polymer relative to the pure liquid polymer as standard state.

$$\mu_2 - \mu_2^0 = RT [\ln v_2 - (x - 1) (1 - v_2) + \chi_1 x (1 - v_2)^2] \quad (2.17)$$

From the chemical potential an expression for the osmotic pressure π of the solution may be written, using standard relations of thermodynamics. For the osmotic pressure $\pi v_1 = - (\mu_1 - \mu_1^0)$,

$$\pi = - \frac{RT}{v_1} [\ln (1 - v_2) + (1 - 1/x) v_2 + \chi_1 v_2^2] \quad (2.18)$$

where v_1 is the molar volume of the solvent [1,5].

2.1.5. Dilute Polymer Solutions

In dilute solutions, coils of flexible macromolecules, representing high local concentration of segments, are separated by large regions of polymer free solvent. The inhomogeneity in segment distribution in solution makes the Flory-Huggins theory inapplicable because the assumption that the probability of occupancy of a lattice site is equal to the overall fraction occupied sites becomes clearly invalid. Flory and Krigbaum have provided a model to describe the thermodynamics of a dilute polymer solution in which individual polymer chains are isolated and surrounded by regions of solvent molecules. In contrast to the case of a semi dilute solution addressed by the Flory-Huggins theory, segmental density can no longer be considered to be uniform. In their development Flory and Krigbaum viewed the dilute solution as a dispersion of clouds consisting of polymer segments surrounded by regions of pure solvent. They assumed such a model in which each cloud of segments is approximately spherical with an average density which is maximum at the center and decreases in a continuous manner with the distance from the center. Each molecule in a very dilute polymer solution in a good solvent (low χ_1) will tend to exclude all others from the volume which it occupies. Conversely, the excluded volume decreases in poor solvent. Therefore excluded volume is related to the interaction parameter. In evaluating the excluded volume, Flory and Krigbaum considered the centers of two coils approaching each other so that a volume element δV contains segments from both molecules[15].

Let assume that the number of polymer molecules in the volume element is zero. It is as if the molecular weight were infinite, in which case would be zero. Then the free energy of mixing of polymer segments with solvent in the volume element δV is,

$$\delta(\Delta G_m) = kT[\delta n_1 \ln (1 - v_2) + \chi_1 \delta n_1 v_2] \quad (2.19)$$

where δn_1 is the number of solvent molecules in the volume element. The volume fraction v_2 appearing here and in the following equations refers to the volume element and not to the solution as a whole.

The chemical potential of the solvent in the volume element, obtained by differentiating Equation (2.19), is

$$(\mu_1 - \mu_1^0)_E = RT [\ln (1 - v_2) + v_2 + \chi_1 v_2^2] \quad (2.20)$$

which also follows directly from the previous Equation (2.16) when x is taken to be infinite. Expanding in series

$$(\mu_1 - \mu_1^0)_E = - RT [(1/2 - \chi_1) v_2^2 + v_2^3 / 3 + \dots] \quad (2.21)$$

These expressions comprise the nonideal terms in the previous equations for the chemical potential. They may therefore be regarded on the excess relative partial molar free energy or chemical potential.

If the concentration of polymer in the volume element is very small, higher terms in such a series expansion may be neglected and the equation is rewritten as

$$(\mu_1 - \mu_1^0)_E = RT (\kappa_1 - \Psi_1) v_2^2 \quad (2.22)$$

where κ_1 and Ψ_1 are heat and entropy parameters such that the excess enthalpy and excess entropy is

$$\overline{\Delta H}_1 = RT \kappa_1 v_2^2 \quad (2.23)$$

$$\overline{\Delta S}_1 = R \Psi_1 v_2^2 \quad (2.24)$$

χ_1 of the preceding treatment may be related to these parameters by comparing Equation (2.21) with Equation (2.22). Then

$$\kappa_1 - \Psi_1 = \chi_1 - 1/2 \quad (2.25)$$

The ratio of ΔH_1 and ΔS_1 , is defined by Flory as the "ideal" temperature θ ,

$$\theta = \kappa_1 T / \Psi_1 \quad (2.26)$$

such that

$$\Psi_1 - \kappa_1 = \Psi_1 (1 - \theta / T) = 1 / 2 - \chi_1 \quad (2.27)$$

Hence the excess chemical potential may be written,

$$(\mu_1 - \mu_1^0)_E = -RT \Psi_1 (1 - \theta / T) v_2^2 \quad (2.28)$$

At temperature T equal to θ , the excess enthalpy and entropy contributions cancel each other. The θ point can be reached by changing either the temperature of the solution or the nature of the solvent. The size of the macromolecule in θ solvent corresponds to the unperturbed dimensions[1,14].

2.2. Swelling of Network Structures

A three dimensional network polymer such as vulcanized rubber, although incapable of dispersing completely, may nevertheless absorb a large quantity of a suitable liquid with which it is placed in contact. Swelling occurs under these conditions for the same reason that the solvent mixes spontaneously with an analogous linear polymer to form an ordinary polymer solutions; the swollen gel is in fact a solution, although an elastic rather than a viscous one. Thus an opportunity for an increase in entropy is afforded by the added volume of the polymer throughout which the solvent may spread. This mixing tendency, expressed as the entropy of dilution, may be augmented ($\chi_1 < 0$) or diminished ($\chi_1 > 0$) by the heat (or first neighbour interaction free energy) of dilution. As the network is swollen by the absorption of solvent, the chains between network junctions are required to assume elongated configurations, and a force akin to the elastic retractive force in rubber consequently develops in position to the swelling process. As swelling proceeds, this

force increases and the diluting force decreases. Ultimately, a state of equilibrium swelling is reached in which these two forces are in balance.

A close analogy exists between swelling equilibrium and osmotic equilibrium. The elastic reaction of the network structure may be interpreted as a pressure acting on the solution, or swollen gel. In the equilibrium state this pressure is sufficient to increase the chemical potential of the solvent in the solution so that it equals that of the excess solvent surrounding the swollen gel. Thus the network structure performs the multiple role of solute, osmotic membrane and pressure-generating device[1-cp13].

2.2.1. Definition for Topological Structure of Networks

A network chain (a chain between two junction points) forms the basis of the elementary molecular theory of amorphous polymeric networks[1,18-20].

In general, network chains exhibit a distribution of molecular weights about an average, which serves as a representative reference quantity in describing network structure. The number of chains meeting at each junction is called the functionality ϕ of that function. A network may have two or more sets of junctions with different functionalities; it may then be characterized by an average functionality. A chain connected to a junction of the network at only one end is called a dangling chain, and one having both its ends attached to the same junctions is called a loop. A network with no dangling chains or loops and in which all junctions have a functionality greater than two is called a perfect network can never be obtained in reality, it forms a simple reference structure around which molecular theories are constructed[19,21].

The topological structure of a perfect network may be derived by various parameters: the average molecular weight between junctions, M_c ; the average functionality ϕ^* ; the number of network chains v ; the number of junctions μ ; and the cycle rank ξ , which denotes the number of chains that have to be cut in order to reduce the network to a tree with no closed cycles. These five parameters are not independent, however, and are related by three equations[19].

For the network to be perfect the number of chain ends, $2v$, has to be equal to the number of functional groups, $\phi^* \mu$, on the end-linking molecules, Thus,

$$\mu = \frac{2\nu}{\phi^*} \quad (2.29)$$

which states, for example, that to get ν chains in a perfect tetrafunctional network only $\mu = \nu / 2$ junctions are required. The other two equations are

$$\xi = \left(1 - \frac{2}{\phi^*}\right)\nu \quad (2.30)$$

$$\frac{\xi}{V_0} = \frac{\left(1 - \frac{2}{\phi^*}\right)\rho}{M_c / N_A} \quad (2.31)$$

where V_0 is the volume of the network in the state of formation, ρ is the corresponding density and N_A is the Avogadro's number[1-cp11,19-20].

2.2.2. Theory of Swelling

The thermodynamics of the system may be described by the change in the Gibbs free energy ΔG of the system. The total change results from the change in the elastic free energy ΔG_{el} of the network upon isotropic (i.e.unstrained) dilation with the introduction of the solvent, and from the change in the free energy of mixing ΔG_m of the solvent molecules with the chains constituting the network [1-cp11,18].

It is assumed that the change in total free energy is the direct sum of ΔG_{el} and ΔG_m . Thus,

$$\Delta G = \Delta G_{el} + \Delta G_m \quad (2.32)$$

For the free energy of elastic deformation ΔG_{el} , several theories are available[22-30]. In the simplest affine network model, the junction points are assumed to be embedded in the network. As a result of this assumption, components of each chain vector transforms linearly with macroscopic deformation.

Elastic free energy of the affine network

$$\Delta G_{el} = 1/2 v_e k T (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln \alpha_x \alpha_y \alpha_z) \quad (2.33)$$

where v_e is the effective number (number of moles) of chains in the network and

$$\alpha_x^2 = \frac{\langle x^2 \rangle}{\langle x^2 \rangle_0}, \quad \alpha_y^2 = \frac{\langle y^2 \rangle}{\langle y^2 \rangle_0}, \quad \alpha_z^2 = \frac{\langle z^2 \rangle}{\langle z^2 \rangle_0} \quad (2.34)$$

If we let α_s represent the linear deformation factor, then by the condition of isotropy $\alpha_s = \alpha_x = \alpha_y = \alpha_z$, and Equation (2.33) is expressed as

$$\Delta G_{el} = 1/2 v_e k T (3\alpha_s^2 - 3 - 3\ln \alpha_s) \quad (2.35)$$

$$\alpha_s = (V / V_0)^{1/3} \equiv (v_2^0 / v_{2m})^{1/3} \quad (2.36)$$

where V is the volume of polymer network at equilibrium degree of swelling, V_0 is the volume of polymer network in the state of formation, v_{2m} is the volume fraction of polymer network at equilibrium degree of swelling when exposed to excess solvent and v_2^0 is the volume fraction of the polymer network after preparation.

Substituting Equation (2.36) in to Equation (2.35), respectively, leads to

$$\Delta G_{el} = 3/2 v_e k T [(v_2^0 / v_{2m})^{2/3} - 1 - \ln (v_2^0 / v_{2m})^{1/3}] \quad (2.37)$$

The second term of Equation (2.32), ΔG_m , for mixing polymer chains with solvent is given by the Flory-Huggins relationship[1,32]

$$\Delta G_m = kT \left[\sum_i n_i \ln v_i + \sum_{i < j} \chi_{ij} n_i v_j \right] \quad (2.38a)$$

$$\Delta G_m = kT (n_1 \ln v_1 + n_2 \ln v_2 + \chi_{12} n_1 v_2) \quad (2.38b)$$

where n_1 and n_2 are the numbers of solvent and polymer molecules, respectively. For a cross-linked network, $n_2 = 1$. The quantity χ_{12} is the interaction parameter for the solvent - polymer system [18].

Introduction of solvent molecules into the system results in

- (1) an increase in ΔG_{el} due to the decrease of the entropy of the network chains upon dilation, and
- (2) a decrease in ΔG_m primarily due to the increase in entropy of mixing the solvent molecules with the network chains.

A state of equilibrium swelling is obtained when the two changes balance each other. Mathematically this state is expressed as

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{T,P} = \left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{T,P} + \left(\frac{\partial \Delta G_{el}}{\partial n_1}\right)_{T,P} = 0 \quad (2.39)$$

where the subscripts, T, P indicate that the differentiation are made at constant temperature and pressure. Performing the differentiations indicated in Equation (2.39) one obtain

$$\ln(1 - v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2 + v_1 (v_e / V_0) (v_2^{0,2/3} v_{2m}^{1/3} - v_{2m} / 2) = 0 \quad (2.40)$$

or, adopting the terminology

$$\frac{v_1 \rho}{M_c} = N^{-1} = \frac{v_e v_1}{V_0} \quad (2.41)$$

$$\ln(1 - v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2 = - N^{-1} (v_2^{0,2/3} v_{2m}^{1/3} - v_{2m} / 2) \quad (2.42)$$

where M_c is the average molecular weight between junctions, ρ is the density of the polymer network and N is the number of segments in a network chain.

The left hand member in this equation represents the lowering of the chemical potential owing to mixing of polymer and solvent; that on the right gives the increase from the elastic region of the network. The latter corresponds to the increase πv_1 in the chemical potential resulting from an osmotic pressure π at equilibrium.

It is customary to employ the swelling ratio, q , equal to the ratio V / V_0 of the volumes of the swollen and unswollen structures. Thus, $q = 1 / v_2$. At swelling equilibrium, $1 / v_{2m}$ may be replaced by q_m , the subscript m indicating equilibrium swelling. At large M_c values of 10000 or more, q_m in a good solvent will exceed 10. Then $v_{2m} / 2$ is considerably smaller than $v_{2m}^{1/3}$ and can be neglected. Also the higher terms in the series of expansion of the first term member of Equation (2.40) may be neglected. The swelling equilibrium equation may then be solved for $v_{2m} = 1 / q_m$ with the following result.

$$q_m^{5/3} \cong (V_0 / v_e) (1/2 - \chi_{12}) v_1 \quad (2.43)$$

This simplified relationship offer a clearer insight into the dependence of the equilibrium swelling ratio q_m on the quality of the solvent as expressed by χ_{12} , and on the extent of cross-linking. Because of the nature of the approximation introduced to obtain Equation (2.43), its use as quantitative expressions must be limited to networks of very low degrees of cross-linking in good solvents [1-cp13].

2.2.3. Swelling of Ionic Networks

If the polymer chains making up the network contain ionizable groups, the swelling forces may be greatly increased as a result of the localization of charges on the polymer chains.

The character of the behavior of the ionic network depends essentially on the fact whether network chains carry charged units of the same or opposite sign. It is possible to consider two limiting cases. When network chains contain only charged units of the same sign and oppositely charged counterions move freely within the sample, it is called a polyelectrolyte network. In the opposite case, when network

chains carry both negative and positive charges in equal quantities and counter ions are absent, the network is called an isoelectric network[32].

Cross-linked polyacrylic acid and polymethacrylic acid afford appropriate examples for polyelectrolyte network. When neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion which tends to expand the network.

The exchange of ions and solvent between a swollen ionic network and the surrounding electrolyte is represented in Figure 2.2, where the fixed ion is taken to be a cation. It is apparent that the equilibrium between the swollen ionic gel and its surroundings closely resembles Donnan membrane equilibria. The polymer acts as its own membrane preventing the charged substituents from diffusing into outer solution. The swelling force resulting from the presence of these fixed charges may be identified with the swelling pressure or osmotic pressure, across the semipermeable membrane in a typical Donnan equilibrium.

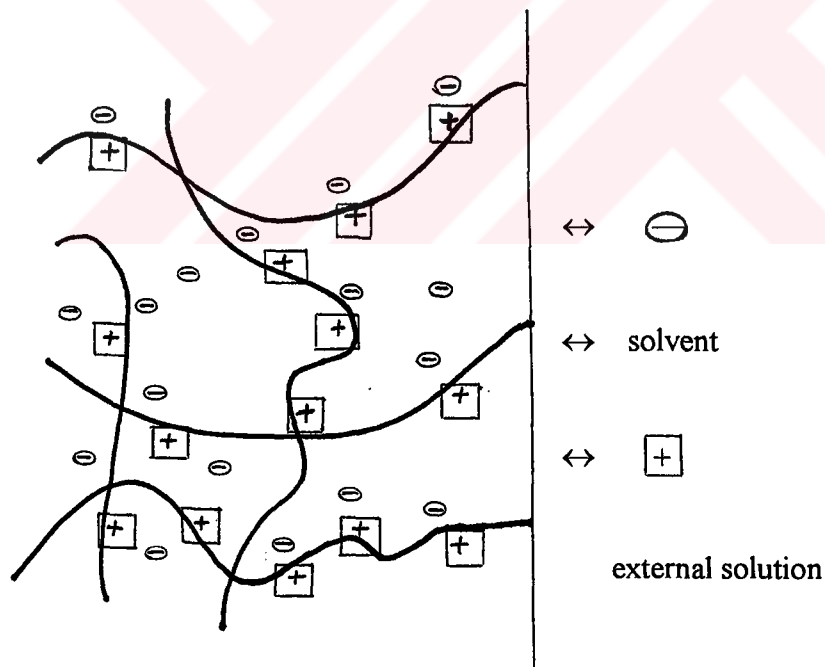


Figure 2.2. Diagram of swollen ionic gel in equilibrium with electrolyte solution. Fixed chages are represented by + [1].

The free energy of such a network can be written as the sum of at least three terms:

$$\Delta G = \Delta G_{el} + \Delta G_m + \Delta G_i \quad (2.44)$$

where ΔG_i is the free energy of electrostatic interactions. In the case of a weakly charged polyelectrolyte network, in order to describe the effect of charges it is sufficient to take into account only the translational entropy of counterions. If i represents the number of ions in $(x n_2 + i)$ units, then the mean number of ionic units between successive junctions in a network chain, f , can be written as:

$$f = \frac{N i}{x n_2 + i} \quad (2.45)$$

where N is the number of segments in a network chain. Then the free energy of electrostatic interactions ΔG_i may be written as follows: [1-cp13, 33-34]

$$\Delta G_i = kT (f / N) (v_2 / v_1) n_1 \ln (f v_2 / N) \quad (2.46)$$

CHAPTER 3

PHASE EQUILIBRIA IN POLYMER SYSTEMS

The mutual solubility of a polymer-solvent system can be best understood by referring to the free energy of the system as a function of composition. If two separate phases were present in the system, they will always correspond to a higher free energy and hence, are unstable with respect to the homogeneous phase. For total miscibility, it is necessary that both

$$\Delta G_m < 0 \quad (3.1)$$

and that the second derivative of ΔG_m with respect to the volume fraction of solvent or polymer be greater than zero.

$$\left(\frac{\partial^2 \Delta G_m}{\partial v_2^2} \right)_{P,T} > 0 \quad (3.2)$$

over the entire composition range.

The phase equilibrium is strongly affected by solution temperature. If the solvent chosen for a given polymer becomes progressively poorer as the temperature is lowered, eventually a temperature may be reached below which the solvent and the polymer no longer are miscible in all proportions. At each lower temperature, mixtures of the polymer and solvent over a certain composition range will separate into two phases. If the polymer consists of a sufficiently narrow range of molecular species then the mixtures of solvent and polymer may be treated as binary solution system. The temperature-composition phase diagram consists of a boundary curve distinguishing the homogeneous region from the heterogeneous region and it is called the binodal. The binodal is the loci of points that satisfy the conditions for

thermodynamic equilibrium of a binary mixture. The maximum in the binodal curve is a critical point for the binary system; the compositions of the coexisting phases merge at this point, and at temperatures above the critical temperature, T_c , the system is homogeneous for all compositions[15,16].

3.1. Binary Polymer- Solvent Systems

The conditions for equilibrium between two phases in a binary system are expressed by stipulating equality of the chemical potentials in the two phases; that is

$$\mu_1 = \mu_1' \quad (3.3)$$

$$\mu_2 = \mu_2' \quad (3.4)$$

where the prime is adopted as the designation for the more concentrated phase. Equations (2.16) and (2.17) express the chemical potentials μ_1 and μ_2 as a function of the volume fraction v_2 of polymer. The single parameter χ_{12} occurs in these functions. There must be two concentrations at which the chemical potential μ_1 has the same value and this requires that μ_1 pass through a minimum and then a maximum as a v_2 is increased from zero to unity. Since μ_1 and μ_2 are derived by differentiating the same free energy function, Equation (2.14), it is easy to show that the one must pass through a maximum where the other is at its minimum. Confining attention to μ_1 , the inflection point characterized by the condition of zero curvature ($\partial^2 \mu_1 / \partial v_2^2$)_{T,P} = 0 must necessarily occur between the minimum and the maximum in the curve. At both the maximum and the minimum ($\partial \mu_1 / \partial v_2$)_{T,P} = 0. If the curve representing μ_1 as a function of composition decreases monotonically with v_2 total miscibility is assured. In passing to progressively poorer solvents, eventually a minimum and a maximum will appear in the curve, their appearance signifies incomplete miscibility.

The critical solution temperature T_c , is an important quantity. At this temperature incipient phase separation will be encountered. Hence the conditions for incipient phase separation are

$$(\partial \mu_1 / \partial v_2)_{T,P} = 0 \quad (3.5)$$

$$(\partial^2 \mu_1 / \partial v_2^2)_{T,P} = 0 \quad (3.6)$$

Application of these critical conditions to Equation (2.16) leads to the first derivative of that equation

$$(1 - v_{2c})^{-1} - (1 - 1/x) - 2\chi_{1c} v_{2c} = 0 \quad (3.7)$$

while the second derivative is

$$(1 - v_{2c})^{-2} - 2\chi_{1c} = 0 \quad (3.8)$$

where the subscript c denotes critical conditions. The critical composition at which phase separation is first detected is then

$$v_{2c} = 1 / (1 + x^{1/2}) \quad (3.9)$$

$$\chi_{1c} = 1/2 (1 + x^{-1/2})^2 \quad (3.10)$$

It is seen that for very large values of x, the above expressions reduce to

$$v_{2c} = x^{-1/2} \quad (3.11)$$

$$\chi_{1c} = 1/2 \quad (3.12)$$

The critical value of χ_1 approaches a limiting value of 1/2 for infinite molecular weight. This corresponds to the θ point in Equation (2.27), i.e., $T_c = \theta$ for $x \rightarrow \infty$, Equation (2.27) can be rewritten as

$$1/2 - \chi_{1c} = \Psi_1 (1 - (\theta / T_c)) \quad (3.13)$$

Combination with Equation (3.10) gives

$$\frac{1}{T_c} = \frac{1}{\theta} \left[1 + \frac{1}{\psi_1} \left(\frac{1}{x^{1/2}} + \frac{1}{2x} \right) \right] \quad (3.14)$$

which predicts a linear relation between $1 / T_c$ and $(1 / x^{1/2} + 1 / 2x)$ and is verified by experimental results (Shultz and Flory; 1952). It can be seen from Equation (3.14) that the theta temperature is also the critical miscibility temperature in the limit of infinite molecular weight [1-cp13, 15-16].

3.2. Ternary Solvent-Network-Polymer Systems

The state of an equilibrium swelling of a network immersed in a polymer solution is obtained when the solvent and the polymer inside the network are in thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential μ of these components in both phases. If the subscript $i = 1, 2, 3$ denotes the solvent, the network and the linear polymer, respectively, at swelling equilibrium,

$$\Delta\mu_1^{gel} - \Delta\mu_1^{sol} = 0 \quad (3.15)$$

$$\Delta\mu_3^{gel} - \Delta\mu_3^{sol} = 0 \quad (3.16)$$

Substitution of Equations (2.37), (2.38a) and (2.46) into Equation (2.44) and differentiating with respect to the number of moles of solvent n_1 and polymer molecules n_3 yield the following set of equations for the excess chemical potentials of the solvent and polymer in both the gel ($\Delta\mu_i^{gel}$) and the solution phases ($\Delta\mu_i^{sol}$): [34]

$$\begin{aligned} \frac{\Delta\mu_1^{gel}}{RT} = N^{-1} & \left(v_2^{1/3} v_2^{o2/3} - v_2/2 \right) + \ln v_1 + (1 - v_1) - v_3/y + \\ & (\chi_{12} v_2 + \chi_{13} v_3)(1 - v_1) - \chi_{23} v_2 v_3 - v_2 f / N \end{aligned} \quad (3.17)$$

$$\frac{\Delta\mu_1^{\text{sol}}}{RT} = \ln(1-\phi) + \phi(1-1/y) + \chi_{13}\phi^2 \quad (3.18)$$

$$\begin{aligned} \frac{\Delta\mu_3^{\text{gel}}}{yRT} = & N^{-1} \left(v_2^{1/3} v_2^{2/3} - v_2/2 \right) + (1/y) \ln v_3 + (1/y)(1-v_3) - v_1 \\ & + (\chi_{13}v_1 + \chi_{23}v_2)(1-v_3) - \chi_{12}v_1v_2 - v_2 f / N \end{aligned} \quad (3.19)$$

$$\frac{\Delta\mu_3^{\text{sol}}}{yRT} = (1/y) \ln \phi - (1-\phi) + (1/y)(1-\phi) + \chi_{13}(1-\phi)^2 \quad (3.20)$$

where y is the number of segments in the linear polymer, ϕ is its volume fraction in the solution phase and N is called the number of segments in a network chain,

In terms of the osmotic pressure π , Equation (3.15) can also be written as:

$$\pi = - \frac{(\mu_1^{\text{gel}} - \mu_1^{\text{sol}})}{v_1} = 0 \quad (3.21)$$

osmotic pressure π of a gel determines whether the gel tends to expand or to shrink. When nonzero, π provides a driving force for gel volume change. Solvent moves into or out of the gel until $\pi = 0$; i.e., until the forces acting on the gel are balanced.

From the equality of "chemical potential" inside and outside the network (Equations (3.15) and (3.16)) and the equality of osmotic pressure exerted by solvent and polymer inside and outside the network,

$$\frac{(\Delta\mu_1^{\text{gel}} - \Delta\mu_1^{\text{sol}})}{RT} = \frac{(\Delta\mu_3^{\text{gel}} - \Delta\mu_3^{\text{sol}})}{RT} \quad (3.22)$$

Inserting Equations (3.17)-(3.20) into Equations (3.15) and (3.16), the system of equations is obtained,

$$\frac{1}{y} \ln\left(\frac{v_3}{\phi}\right) - \ln\left(\frac{1-v_2-v_3}{1-\phi}\right) + 2\chi_{13}(\phi-v_3) + (\chi_{23}-\chi_{12}-\chi_{13})v_2 = 0 \quad (3.23)$$

$$N^{-1} \left(v_2^{1/3} v_3^{2/3} - v_2/2 \right) + \ln \left(\frac{1-v_2-v_3}{1-\phi} \right) + (v_2 + v_3 - \phi) - (v_3 - \phi)/y + \chi_{12} v_2^2 + \chi_{13} (v_3^2 - \phi^2) + (\chi_{12} + \chi_{13} - \chi_{23}) v_2 v_3 - v_2 f / N = 0 \quad (3.24)$$

where χ_{12} , χ_{13} and χ_{23} are the solvent-network, solvent-polymer and network-polymer interaction parameters.

In ionic gels, triphasic equilibrium in which two swollen gel phases may coexist with the polymer solution for a certain values of ϕ . In these cases, the composition of the gels in coexisting phases is calculated by equating chemical potentials of the network chains in both gel phases[34].

$$\Delta\mu_2^{\text{gel-1}} = \Delta\mu_2^{\text{gel-2}} \quad (3.25)$$

where gel-1 and gel-2 denotes swollen and collapsed states of the gel.

Substitution the Equations (2.37), (2.38a) and (2.46) into Equation (2.44) and differentiating with respect to the number of moles of network chains, n_2 gives,

$$\begin{aligned} \frac{\Delta\mu_2}{xRT} = & -N^{-1} \left(v_2^{1/3} v_3^{2/3} - v_2/2 \right) \left(\frac{1-v_2}{v_2} \right) + -v_1 - (v_3/y) \\ & + (\chi_{12} v_1 + \chi_{23} v_3)(1-v_2) - \chi_{13} v_1 v_3 + N^{-1} f \left[(1-v_2) + \ln(fN^{-1} v_2) \right] \end{aligned} \quad (3.26)$$

Then the result obtained on equating $\mu_2^{\text{gel-1}}$ to $\mu_2^{\text{gel-2}}$ according to the equilibrium conditions yields volume fractions $v_2^{\text{gel-1}}$ and $v_2^{\text{gel-2}}$ indicating the coexistence of two gel phases with different conformations and appearance of van der Waals loops in the swelling curves.

3.3. Critical Phenomena and Gel Collapse

The osmotic compressibility or the chemical potential of a network depends on temperature and solvent activity. If the network chains carry ionic groups, then

the pH, ionic strength of the solvent or an electric field acting across the gel, also affects the osmotic compressibility. It has been shown experimentally that very large changes in the state of a gel may be induced by small changes in the external conditions.

When certain critical conditions are reached, the osmotic compressibility becomes infinitely large indicating that the network shrinks strikingly and can continue almost indefinitely under a slight increase in external pressure. At this state, pure solvent phases appear in the network and their sizes reach macroscopic dimensions. This indicates the onset of large fluctuations in the system.

The first and second derivatives of the solvent chemical potential with respect to v_2 equate to zero at the critical point for a polymer- solvent system. Thus,

$$\Delta\mu_1 = RT \ln a_1, \quad \frac{\partial \Delta\mu_1}{\partial v_2} = 0, \quad \frac{\partial^2 \Delta\mu_1}{\partial v_2^2} = 0 \quad (3.27)$$

A network-solvent system may also exhibit phase separation where three phases of different concentrations may exist in equilibrium inside the swollen network. One of the phases is pure solvent ($v_2 = 0$). The remaining two phases are a less swollen and a highly swollen phase. Such a state is referred to as triphasic equilibrium, described by equations

$$\Delta\mu_1 (v_2') = \Delta\mu_1 (v_2'') = RT \ln a_1 \quad (3.28)$$

$$\int \Delta\mu_1 dn_1 = 0 \quad (3.29)$$

where v_2' and v_2'' represent the two coexisting polymer concentration. This state may be reached by varying the temperature, which in turn varies $\chi_1 (T)$ and $\chi_2 (T)$. Alternatively, triphasic conditions may be obtained by varying the activity or the pH of the solvent in which the gel is immersed. The results of typical calculations are shown in Figure 3.1 for triphasic equilibrium obtained by varying the temperature.

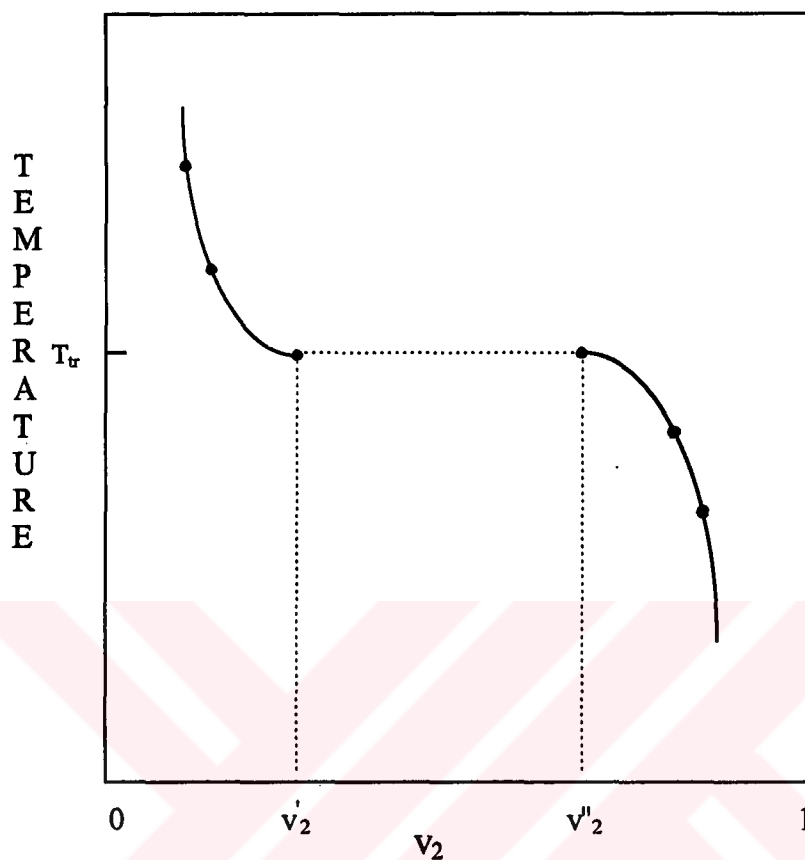


Figure 3.1. Temperature-composition diagram for a swollen network showing a transition. T_r indicates the temperature of transition at which triphasic equilibrium obtains. The quantities v_2' and v_2'' denote polymer volume fractions in the less swollen and the more highly swollen phases at this state, respectively. Circles show representative data from corresponding experiments [19].

The horizontal line identifies the temperature at which the transition takes place. At higher temperatures $v_2 < v_2'$ and the network is highly swollen. At lower temperatures, $v_2 > v_2''$ and the network is collapsed. The width of the horizontal line at the transition depends on various parameters such as the presence of ionic groups on the network chains, the degree of cross-linking, and the amount of solvent during cross-linking[19].

3.4. Fundamental Interactions for Volume Phase Transition of Gels

Four fundamental molecular interactions play an essential role in determining the structures and specific functions of macromolecules and their assemblies: These are van der Waals, hydrophobic, hydrogen bonding and electrostatic interactions (Figure 3.2) [35,36]. A gel can be one macroscopic molecule. Because of this reason, the size of a gel is very sensitive to the change in the molecular interactions. Therefore, by measuring the size of a gel as a function of external intensive variables, such as temperature, pH, solvent composition, one can investigate the local environment of polymer chains. Since gels are simply obtained by cross-linking these polymer chains, gels can be a good system for studying molecular interactions[37].

3.4.1. Van der Waals Interaction

A partially hydrolyzed polyacrylamide gel undergoes a phase transition in acetone / water mixtures[8]. The main polymer -polymer affinity is due to the van der Waals interaction. Acetone, a nonpolar poor-solvent had to be added to water in order to increase the attractive interaction between polymers in the networks to induce the transition. The transition is also observed when the temperature was varied while the solvent composition fixed near the transition threshold at room temperature. The gel swells at higher temperatures and shrinks at lower temperatures.

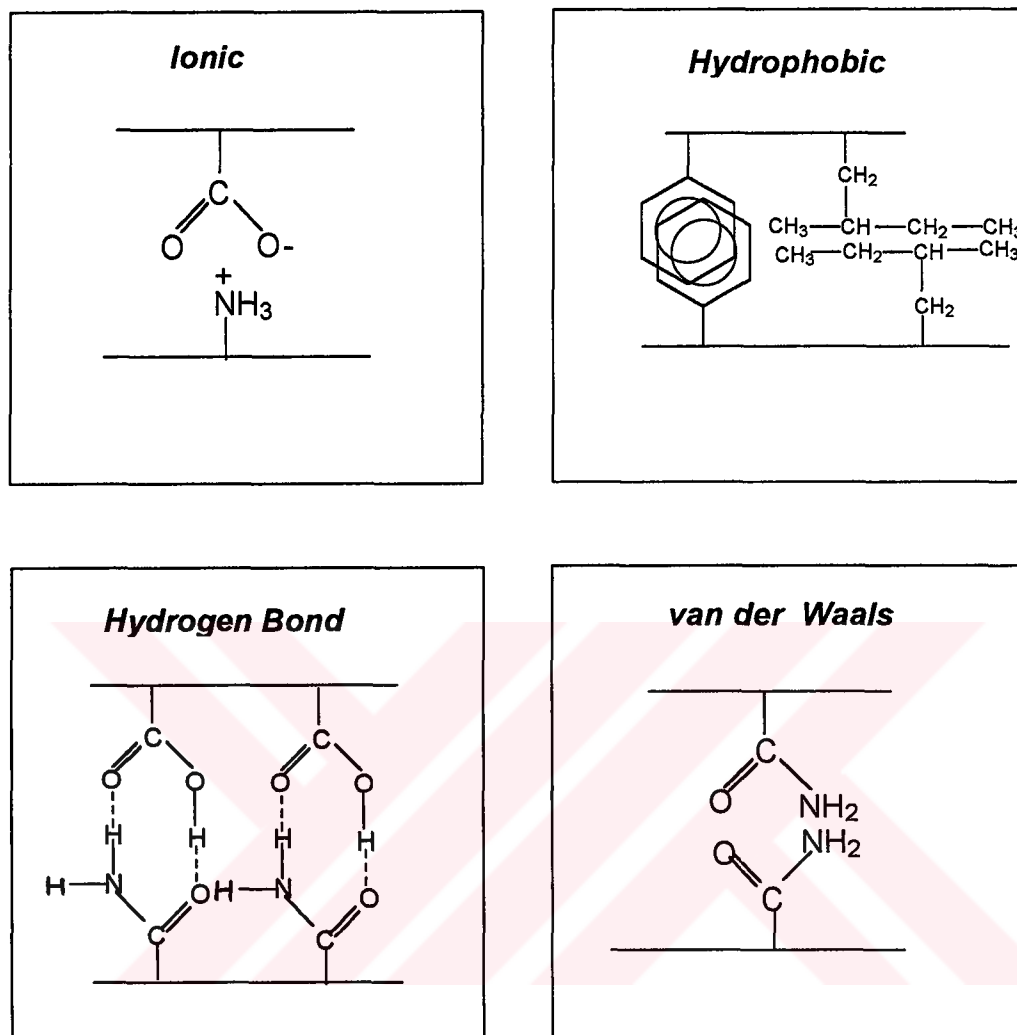


Figure 3.2. Schematic representation showing the four fundamental molecular interactions.

3.4.2. Hydrophobic Interactions

In an attempt to find a gel that undergoes a volume phase transition in pure water Hirokawa studied with poly(N-isopropyl acrylamide) gels which had side groups with more hydrophobicity than that of acrylamide[10]. They observed the collapsing transition at approximately 33.2 °C by increasing temperature.

It is interesting to observe that gels swell at lower temperatures and collapse at higher temperatures. This temperature dependence, which is opposite to the transition induced by van der Waals interaction, is due to the hydrophobic interaction of the polymer network and water. At higher temperatures the polymer network shrinks and becomes more ordered, but the water molecules excluded from the polymer network become less ordered[11].

3.4.3. Hydrogen Bonding

A volume phase transition via the hydrogen bonding interaction was demonstrated with an interpenetrating polymer network (IPN) consisting of two independent networks intermingled with each other[38]. For example, one network is poly(acrylic acid) and the other polyacrylamide. The gel was originally designed and developed by Okano and his colleagues who found that the gel is shrunken at low temperatures in water, and the volume increased as temperature rose. There was a sharp but continuous volume change at about 30 °C. These researchers identified the main interaction to be hydrogen bonding and also pointed out the importance of the so-called "zipper" effect, which described the cooperative nature of the interaction between two polymers[39]. By slightly ionizing the gel, Ilmain, Tanaka, and Kokufata succeeded in inducing the discontinuous volume transition of the IPN in pure water [38].

3.4.5. Electrostatic Interaction

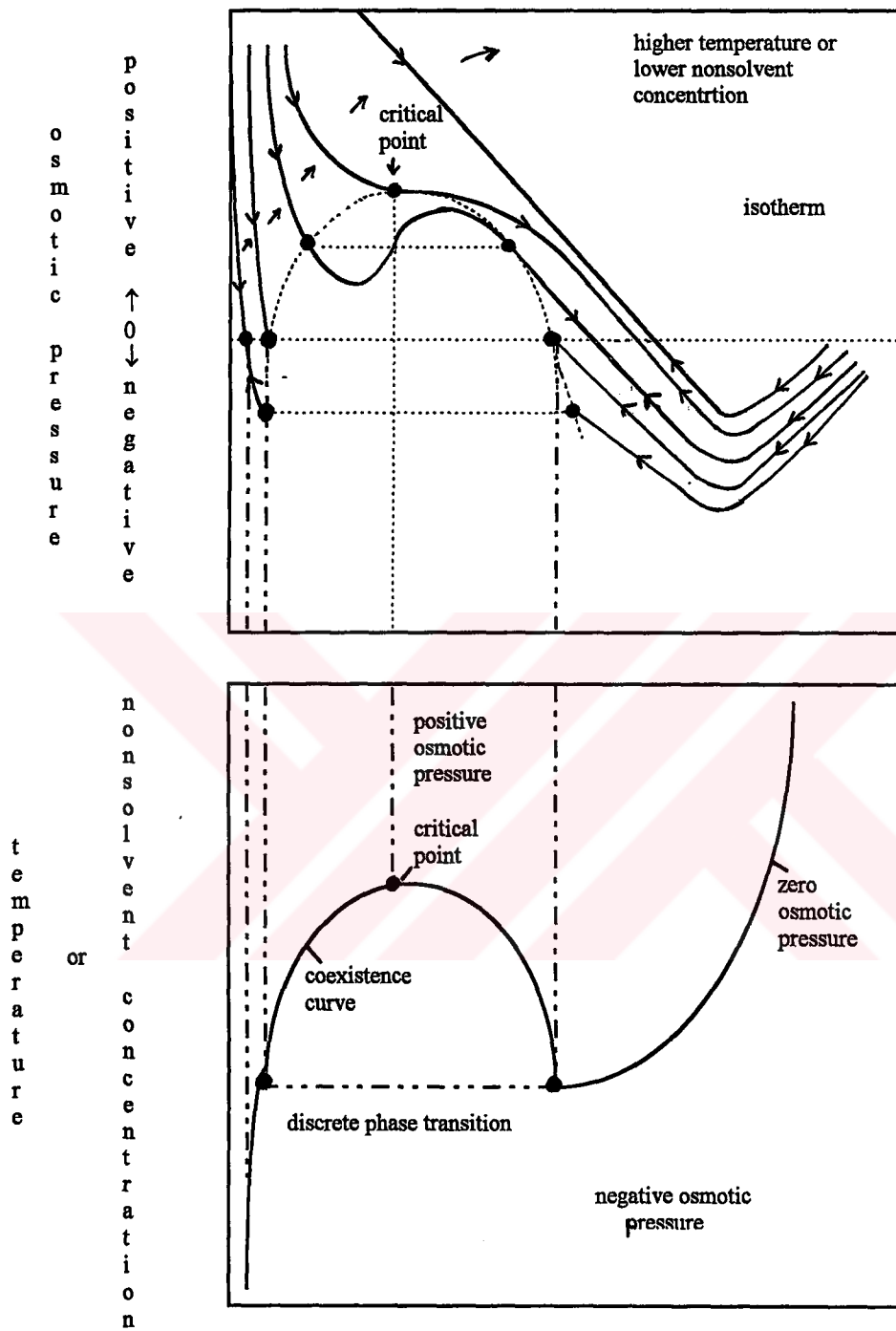
The electrostatic interaction is a long-range order interaction. The electrostatic interaction is inversely proportional to the dielectric constant of the

medium. In synthetic polymers, either positive or negative charges is introduced on the polymer chains by copolymerization or partial ionization, which give rise to a strong repulsive interaction. Since a free movement of the charges is not allowed because the charges are fixed on the polymer chain, the counter ions have to be localized near the polymer chains so as to keep the electroneutrality. As a result Donnan potential is created between the inside and outside of the gel, resulting in an increase in the osmotic pressure[37].

3.5. Phase Diagram of a Gel

Phase diagram of a gel (Figure 3.3) is constructed by calculating the osmotic pressure for many combinations of volume and either temperature or solvent concentration. In the upper diagram this information is presented as a series of isotherms, which are curves that specify all possible combinations of pressure and volume at a given temperature (or solvent composition). The lower diagram was derived from the upper, but it gives the volume of the gel as a function of temperature or solvent concentration.

The complete phase diagram for the gel has three regions. Below the swelling curve the gel has a negative osmotic pressure and is always unstable; it will expel fluid and shrink until it reaches the zero-pressure swelling curve. Another region represents states with a positive osmotic pressure, which are stable only if there is no excess fluid the gel could absorb in order to expand. Between these realms is the dominant of dual stability, where some parts of the gel shrinks and another part swells. The boundary of this region is the coexistence curve for the two phases. The difference in volume between the two phases is greatest along the swelling curve, and it decreases steadily at higher temperature ultimately the coexistence curve reaches a maximum temperature where the two phases are identical or in other words where they cease to exist as distinguishable phases. That is critical point of the gel[40].



shrunk ← gel volume → swollen

Figure 3.3. Phase Diagram of a Gel[40].

CHAPTER 4

COIL-GLOBULE TRANSITION IN LINEAR POLYMER CHAINS

Polymer chains in solution exhibit different conformations depending on the nature of the polymer and the solvent conditions. In a good solvent where the solvent-segment contacts are favored, the polymer has an extended coil configuration. In a poor solvent, segment-segment interaction is attractive and the complete collapse of the chain is hindered only by the steric repulsion between segments. The transition from an expanded coil to a collapsed globule state effected by changing the quality of the solvent has been focus of many theoretical studies. It can be induced by a change in temperature, a change in pressure, or by mixing two or more solvents of different qualities. There has been extensive experimental information gathered on the dynamic and static properties of chain conformation at and above θ temperature using static and quasi-elastic light scattering techniques as well as intrinsic viscosity measurements of dilute polymer solutions[41-45].

4.1. Configuration of Polymer Molecules in Dilute Solutions

In dilute solution, a polymer molecule is a randomly coiling mass most of whose configurations occupy many times the volume of its segments alone. The size of a molecular coil is very much influenced by the polymer-solvent interaction forces. The random coil arises from the relative freedom of rotation associated with the chain bonds of most polymers and formidably large number of configurations accesible to the molecule.

One of this configuration is fully extended chain has special interest because its length, can be calculated in a straight forward way. In all other cases, the size of the random coil must be expressed interms of statistical parameters such as the root-mean-square distance between its ends. $\langle r^2 \rangle^{1/2}$, or its radius of gyration, the root-

mean- square distance of the elements of the chain from its centre of gravity, $\langle s^2 \rangle^{1/2}$. For linear polymers the mean square end-to-end distance and the square of the radius of gyration are simply related:

$$r^2 = 6 s^2 \quad (4.1)$$

The freely jointed chain is a simple model of a polymer chain that consists of a series of x links of length l jointed in a linear sequence with no restriction on the angles between successive bonds. The most important result of the calculation is that end-to-end distance is proportional to the square root of the number of links.

$$\langle r_f^2 \rangle^{1/2} = l x^{1/2} \quad (4.2)$$

where subscript f indicates the random-flight end-to-end distance. The freely jointed or random-flight model seriously underestimates the true dimensions of real polymer molecules for two reasons: first, restrictions to completely free rotation, such as fixed bond angles and steric hindrances, provide short-range interactions leading to larger dimensions than calculated above; and second, long-range interactions resulting from the inability of chain atoms far removed from one another to occupy the same space at the same time result in a similar effect[14].

4.1.1 Short-range interactions

Flory and his collaborators (Flory 1969) have calculated completely and accurately the effect of short-range interactions on the dimensions of random coil polymers. Several effects are involved. The restriction fixed bond angle θ expands the chain by a factor of $[1 - \cos\theta / 1 + \cos\theta]^{1/2}$, equal to $\sqrt{2}$ for carbon-carbon bonds. Restricted rotation, whether resulting from steric hindrances and resulting potential-energy barriers or from resonance leading to rigid planar conformations, increases dimensions still more. Finally, configurations that would place two atoms close together along the chain too close to one another are not allowed, leading to further expansion.

The net results of these short-range interactions can be expressed as a characteristic ratio of the square of the actual chain dimensions in the absence of long-range interactions (called the unperturbed dimensions) and given the symbol $\langle r_0^2 \rangle$ and the square of the random-flight end to end distance, l^2 .

4.1.2. Long-range interactions and the excluded volume

Correction of polymer chain dimensions for short-range interactions still fails to eliminate configurations in which two widely separated chain segments occupy the same space. Each segment of a real chain exists within a volume from which all other segments are excluded. Practically, the effect of the long-range interaction is to cause a further expansion of the chain over its unperturbed dimensions, since more of the compact conformations, with small values of r^2 , must be excluded. The actual dimensions of the real chain can be expected to exceed its unperturbed dimensions by an expansion factor α , thus

$$\langle r^2 \rangle^{1/2} = \alpha \langle r_0^2 \rangle^{1/2} \quad (4.3)$$

The value of α depends on the nature of the solvent: a solvent for which α is large is said to be a thermodynamically "good" solvent for that polymer, and vice versa.

In a sufficiently poor solvent, or at sufficiently low temperature, it is possible to achieve the condition $\alpha = 1$, where the chain attains its unperturbed dimensions. This special point is called the Flory temperature θ ; a solvent used at $T = \theta$ is called θ solvent.

4.2. The Molecular Expansion Factor α and the General Dependence of the Intrinsic Viscosity on Molecular Weight.

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognized ever since the early work of Staudinger (1930). Solution viscosity is basically a measure of the size or extension in space of polymer molecules. The size of a dissolved polymer molecule, which can be estimated by means of its

intrinsic viscosity, depends upon a number of factors. These include the molecular weight, the local chain structure and the perturbations reflected in α [14].

The viscosity of a suspension of a rigid non-interacting spheres is given by the Vand equation[46]

$$\eta = \eta_0 [1 + 2.5 \phi_2 + 7.349 \phi_2^2 + \dots] \quad (4.4)$$

where η and η_0 are the viscosities of the suspension and the pure solvent, respectively, and ϕ_2 is the volume fraction of the spheres. If the spheres are considered to be impermeable polymer coils of hydrodynamic volume V_h then

$$\phi_2 = (c / M) N_A V_h \quad (4.5)$$

where c is the polymer concentration (mass per unit volume), M is the molecular weight of the sample (mass per mol) and N_A is the Avogadro's number[17]. Substituting this equation into Equation (4.4) and simplifying gives

$$\eta_{sp} = 2.5 (c / M) N_A V_h \quad (4.6)$$

where $\eta_{sp} = (\eta - \eta_0) / \eta_0$ and is known as the specific viscosity. Non-interaction of the polymer coils requires infinite dilution and this is achieved mathematically by defining a quantity called the intrinsic viscosity, $[\eta]$, according to the equation

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp} / c) \quad (4.7)$$

Theories (Debye 1948; Kirkwood 1948, Flory 1949, 1950, 1951) of the frictional properties of polymer molecules in solution show that the intrinsic viscosity is proportional to the effective hydrodynamic volume of the molecule in solution ($V_h \propto (\alpha_{\eta} \langle r_0^2 \rangle^{1/2})^3$) and the intrinsic viscosity is given by the relationship[1]

$$[\eta] = \Phi \langle r_0^2 \rangle^{3/2} \alpha^3 M^{-1} \quad (4.8)$$

where Φ is an universal constant and the factor

$$\alpha = (\langle r^2 \rangle / \langle r^2 \rangle_0)^{1/2} \quad (4.9)$$

characterizes the extent to which polymer-solvent interactions expand the chain dimensions over their unperturbed values, and is thus unity in a θ solvent.

It is well established that viscosity measurements performed on solutions under θ conditions can yield information on the unperturbed dimensions with the aid of the following relations:

$$[\eta] = [\eta]_0 \alpha_\eta^3 \quad (4.10)$$

$$[\eta]_0 = K_0 M^{1/2} \quad (4.11)$$

where $[\eta]$ and $[\eta]_0$ represent the intrinsic viscosities in ordinary and θ solvent, respectively, M is the molecular weight and K_0 is a constant. However, since the hydrodynamic radius of a polymer chain increases less rapidly than the statistical radius as the excluded volume increases, theoretical considerations indicate that the expansion factors given in Equations (4.8) and (4.10) are not identical but $\alpha_\eta \leq \alpha$ [47]. For practical purposes, Kurata and Stockmayer proposed to use the following exponential type of expansion factor in calculations[48]

$$\alpha_\eta^3 = \alpha^{2.43} \quad (4.12)$$

4.3. Theory of Coil-Globule Transition in Linear Macromolecules

The theory of the random coil-globule transition has been developing for over 40 years. Many authors, Stockmayer[49], de Gennes[50] and Sanchez[51] have investigated this problem on the basis of a simple Flory scheme. Williams et al. [42] summarized the contributions made by end of 1970s, and Fujita[51] presented a review on this subject at 1990. Recently, Chu et.al. have studied the transition of polymer dimensions from θ to collapse regime for polystyrene solutions at extremely

low concentrations by quasi-elastic light scattering techniques as well as intrinsic viscosity measurements of dilute polymer solutions[43, 53-55].

On the other hand, Birshtein and Pryamitsyn studied the entropic force and they indicated that the evaluation of the configurational entropy (and entropy force) in earlier papers published on the coil-globule transition were based on an expression in applicable to the contraction of the chains but valid for the case of chain expansion[44].

The following asymptotic expressions may be written for chain expansion and contraction.

$$f_{el} = (\pi^2 / 2) \alpha_{av} (1 - \alpha_{av}^{-2}) \quad \alpha_{av} > 1 \quad (4.13)$$

$$f_{el} = - (9 / 2) \alpha_{av}^{-3} (1 - \alpha_{av}^2) \quad \alpha_{av} < 1 \quad (4.14)$$

where f_{el} and α_{av} are the elastic force and the averaged value of chain deformation, respectively.

A non-averaged value of α is used in the following relations of the expansion factors,

$$\alpha_s^2 = \langle s^2 \rangle / \langle s_0^2 \rangle \quad (4.15)$$

$$\alpha_{av}^2 = \langle \alpha^2 \rangle \quad (4.16)$$

The equilibrium average size of a chain is calculated as a function of an interaction parameter using the following equation of the free energy of the chain.

$$\Delta G = \Delta G_{el}(\alpha_{av}) + \Delta G_{int}(\alpha_{av}, N^*) \quad (4.17)$$

where the terms on the right hand-side represent the usual elastic and interaction free energies. $\Delta G_{int}(\alpha_{av})$ is calculated using a mean field approximation, assuming that the change in the chain size is determined by a change in the interaction between units distant from each other along the chain[44]. Standard methods of derivations of the

theory of random coil-globule transition give the following expressions for the force determined by the interaction between segments located far from each other.

$$f_{\text{int}} = -\frac{9}{2} \alpha_{\text{av}}^{-4} [N^{1/2} B \tau + C (\alpha_{\text{av}}^{-3} - 1)] \quad (4.18)$$

where N^* represents the number of the Kuhn segments in the chain, B and C are parameters that do not depend on molecular weight and temperature T but depend on chain stiffness, $\tau = \left(\frac{T - \theta}{\theta} \right)$ is the reduced temperature. The equilibrium condition of forces is given as follows,

$$f_{\text{el}} = -f_{\text{int}} \quad (4.19)$$

Birshtein and Pryamitsyn obtained the following equations for α using Equations (4.13), (4.14) and (4.18) in Equation (4.19)

$$\frac{\alpha^3 - \alpha}{1 - \alpha^{-3}} = \frac{B N^{*1/2} \tau}{(1 - \alpha^{-3})} + C \quad T < \theta \quad (4.20)$$

$$\alpha^5 - \alpha^3 = \frac{9}{\pi^2} B N^{*1/2} \tau \quad T > \theta \quad (4.21)$$

Equation (4.20) is related to the transition of a Gaussian chain to a compact globule, whereas Equation (4.21) represents a relation for the conditions of chain expansion.

CHAPTER 5

EXPERIMENTAL WORK

5.1. Materials and Chemicals

Acrylamide: Acrylamide was a product of Fluka Chemical Company and was used as monomer in the polymerization. It was used after recrystallization in acetone-ethanol mixture. It had a melting point of 84-85 °C. Its molecular weight was 71.08.

Acrylic acid: Acrylic acid was obtained from Fluka Chemical Company. It had a melting point 12-15 °C and a boiling point 139 °C. Its molecular weight was 72.06. It was added to the polymerization system as a comonomer containing ionic groups. It was freed from inhibitor by vacuum distillation under reduced pressure before use. (bp 50-52 °C at 400 mm-Hg)

N-isopropyl acrylamide: N-isopropyl acrylamide was a product of Eastman Kodak Company. Its molecular weight was 113.16. It was used as a monomer in the polymerization step and used without further purification.

N,N'-Methylenebis(acrylamide): N,N'-Methylenebis(acrylamide) was obtained from Aldrich Chemical Company, Inc. It had a melting point greater than 300 °C. Its molecular weight was 154.17. It was used as a crosslinking agent in the polymerization and used without further purification.

N,N,N',N'-Tetramethylethylenediamine: N,N,N',N'-Tetramethylethylenediamine was a product of Aldrich Chemical Company, Inc. It had a boiling point of 120-122 °C. Its molecular weight was 116.21. It was used as an accelerator in the polymerization.

Ammonium peroxodisulfate: Ammonium peroxodisulfate was obtained from Aldrich Chemical Company, Inc. It had a melting point of 120 °C . Its molecular weight was 228.20. It was used as initiator in the polymerization step.

Potassium persulfate: Potassium persulfate was obtained from Fluka Chemical Company. Its molecular weight was 270.33. It was used as a redox initiator system with sodium thiosulfate in the presence of sodium bicarbonate buffer in acrylamide polymerization without further purification.

2,2'-Azobisisobutyronitrile: 2,2'-Azobisisobutyronitrile was a product of Fluka Chemical Company. It was recrystallized twice from chloroform and methanol, then dried in a vacuum oven at room temperature. It had a melting point of 102-104 °C. It was used as initiator in the radical polymerization of acrylamide.

Thioglycolic acid: Thioglycolic acid was obtained from Fluka Chemical Company. Its molecular weight was 92.12. It was used as a chain transfer agent in the polymerization of acrylamide without further purification.

Isopropyl alcohol: Isopropyl alcohol was provided from Merck A.G. Its molecular weight was 60.10. It was used as a chain transfer agent in the polymerization of acrylamide and used as received.

Sodium thiosulfate anhydrous: Sodium thiosulfate anhydrous was obtained from Fluka Chemical Company. Its molecular weight was 158.11. It was used as a redox initiator system with potassium persulfate in the presence of sodium bicarbonate buffer in acrylamide polymerization without further purification.

Sodium bicarbonate: Sodium bicarbonate was obtained from Fluka Chemical Company. Its molecular weight was 84.01. It was used as a buffer in acrylamide polymerization. It was used without further purification.

Paraffin oil: Paraffin oil was provided from Merck A.G. and used as a continuous phase in the inverse suspension polymerization of N-isopropyl acrylamide.

Bovine Serum Albumin: Bovine Serum Albumin was a product of Sigma Chemical Company. Its molecular weight was 60,000 and it was used as a model protein in the separation experiments.

6-Aminopenicillanic acid: 6-Aminopenicillanic acid was provided from Unifar Pharmaceutical Company. Its molecular weight was 218.26. It was used as a bioactive compound in the separation experiments.

Penicillin G Acylase (E.C 3.5.1.11): Penicillin G Acylase was purified in Enzyme and Fermentation Technology Laboratory of TÜBİTAK Marmara Research Center. It was used as an enzyme in the separation experiments. Its molecular weight was 90,000 and had a specific activity of 14.1 u / mg.

Poly(methyl methacrylate): Poly(methyl methacrylate) was a product of Poly Sciences, Inc. Its molecular weight was 2,300,000. It was used as a linear polymer chain in the coil-globule transition phenomena .

Tert-Butyl alcohol: *Tert*-Butyl alcohol was obtained from Merck A.G and it was purified by fractional distillation. Its boiling point was 82 °C. On the coil-globule transition of PMMA, a mixed solvent of *tert*-butyl alcohol + water (97.5% v/v *tert*-butyl alcohol) was used as the θ solvent.

Acetone , Methanol and Toluene were products of Merck A.G. These were used as solvents in the fractionation of polyacrylamide and poly(methylmethacrylate).

Poly(ethylene glycols) were purchased from Fluka Chemical Company (PEG 300, 600, 1540, 2000 and 35000), Union Carbide Corp. (PEG 5000, 6000 and 20000) and Aldrich Chemical Company, Inc. (Tetraethylene glycol). Diethylene glycol and

monoethylene glycol were obtained from Fluka Chemical Company. All products were used without further purification.

5.2. Experimental Set-up and Equipment:

The experimental set-up and equipment used for this work consisted of an incubator, an analytical balance, an electronic digital caliper, a vacuum oven and a pump, a vacuum distillation apparatus, a mechanical stirrer and a reactor system and other auxiliary equipments such as tubes, pipettes, volumetric flasks, vials, sieves (porosity between 125 μm -2500 μm). The equipments used for the characterization tests were refractometer, optical microscopy, scanning electron microscopy (SEM), viscosimetry, UV-visible spectrometer, nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), vapor pressure osmometer (VPO).

5.2.1. Incubator

An incubator was used for providing a constant temperature surrounding to the gels during the swelling experiments. It was an EN 400 type of incubator from Nüve and operated from ambient to 90°C within $\pm 0.1^\circ\text{C}$. It was controlled digitally and had a capacity of 0.04 m^3 .

5.2.2. Analytical Balance

The analytical balance of Mettler AT 200 was used in the experiments. It featured a bright VFD display to four decimal places. Its weighing capacity was 205g.

5.2.3. Electronic Digital Caliper

The measurements of the diameters of the cylindrical gel samples were done by using an electronic digital caliper. The device had a measuring range between 0-150 mm with an accuracy of ± 0.02 mm.

5.2.4. Vacuum Oven

A vacuum oven (EV 018 Nüve) was used for removal of solvents from gel and polymer samples. There were a digital temperature control system and manometer on the oven. The pump to provide vacuum in the oven was from Germany.

5.2.5. Tubes

5.8 mm diameter and 10 cm long glass tubes were used in experiments. Gelation occurred in these tubes.

5.2.6. Vacuum Distillation Apparatus

Vacuum distillation was used in the purification of monomeric acrylic acid. The diagram of vacuum distillation apparatus is shown in Figure 5.1.

5.2.7. Mechanical Stirrer and A Reactor System

Gelation of Poly(N-isopropyl acrylamide) was conducted in a 500 ml of round bottom, four neck flask, fitted with a mechanical stirrer, nitrogen inlet and pipette outlet. A Janke & Kunkel IKA-WERK RW 18 Nr type mechanical stirrer was used with a speed range from 25 - 2500 rpm. The diagram for the apparatus is shown in Figure 5.2.

5.2.8. Refractometry

Refractive indices of dilute polymer solutions was measured by refractometry using an Abbe refractometer at 20 °C.

- A : manostat pressure regulator
 B : vacuum pump
 C : cold trap
 D : sample collector
 E : condenser
 F : thermometer
 G : distillation flask
 H : heating mantle
 I : heater

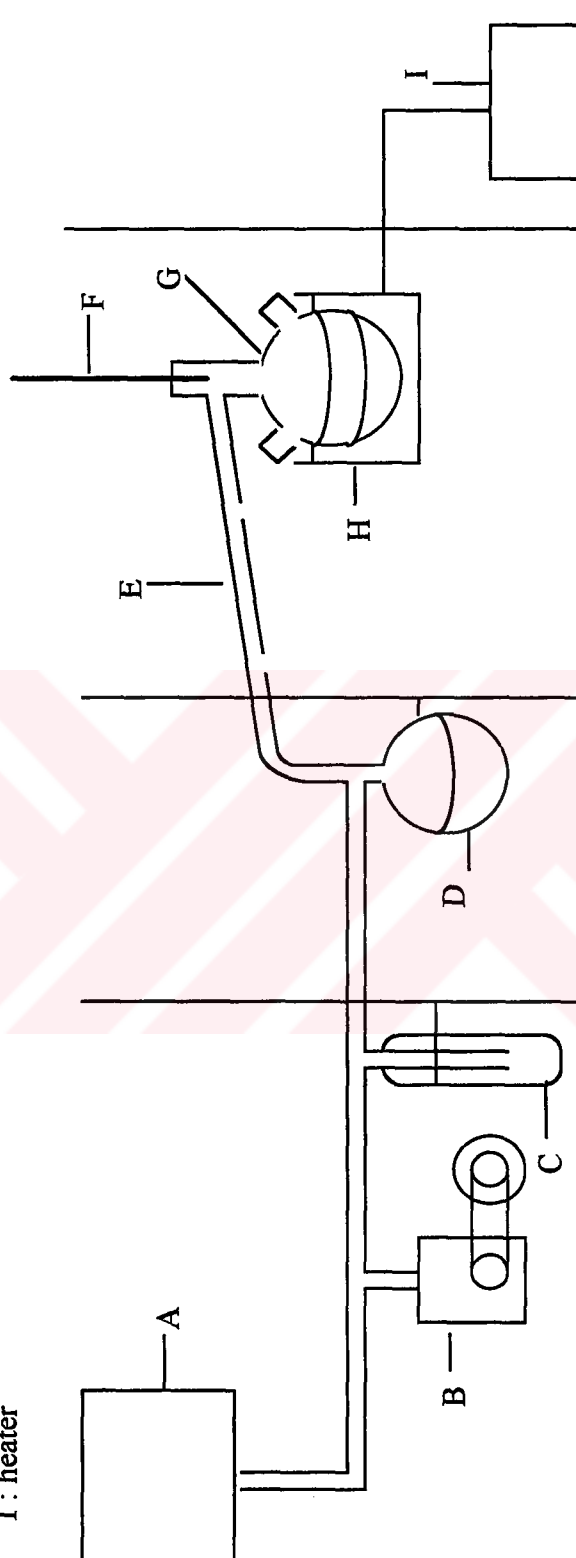


Figure 5.1. Vacuum distillation apparatus

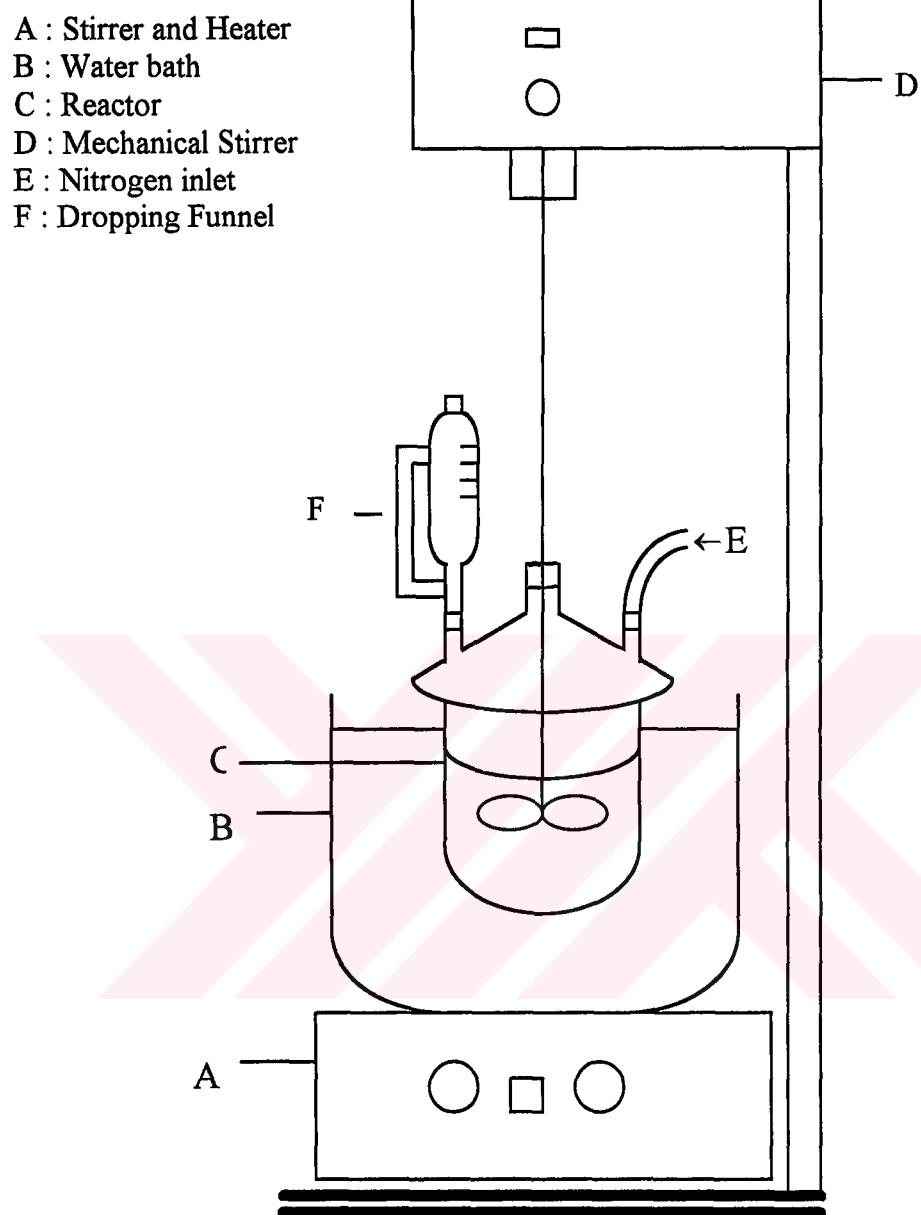


Figure 5.2. Mechanical stirrer and a reactor system for suspension polymerization.

5.2.9. Optical Microscopy

Optical micrograph of the Poly(N-isopropyl acrylamide) gel particles was obtained using Light Ortho Plan / MParis - Sp.Fotometer type microscope. Magnification = 40x

5.2.10. Scanning Electron Microscopy (SEM)

Micrographs were obtained using Jeol JXA-840 A scanning electron microscope. The experiments were done in the laboratories of TUBITAK Marmara Research Center.

5.2.11. Viscosimetry

The instrument was a Cannon 75 M 710 Model Ubbelohde type glass viscosimeter which has a time resolution of ± 0.001 s. Since it has a quite large reservoir, 5 successive data can be taken by 5 ml per dilution. Figure 5.3. gives a picture of Ubbelohde type viscosimeter.

A cylindrical glass bath filled with deionized water was used as constant temperature bath. A polyscience Model 71 type heater-circulator capable of thermostatic temperature control was immersed into this bath. Temperature of bath was measured by glass mercury thermometer. To set the temperature of water-bath below the room temperature, a mgw LAUDA ETK 70 type cryostat was used.

5.2.12. UV- Visible Spectrometer

The optical densities of enzyme solutions were measured by using Varian DMS 90 UV-visible spectrometer.

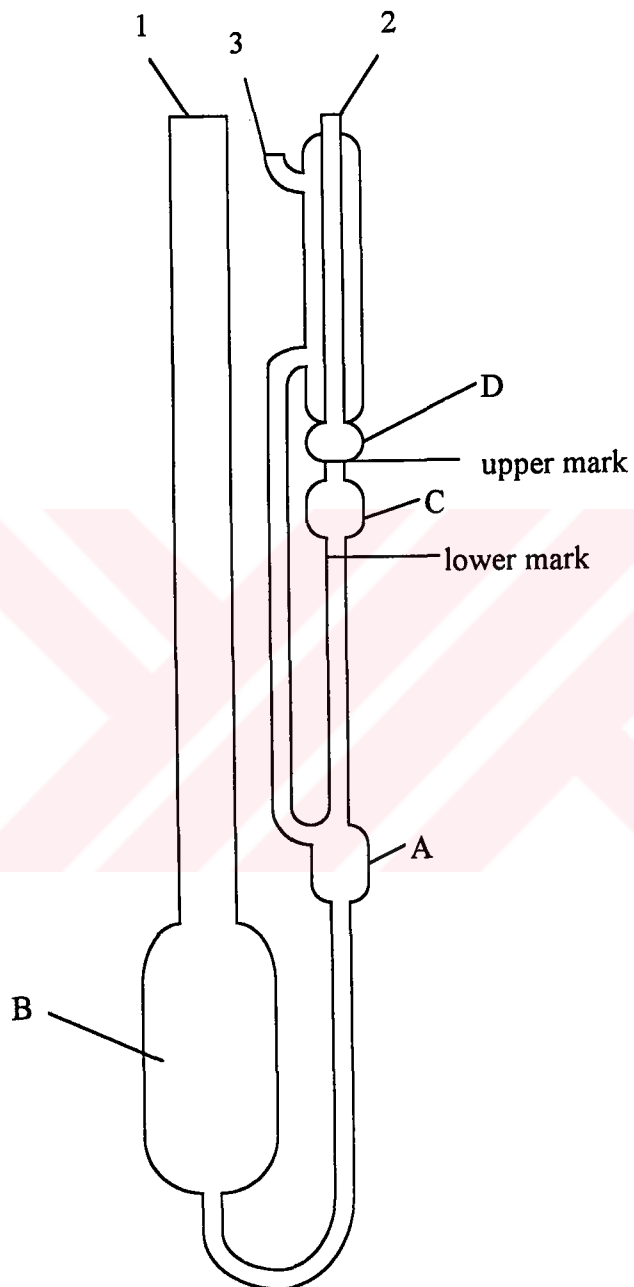


Figure 5.3. Ubbelohde type viscometer. 1: Charge inlet; 2: Opening to air; 3: Close / Open tube; A : Drain bulb; B : Reservoir; C : Measure bulb; D : Initial head bulb.

5.2.13. Nuclear Magnetic Resonance (NMR)

For tacticity determination, ^1H NMR spectrum of PMMA in CDCl_3 was recorded on a Bruker AC 200L instrument at 200.133 MHz proton frequency, with 3.3 μs pulses and 0.1 s relaxation delay.

5.2.14. Gel Permeation Chromatography (GPC)

Gel permeation chromatographs were obtained on a Waters Instruments (Waters 510 Pump- Waters 410 Refractometer). Stragel HT6E and HR1 columns were used. Tetrahydrofuran served as eluent at 25 °C. The flow rate was 1 ml / min.

5.2.15. Vapor Pressure Osmometry (VPO)

Vapor Pressure Osmometer (VPO) measurements for determining molecular weights up to approximately 25,000 were conducted in a Knauer Instrument. Two syringes for solvent, four syringes for solutions of different concentrations (0.001 Molal - 10 Molal) were used. Operating temperature was adjustable between 25°C and 130°C.

5.3. Experimental Procedure

5.3.1. Preparation of Polymer Gels

5.3.1.1. Preparation of Polyacrylamide and Poly(acrylamide-co-acrylic acid) Gels

The polyacrylamide gels were prepared by free-radical cross-linking copolymerization of acrylamide with a small amount of N,N'-methylenebis(acrylamide) (MBA) in aqueous solution. Acrylic acid (AAc) was used as the ionizable comonomer. Ammonium peroxodisulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TEMED) were, respectively, the initiator and the

accelerator. The reactions were carried out at room temperature ($21 \pm 2^\circ\text{C}$) and the gels were prepared according to the following method [34]:

5 g of the monomer mixture (AAm and AAc), 133 mg MBA and 40 mg APS were dissolved in double distilled water to give a total volume of 100 ml. To eliminate oxygen from the polymerization system nitrogen was bubbled through the solution for 10 min. After addition of 0.24 ml TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. The gelation took place within 5 min. After 3 hours, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess distilled water for 1 h to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1 % after extraction with water.

Polymerization of acrylamide monomer and production of a gel proceeds by way of a chain reaction. The first step in the polymerization is a reaction between ammonium peroxodisulfate and TEMED in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an acrylamide or N,N'-methylenebis(acrylamide) monomer; in the process the unpaired electron is transferred to the acrylamide unit, so that it in turn becomes reactive. As the chain of acrylamide units grows, the active site shifts to the free end. Another monomer can therefore be attached and activated in the same way. The polymer can continue growing indefinitely (or until the supply of monomer is exhausted), with the active center being continually shifted to the free end of the chain. A N,N'-methylenebis(acrylamide) molecule can be incorporated into two growing chains simultaneously and forms a permanent link between them. Hence the presence of N,N'-methylenebis(acrylamide) leads to the formation of cross-links between chains. With an abundance of cross-links the polymer of a gel has a topologically complex configuration, with loops, branches and inter connections[40]. The polymerization mechanism can be seen in Figure 5.4.

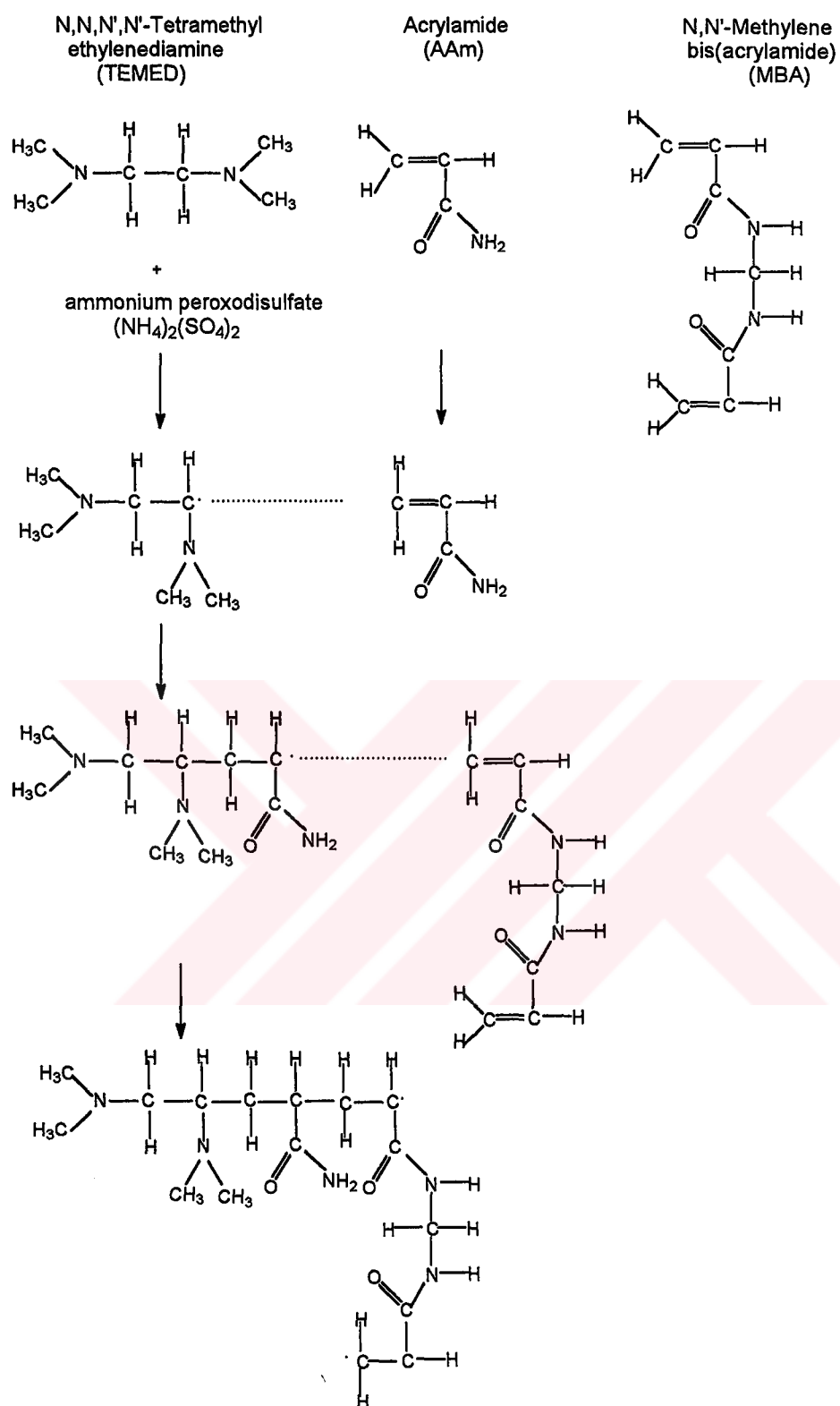


Figure 5.4. Formation of polyacrylamide gels[40].

5.3.1.2 Preparation of Hydrolyzed Polyacrylamide Gels

Non-ionic Polyacrylamide (PAAm) gels were prepared according to the procedure above (section 5.3.1.1.) without using any ionizable comonomer. To convert the non-ionic PAAm gels into ionic (hydrolyzed) gels, they were placed in aqueous solutions of sodium hydroxide (NaOH) with a pH of 10.7 and 12 [56]. After predetermined hydrolysis times, the gels were washed with distilled water for several times until neutral pH in the external solution was obtained. Figure 5.5 shows the simple representation of hydrolysis process.

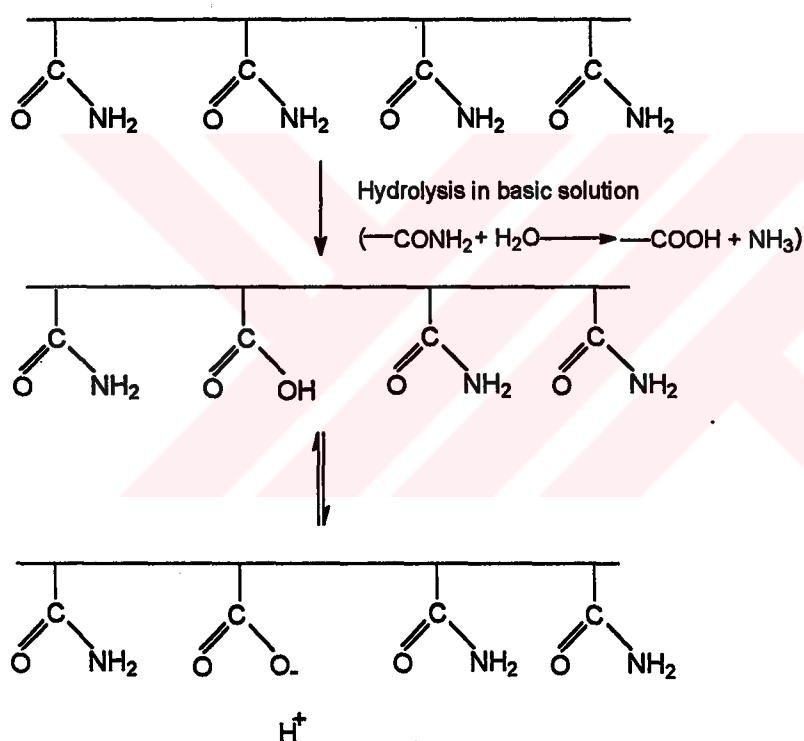


Figure 5.5. Simple representation of hydrolysis process[40].

5.3.1.3. Preparation of Poly(N-isopropyl acrylamide) Gels by Solution and Inverse Suspension Polymerization Techniques

Poly(N-isopropyl acrylamide) (PNIPA) gels were prepared by free radical cross-linking copolymerization of the monomer N-isopropyl acrylamide (NIPA) with a small amount of the cross-linker N,N'-methylenebis(acrylamide) (MBA) in aqueous solutions. The gels were prepared by solution and inverse suspension polymerization techniques as follows [57]:

5.3.1.3.i. Solution Polymerization

8.0 g of the monomer mixture (NIPA and MBA) and 80 mg of APS were dissolved in double distilled water to give a total volume of 100 ml. The solution was then purged with nitrogen gas for 10 min to eliminate dissolved oxygen in the system. After addition of 0.24 ml of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. After 2 hours of polymerization at a predetermined temperature, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of water to wash out any unreacted monomers and initiators.

5.3.1.3.ii. Inverse Suspension Polymerization

Copolymerization was conducted in a 500 ml round bottom, four-neck flask, fitted with a mechanical stirrer, nitrogen inlet, and pipette outlet. Clean PNIPA gel beads were prepared without using an external emulsifier in a water insoluble continuous phase. Paraffin oil was used as the continuous phase as reported by Park and Hoffman[58]. 200 ml of paraffin oil were first introduced into the reactor and stirred at 100 rpm under nitrogen atmosphere. 4.03 g of the monomer mixture (NIPA and MBA) and the initiator APS (40 mg) were dissolved in distilled water (20 ml) and then, N₂ was bubbled through the solution for 10 minutes. This solution was transferred into the reactor and, after 1 min, TEMED (0.12 ml) was added to the mixture to initiate the polymerization. The reaction was allowed to proceed for 3 h. The reactions were carried out at three different temperatures, namely at 4, 10, and

25°C. After polymerization, the beads were separated from the oil phase and washed several times with acetone and water. The diameter of the hydrogel beads in the swollen state ranged from 0.25 mm to 2.8 mm. The particles were sieved using ASTM sieves and those of selected fractions were used for further experiments.

5.3.2. Preparation of Linear Polyacrylamide

Linear polyacrylamide (PAAm) samples were prepared according to two different polymerization methods [59].

To obtain PAAm's of molecular weights ranging from 2.5×10^4 to 1×10^5 g/mol; 7 g AAm, 0.54 g potassium persulfate (KPS), 0.136 g sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), 0.168 g sodium bicarbonate (NaHCO_3), and 16 ml isopropyl alcohol were dissolved in 200 ml distilled water. Polymerization was conducted at 40°C for 2 hours under nitrogen atmosphere. The conversion to polymer was 95%. The polyacrylamide was fractionated into 21 fractions in water-methanol mixture at 30°C by the fractional precipitation technique[60]. 2nd, 5th, 18th fractions with $10^4 M_w = 10, 6, \text{ and } 2.5$ g/mol, respectively, were used as polymer samples in swelling experiments.

To obtain lower molecular weight PAAm's; 7 g AAm, 0.21 g thioglycolic acid, 0.12 g 2,2'-azobisisobutyronitrile (AIBN) and 20 ml THF were placed in a 50 ml flask[61]. Polymerization was carried out at 60°C for 10 min. under nitrogen atmosphere. The resulting polymer was diluted with water and precipitated in methanol. The conversion was 78%. The PAAm was fractionated into 10 fractions. 3rd, 6th, and 10th fractions with $10^4 M_w = 1, 0.5 \text{ and } 0.15$ g/mol, respectively were used in the swelling experiments.

5.4. Characterization Methods

5.4.1. Extraction of Uncross-linked Material

Extraction of the polyacrylamide (PAAm) and poly(N-isopropyl acrylamide) (PNIPA) gels resulted in the removal of soluble, linear material. Samples of each gel

were kept in a large excess of water for two weeks. During the extraction process the solvent was refreshed at least three times. Then the excess extraction solvent was evaporated in rotary evaporator at 40°C in vacuum, and the resultant solution was precipitated in methanol. It was found that the sol fraction in the gels is less than 0.1% after extraction. The calculations of soluble fractions are given in Appendix A.

5.4.2. Post-treatment of gel

The prepared gels were divided into two parts. The first part of the gel samples, which we shall call here after “gel after synthesis”, was subjected to swelling experiments without treatment. The second part was immersed in a large excess of distilled water to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1% after extraction with water. Then, the equilibrium swollen gels in water, called “pre-swollen gels”, were used for swelling experiments.

It is to be noted that the impurities in the gel samples after synthesis may influence their swelling behavior. In order to check this point, part of the pre-swollen gels was successively washed with acetone-water mixtures containing increasing amounts of acetone and, finally, with pure acetone. The gels were then dried in vacuum at room temperature. Using this solvent exchange procedure, the good solvent water in the pre-swollen gels was gradually replaced by the non-solvent acetone. Thus, the gel was transferred from a rubbery to the glassy state without the appearance of heterogeneities due to microsyneresis. It was found that the equilibrium swelling ratio of these “dry” gels is the same as that of the corresponding “gel after synthesis”. Therefore, we conclude that the impurities in the gel samples after synthesis do not affect their swelling behavior[62].

5.4.3. Swelling Measurements

Polyacrylamide (PAAm) gel samples were immersed in vials (100 ml) filled with pure water and poly(ethylene glycol)-water solutions. The volume of the solution in the vial was much larger than the gel volume so that the concentration of the solution was practically unchanged. The vials were set in a temperature-

controlled bath at $25 \pm 0.1^\circ\text{C}$. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions for at least one week. Two different methods were used to measure the equilibrium swelling ratio of the gels, V/V_0 , where V and V_0 are the volumes of gel at equilibrium and reference conditions, respectively. First, the diameter of the gels was measured by a calibrated digital compass and their swelling ratio was calculated as:

$$V / V_0 = (D / D_0)^3 \quad (5.1)$$

where D and D_0 are the diameter of the gels after equilibrium swelling and after synthesis, respectively. Second, the swelling ratio was determined by weighing the specimens in the swollen and dry states. In order to dry the gel samples, they were first swollen in pure water and then successively washed with solutions whose composition were changed gradually from water to pure acetone. This solvent exchange process was used to facilitate final drying of the gel samples. The collapsed samples after the treatment with acetone as a final solvent were dried in a vacuum at 60°C to constant weight. The swelling ratio was calculated as:

$$V / V_0 = v_2^0 \left(1 + \frac{(q_w - 1) \rho}{d_1} \right) \quad (5.2)$$

where v_2^0 is the volume fraction of the polymer network after preparation, q_w is the ratio of the weights of the network in the swollen state and the dry state, and ρ and d_1 are the densities of PAAm and PEG solution, respectively. Assuming additivity of the volumes of water, $d_w = 1\text{g/ml}$, and PEG, $d_{\text{PEG}} = 1.1\text{g/ml}$, and using the values $v_2^0 = 0.035$, $\rho = 1.42\text{g/ml}$, the swelling ratios calculated using Equations (5.1) and (5.2) were found to be in good agreement. Each swelling ratio reported in this thesis is an average of at least two separate measurements performed parallel using both methods; standart deviations of the measured swelling ratios were less than 10 and 5% of the mean for swollen and collapsed gels, respectively.

The calculations of swelling ratio, V/V_0 by two different methods are given in the Appendix B.

The same swelling measurements were performed for poly(N-isopropyl acrylamide) gels which were immersed in vials filled with water and aqueous protein solutions, respectively.

5.4.4. Penetration Measurements

The poly(ethylene glycol) (PEG) concentration inside the gel samples was measured by refractometry using an Abbe refractometer at 20°C as follows. After removing the gel samples from the aqueous solutions of PEG, their surfaces were washed quickly with pure water and then the PEG chains inside the gels were extracted using distilled water as an the extraction solvent at room temperature. Usually, for gel samples of about 3 ml in volume, a total amount of 30 ml of water was used for the extraction experiments. Each extraction process took one week, during which the solvent was refreshed at least three times until the PEG concentration in the solution decreases to 1/10 of the initial value. At this PEG concentration level, the amount of PEG inside the gel that cannot be leached into the solution phase causes a maximum error in the final results of less than 4%. The amount of extracted PEG was measured by refractometry using calibration curves prepared for each PEG sample. All measurements were performed in duplicate; standart deviations of the measured PEG distributions were generally less than 5% of the mean.

The calculations of penetration measurement are given in the appendix C.

5.4.5. Protein Concentrating Experiments

Protein concentrating experiments were carried out in test tubes containing dilute protein solutions. 0.5 g of poly(N-isopropyl acrylamide) (PNIPA) gels were first added into the test tubes and they were allowed to swell until about half of the volume of the external solution was absorbed by the gel (Figure 5.6). Then, the protein content in the outer solution as well as the enzyme activity were determined. Protein concentration in the solution phase was measured by coomassie blue binding method using bovine serum albumin (BSA) as the standart[63,64]. Enzyme penicillin

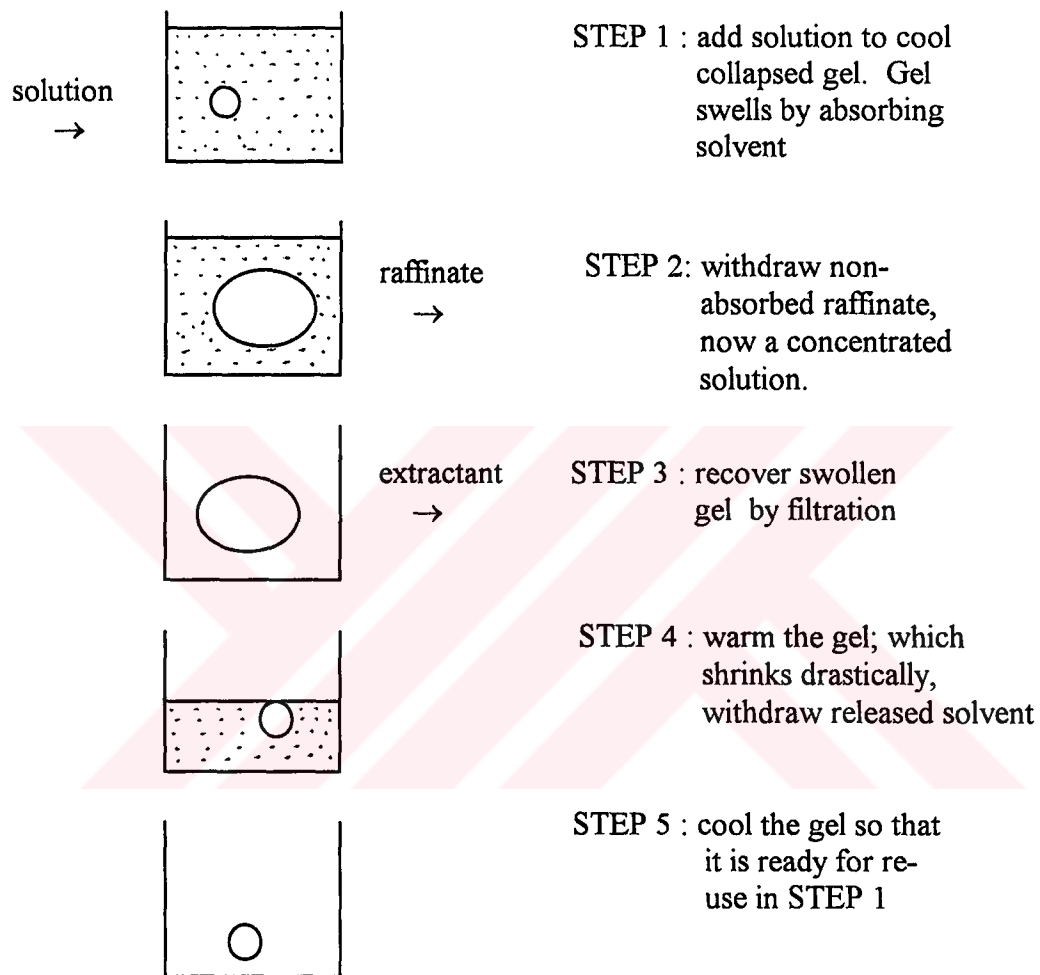


Figure 5.6. Schematic representation of protein concentration by using poly(N-isopropyl acrylamide) gels

G acylase (PGA) activity was measured by p-dimethylamino benzaldehyde (PDAB) method[65]. One unit of enzyme activity is defined as the amount of enzyme required to produce 1 μmol 6-aminopenicillanic acid (6-APA) per minute at 40°C and pH = 8.0 from 15 mM PGA in 50 mM phosphate buffer. Swollen gels after the experiments were collapsed at 55°C by incubating them for 60 min and then re-used in the separation process.

The effectiveness of the protein separation can be quantified an efficiency, η^* which is defined as the actual increase in protein concentration divided by the increase expected from the altered solution volume,[66] i.e.,

$$\eta^* = \frac{c - c_0}{c_0 \left(\frac{V_0}{V^*} - 1 \right)} \times 100 \quad (5.3)$$

where c and V^* are the protein concentration and the volume of the solution phase respectively, and the subscript o denotes the initial values. For example, if half of the feed solution is absorbed by the gel, i.e., $V_0^* / V^* = 2$, and if the raffinate has twice the feed concentration, then the efficiency η^* would be 100%.

The calculation of efficiency are given in appendix D.

5.4.6. Fractional Precipitation Technique

Fractional precipitation in bulk[67] is carried out by adding the nonsolvent to a dilute solution of polymer until a slight turbidity develops at the temperature of fractionation. The precipitated phase is allowed to settle to a coherent layer, and the upper phase is removed. A further increment of precipitant is added to the solution phase to get another fraction (Figure 5.7) [14].

In this thesis, the linear polyacrylamide (PAAm) solution was diluted with water to obtain 0.5 M solution and it was fractionated into several well-fractionated samples in water-methanol mixture at 30°C by fractional precipitation technique[60]. The number-average and weight-average molecular weights of polymer samples were determined by viscometry and vapor pressure osmometry techniques. The weight-

average molecular weights of polymer samples were calculated using the relationship [68]:

$$[\eta] = 6.31 \times 10^{-3} M_w^{0.8} \quad (5.4)$$

where $[\eta]$ is the intrinsic viscosity of PAAm's measured in water solutions at 25°C. The number average molecular weights (M_n) of PAAm's with $M_w \leq 1 \times 10^4$ g/mol were measured in distilled water at 90°C using Knauer vapor pressure osmometer with urea as calibrating substance. The polydispersity index of the polymers M_w/M_n was found to be less than 1.2, showing an effective fractionation. For higher molecular weight PAAm's, because of lack of M_w data, this index is unknown but we can expect that their molecular weight distributions are not very different from low molecular weight PAAm's, because of the fractionation technique.

To study the coil-globule transition of poly(methyl methacrylate) (PMMA) 1 g of linear polymer with $M_w = 2.3 \times 10^6$ and polydispersity index, $M_w / M_n = 1.92$ was dissolved in toluene to produce 0.1 wt% solution and fractionation was effected at 25°C by addition of methanol[69]. The first fraction (0.310 g) is designated as PMMA-1. A portion (0.150 g) of this fraction is dissolved in toluene to produce 0.027 wt-% solution and fractionation again with similar procedure. 0.040 g PMMA is obtained after this second-stage precipitation. This fraction is called PMMA-2. The characterizations of these samples are given in Table 5.1.

Table 5.1. Specification of poly(methyl methacrylate) samples

Sample	$[\eta]^a$ (dl / g)	$M_w \times 10^{-6}$ (g / mol)	M_w / M_n^b
PMMA-1	6.12	2.57	1.35
PMMA-2	10.5	4.73	1.29

^a in chloroform at 20.0°C

^b by GPC measurement

- A : Mechanical Stirrer
B : Water Bath
C : Flask
D : Dropping Funnel

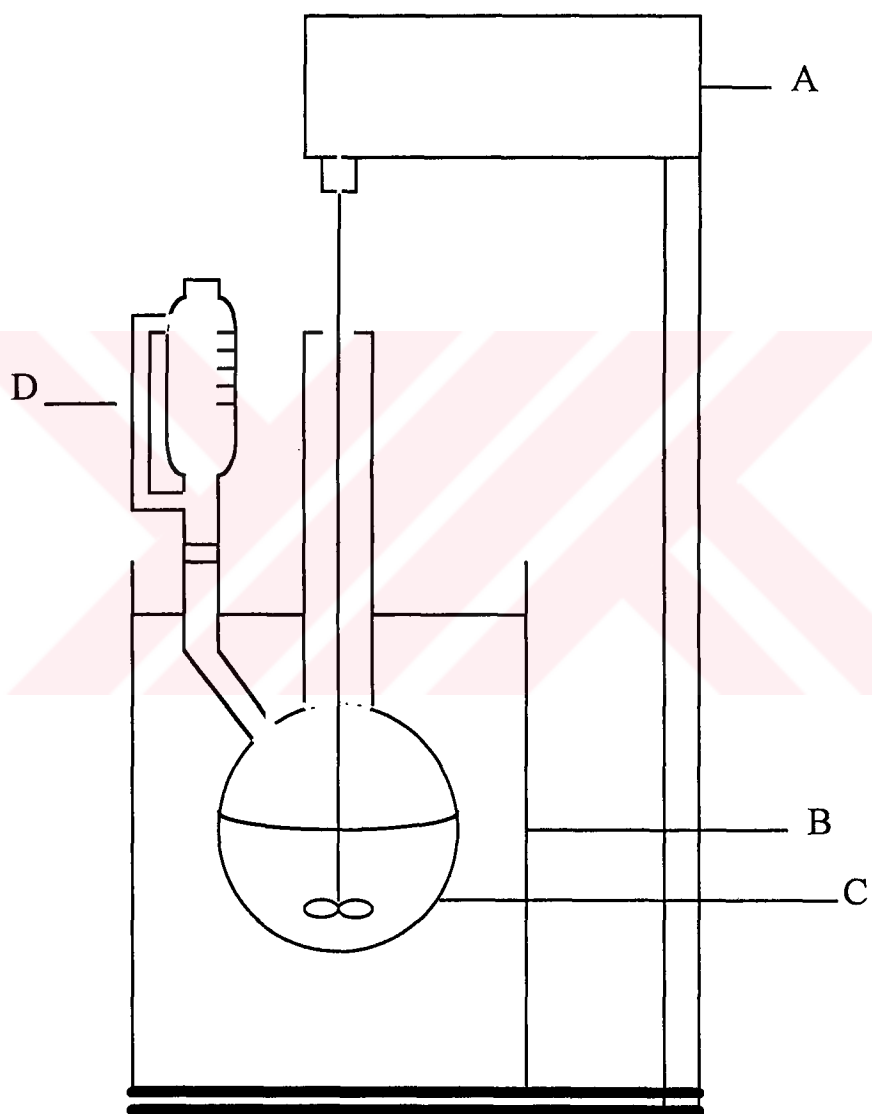


Figure 5.7. Fractional precipitation apparatus

5.4.7. Viscosity Measurements of Poly(methyl methacrylate)

To investigate the transition of linear polymer dimension from θ to collapsed regime, some intrinsic viscosity measurements were performed. Since molecular weight and polydispersity of polymer sample have been shown to play a major role in coil-globule transition, the polymer was fractionated and used in the experiments.

The intrinsic viscosity were calculated using the following relations:

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp} / c) = \lim_{c \rightarrow 0} (\eta_{red}) \quad (5.5)$$

where the specific viscosity $\eta_{sp} = (\eta - \eta_0) / \eta_0$ with η and η_0 being the polymer solution viscosity and the solvent viscosity, respectively, c is the polymer concentration and η_{red} represents the reduced viscosities.

At finite concentrations, in the dilute solution regime

$$\eta_{sp} / c = [\eta] (1 + k_H [\eta] c) \quad (5.6)$$

where k_H is the Huggins interaction coefficient. In our case, as $c (= 2.55 \times 10^{-5} \text{ g/ml})$ is very near infinite dilution (i.e., $k_H [\eta] c \ll 1$), $[\eta] \cong \eta_{sp} / c$.

Intrinsic viscosities $[\eta]$ of poly(methyl methacrylate) solution in *tert*-butyl alcohol + water mixture (97.5/2.5) above and below the θ temperature have been measured using a capillary viscometer[70]. The viscometer was immersed in a constant temperature bath controlled to $\pm 0.01^\circ\text{C}$ over a temperature range $14\text{--}70^\circ\text{C}$. The efflux times for $\sim 1 \text{ ml}$ chloroform and *tert*-butyl alcohol + water mixture were 45.05 s (20.0°C) and 293.28 s (41.5°C), respectively.

PMMA is completely immiscible with water and partially soluble in *tert*-butyl alcohol at high temperature. However, PMMA becomes miscible with the mixed solvent *tert*-butyl alcohol + water in the composition range $0.65 < u_2 < 0.99$. Light scattering measurements showed that second virial coefficient, A_2 , vanishes at 41.5°C . This means that the mixed-solvent *tert*-butyl alcohol + water acts like a single solvent

for PMMA ($M_w = 2.38 \times 10^6$ g/mol) and the temperature 41.5°C can be taken as the θ temperature for the mixed solvent[71].

In our present viscosity studies, the time precision over repeated viscosity measurements of very dilute polymer solutions agreed to better than ± 0.001 s and in worst case ± 0.002 s.

5.4.8. ^1H NMR spectroscopy

For tacticity determination, ^1H NMR spectrum of poly(methyl methacrylate) (PMMA) in deuterated chloroform (CDCl_3) was recorded on a Bruker AC 200L instrument. It can be seen from Figure 5.8 that the three peaks which appear at highest field were used to estimate triad tacticities.

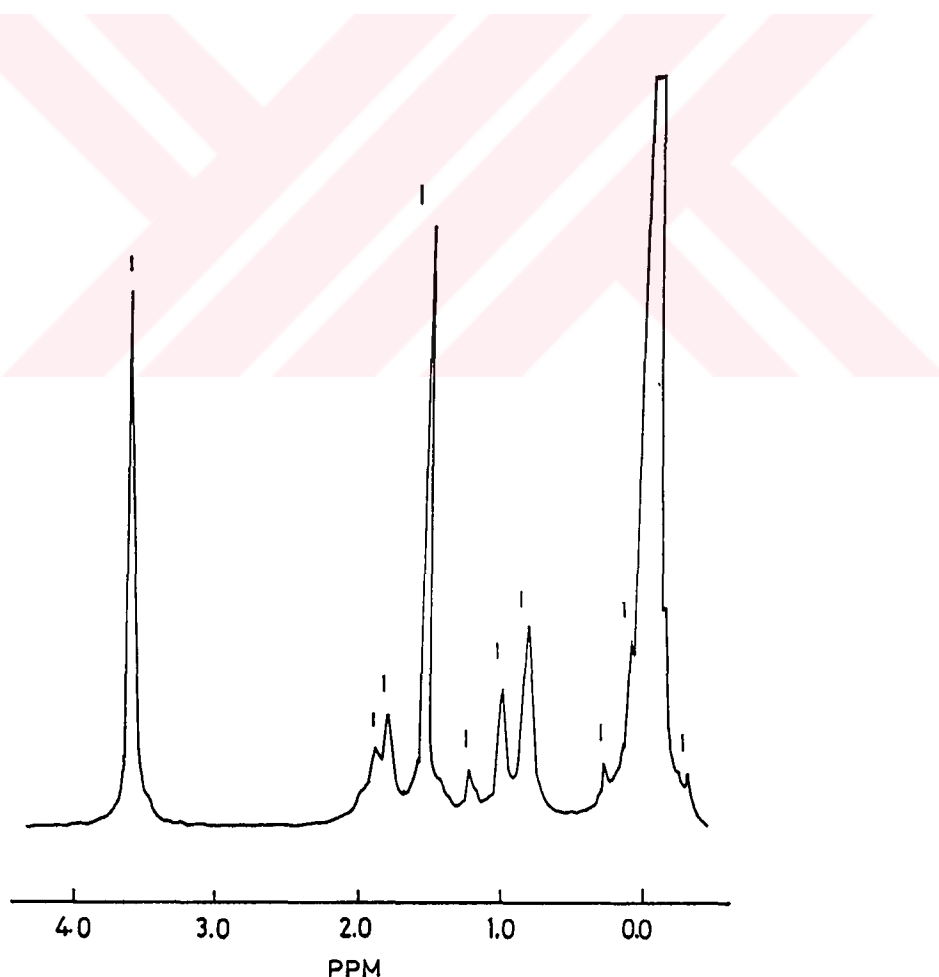


Figure 5.8. ^1H NMR spectrum of poly(methyl methacrylate), (PMMA-2)

The bands at 0.85, 1.00, and 1.25 ppm represent the resonance of syndiotactic, atactic and isotactic methyl groups. The area under each of these three peaks corresponds to the amount of each triad present in the polymer chain. The data is calculated with this method and included in Table 5.2 [72]. The β -methylene proton of PMMA resonances between 1.4 to 2.4 ppm.

The major intensity peak at 1.55 ppm was assigned to the rrr quartet of the predominantly syndiotactic sample. The peak area ratios which illustrate long range syndiotacticity tendency were determined as 1.0 / 0.55 for syndiotactic tetrads, rrr (1.55 ppm), mrr (1.80 ppm) and rmr (1.88 ppm) [16,73].

Table 5.2. Tacticity and long range tacticity determined from ^1H NMR

	triad ^a	tacticity	p(r) or p(m) ^b
PMMA-2	rr	60.2	0.775
	mr	33.9	
	mm	5.9	0.243
		100	
	peak area ratio		
	mrr ^c	0.55	
	rrr	1.00	

^a rr refers to the percent syndiotriads, mr to atactic triads and mm to isotriads.

^b p(r) is the probability of adding a monomer to form a racemic diad, independent of the configuration of the previously added monomer units and p(m) is the probability of adding a meso unit.

^c rrr refers long range tacticity

5.4.9. Morphology

In polymer science, the term morphology generally refers to form and organization on a size scale above the atomic arrangement but smaller than the size and shape of fillers and additives and the size, distribution and association of the structural units within the nanostructure. Microscopy is the study of the fine structure and the morphology of objects with the use of optical, transmission electron and scanning electron microscopes [74].

For the investigation of the morphology of the sample, scanning electron microscope (SEM) was used. The sample was prepared for scanning electron microscopy by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 Angstroms.

The cylindrical hydrogel sample swollen in water was first evacuated for a day at a pressure below 133 Pa in order to sublime water directly from ice at -15°C . By this treatment the structural deformation of the hydrogel network due to surface tension was avoided. The gel sample was then coated with gold and micrographs of polyacrylamide gel was obtained by using a JEOL JXA-840A scanning electron microscope.

CHAPTER 6

RESULTS and DISCUSSION

6.1. Volume Phase Transition of Polyacrylamide Gels in Linear Poly(ethylene glycol) Solutions

6.1.1. Swelling Behavior of Non-Ionic Polyacrylamide Gels in Poly(ethylene glycol) Solutions

Polyacrylamide gels (PAAm) were prepared by free radical cross-linking polymerization as described in section 5.3.1.1. When these gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) solutions with molecular weight ranging from 300 to 20000 g/mol, a decrease in volume was observed. The variation of the degree of swelling of the non-ionic PAAm gel, V/V_0 , with the volume fraction of PEG in the external solution, ϕ , is shown in Figure 6.1. The molecular weights of PEG used were between 300 and 6000 g/mol. For high molecular weights of PEGs, measurements at high polymer concentrations could not be carried out because they were not soluble. Experimental data are shown as symbols. The dotted curves were calculated using the Flory-Huggins theory as discussed in section 3.2. The PAAm gel without any ionizable groups exhibits a continuous change in the swelling volume over the entire concentration and the molecular weight ranges. This behavior is in contrast to poly(N-isopropyl acrylamide) gels (PNIPA gels) which undergo a discontinuous phase transition at PEG molecular weights of 200 and 1000 [75]. Figure 6.1 also shows that, as the PEG concentration outside the gel phase increases, the volume of the gel decreases. Furthermore, at high PEG molecular weights, the swelling ratio becomes rather insensitive to the molecular weight of the linear polymer. This feature is better seen in Figure 6.2 which illustrates the dependence of the swelling ratio on the molecular weight of PEG for fixed concentration of PEG in

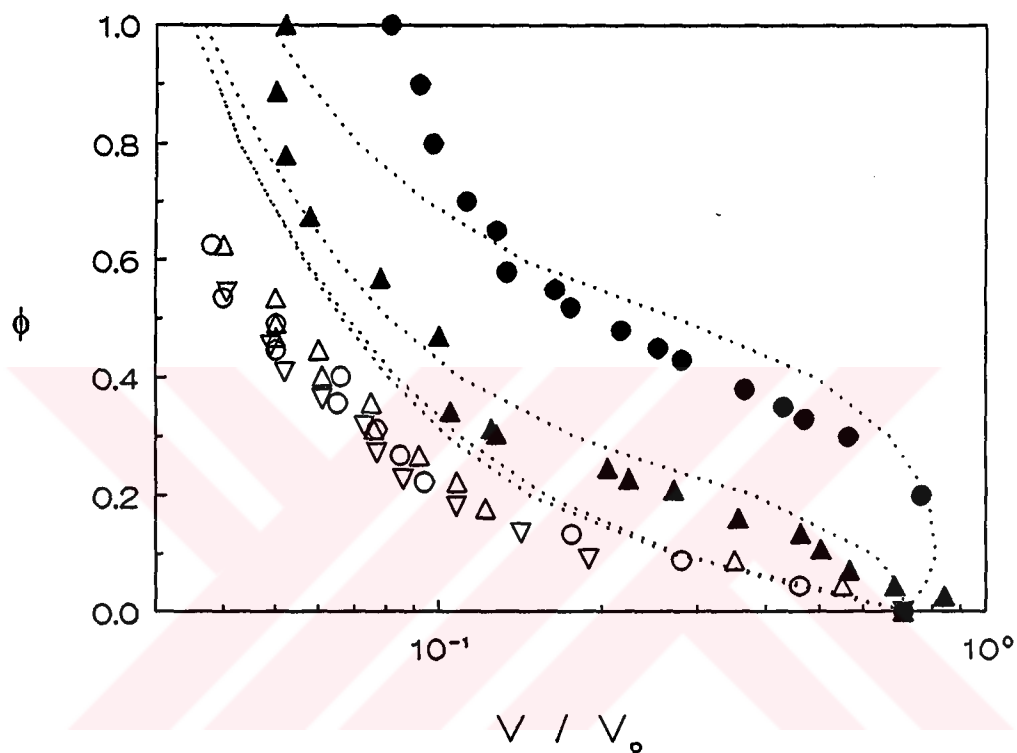


Figure 6.1. Variation of the swelling ratio V/V_0 of the non-ionic PAAm gel with the concentration of PEG in the outer solution. Each PEG concentration is given as volume fraction in the solution phase ϕ . PEG300 ($\bullet$); PEG600 ($\blacktriangle$); PEG1540 (Δ); PEG2000 ($\circ$); and PEG6000 (∇). The curves were calculated using Eqns.(3.17-3.20) for the molecular weights 300(1); 600(2); and 2000-20000 g/mol (3).

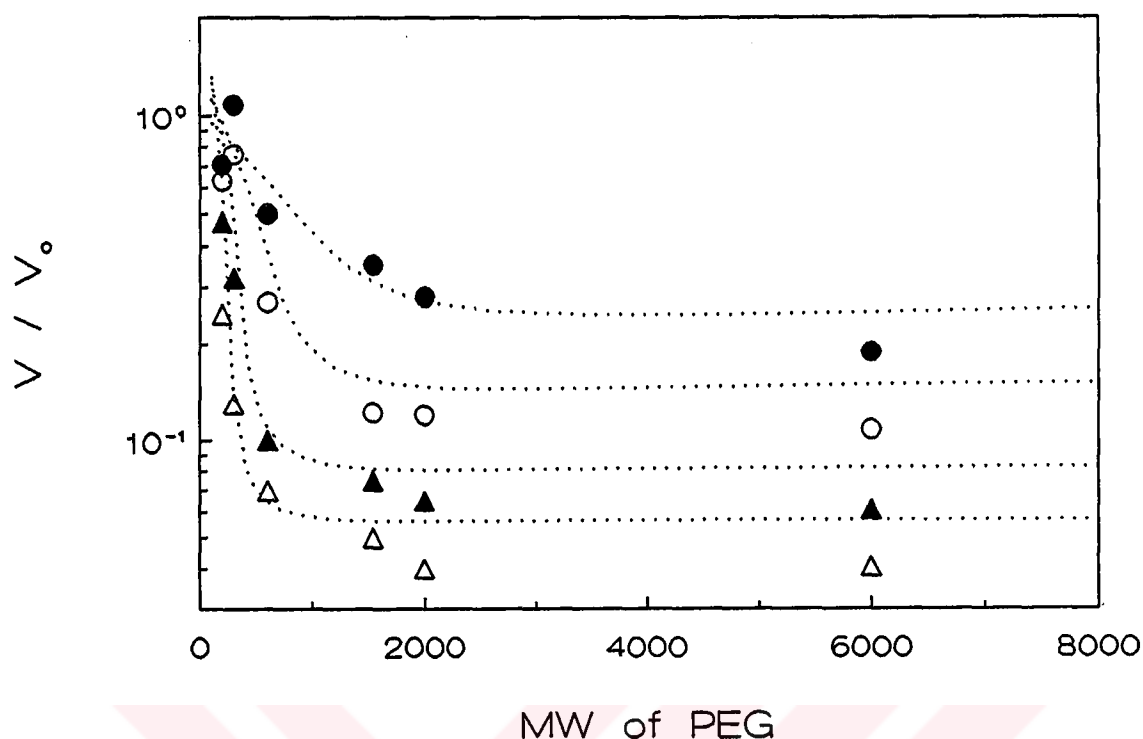


Figure 6.2. Variation of the swelling ratio V/V_0 of the non-ionic PAAm gel with the molecular weight of PEG. The volume fraction of PEG in the outer solution = 0.10 ($\bullet$); 0.20 ($\circ$); 0.40 ($\blacktriangle$); and 0.60 ($\triangle$). The curves were calculated using Eqns.(3.17-3.20).

the external solution. For molecular weights of PEG higher than 2000 g/mol, the swelling ratio is independent of the molecular weight within the limits of experimental error.

In Figure 6.3, the PEG distribution inside and outside the gel phase is shown as a function of the PEG concentration in the solution. The concentration of PEG inside the gel samples was measured by refractometry as discussed in section 5.4.4. In the graph, v_3 / ϕ represents the ratio of the volume fraction of PEG in the gel phase (v_3) to that in the solution phase (ϕ); thus $v_3 / \phi = 1$ means that the PEG concentration inside the gel is equal to that in the solution whereas $v_3 / \phi = 0$ means that the gel excludes all the PEG molecules. Figure 6.3 indicates that a large amount of PEG can penetrate into the gel if the PEG chains are short enough ($M_w = 300$ -600 g/mol). Increasing the volume fraction, ϕ , or molecular weight of PEG in solution decreases the v_3 / ϕ ratio and it approaches zero within experimental accuracy for $M_w = 6000$ g/mol and $\phi > 0.20$. Thus, if the molecular weight of PEG is sufficiently

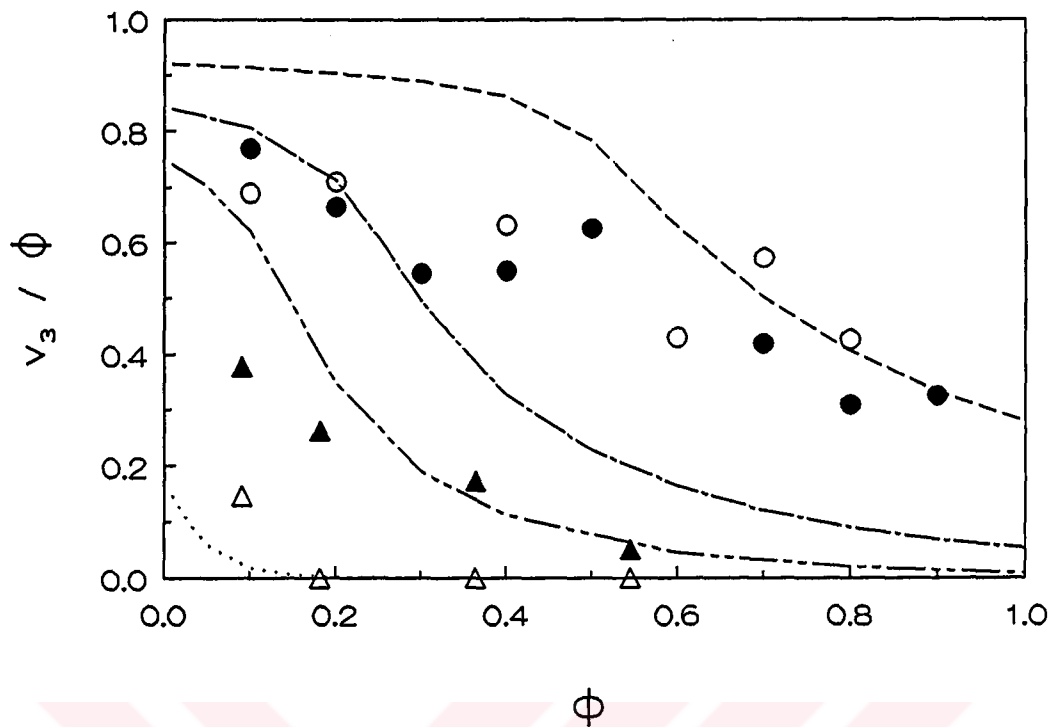


Figure 6.3. Dependence of the PEG distribution inside and outside the gel phase, v_3/ϕ , on the PEG concentration in the solution. PEG300 (●); PEG600 (○); PEG1000 (▲); and PEG6000 (Δ). The curves were calculated using Eqns.(3.17-3.20).

high the linear polymer does not penetrate inside the PAAm network.

6.1.2. Swelling Behavior of Ionic Polyacrylamide Gels in Poly(ethylene glycol) Solutions

Ionic gels were prepared by using acrylic acid as a comonomer in the synthesis of PAAm gels. In Figure 6.4 the swelling ratio of gels containing varying amounts of acrylic acid with respect to the dry copolymers is plotted as a function of the PEG 300 concentration in the outer solution. As expected, the swelling ratio in a given PEG-water mixture increases with increasing acrylic acid content. At low PEG concentrations the PAAm gels are swollen, at high concentrations the gels are collapsed. However, for acrylic acid contents higher than a certain value (28 %) the gels remain in the swollen state over the entire range of the external PEG concentration. For the ionic gels shown in Figure 6.4 with 6-22 % acrylic acid (in the

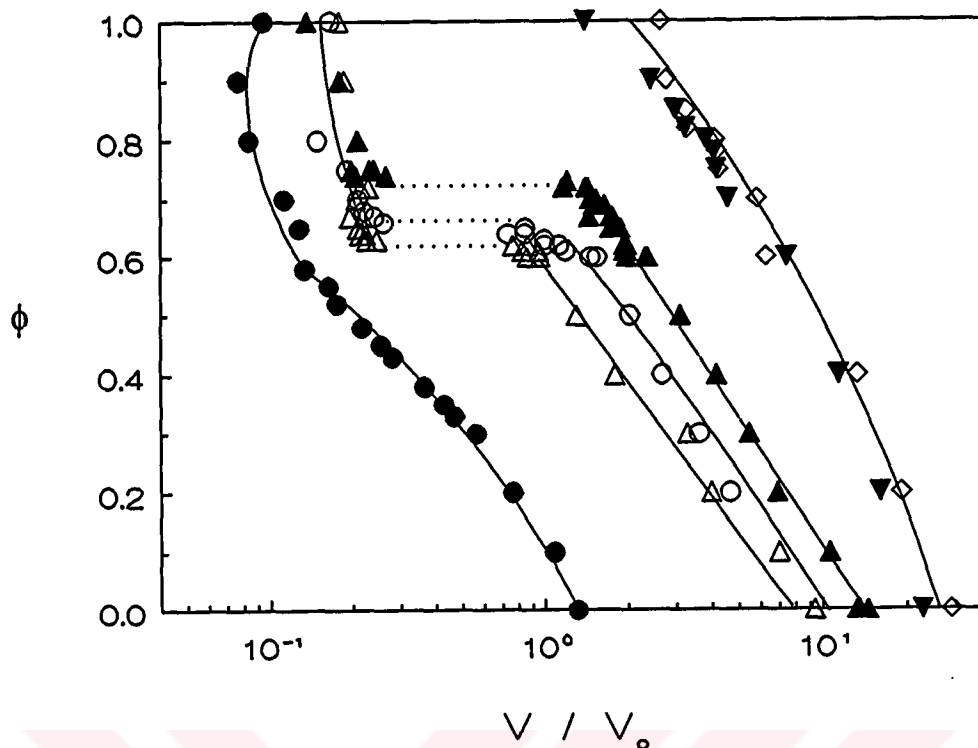


Figure 6.4. Variation of the swelling ratio V/V_0 of ionic PAAm with the concentration of PEG300 in the outer solution. AAc acid content of the dry copolymer = 0($\bullet$); 6(Δ); 13($\circ$); 22($\blacktriangle$); 28($\blacktriangledown$); and 40 w/w% ($\diamond$). The solid curves only show the trend of data.

dry copolymer), the dependence of PEG concentration on the swelling ratio exhibits a discontinuity. In the concentration range marked with horizontal dotted lines, both a swollen and a collapsed state can be observed but never an intermediate state. These findings indicate a first-order transition. The jump of the network volume occurs at the critical volume fraction of PEG ϕ : 0.625, 0.655, and 0.735 for 6, 13, and 22 % acrylic acid, respectively. Thus, the critical value of ϕ at which transition takes place increases with increasing ionic group content of the network. Also, the magnitude of the collapse becomes larger as the ionic group content of the network increases.

Figure 6.5 compares the swelling behavior of ionic and non-ionic gels in PEG 6000 solutions. In the non-ionic gels, the contraction of polymer networks in PEG 6000-water mixture occurs smoothly but it is jumpwise first-order phase transition in ionic gels with the jump at $\phi = 0.26$ for 13 % acrylic acid.

In Figure 6.6a and 6.6b, the swelling ratio of ionic gels containing 13 % of acrylic acid is plotted as a function of the PEG concentration for various PEG

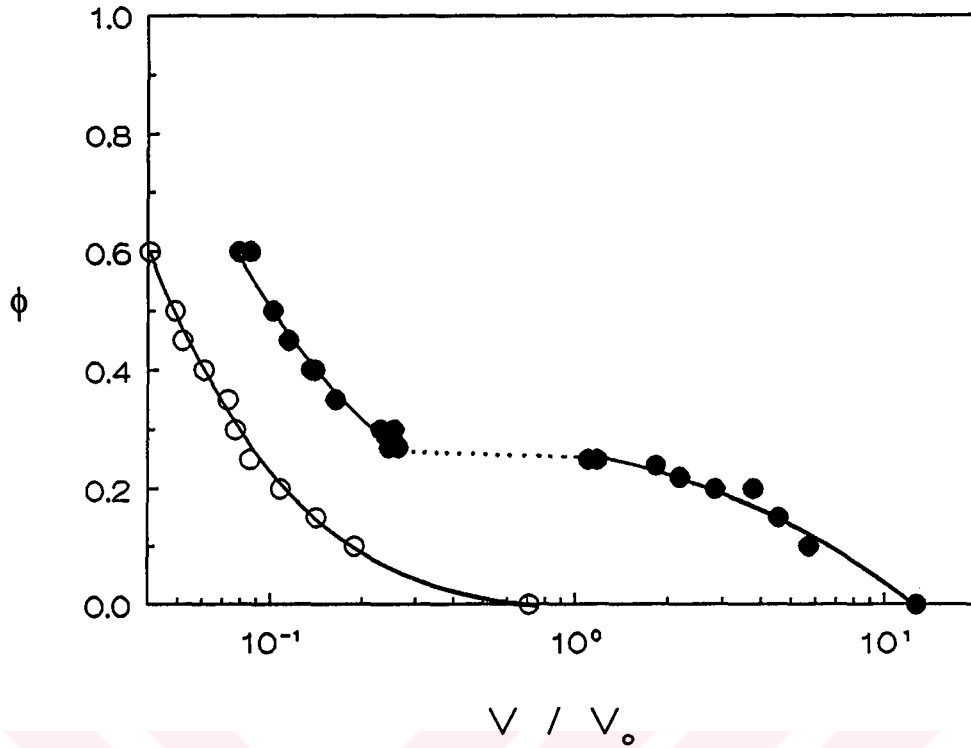


Figure 6.5. Variation of the swelling ratio V/V_0 of PAAm gels with the concentration of PEG 6000 in the outer solution. AAC = 0(o); and 13 w/w% (•).

molecular weights. The critical value of ϕ required for a discontinuous volume collapse is 0.655, 0.45, 0.395, and 0.26, respectively for PEG 300, 1000, 2000, and 6000 (Figure 6.6a). Thus, the critical volume fraction of PEG is shifted towards lower values as the molecular weight of PEG in the outer solution increases. However, in aqueous solutions of PEG with molecular weights higher than 20000 g/mol, or in tetraethylene glycol-water mixtures, the gel changes its volume continuously (Figure 6.6b), indicating that a jumpwise collapse of the gel volume only takes place within a certain molecular weight range of the linear chains.

The distribution of PEG inside and outside the gel phase for the gels shown in Figure 6.6a is given in Figure 6.7. A jumpwise decrease in the content of PEG in the gel phase is observed at the critical ϕ ranges at which the gel shrinks discontinuously.

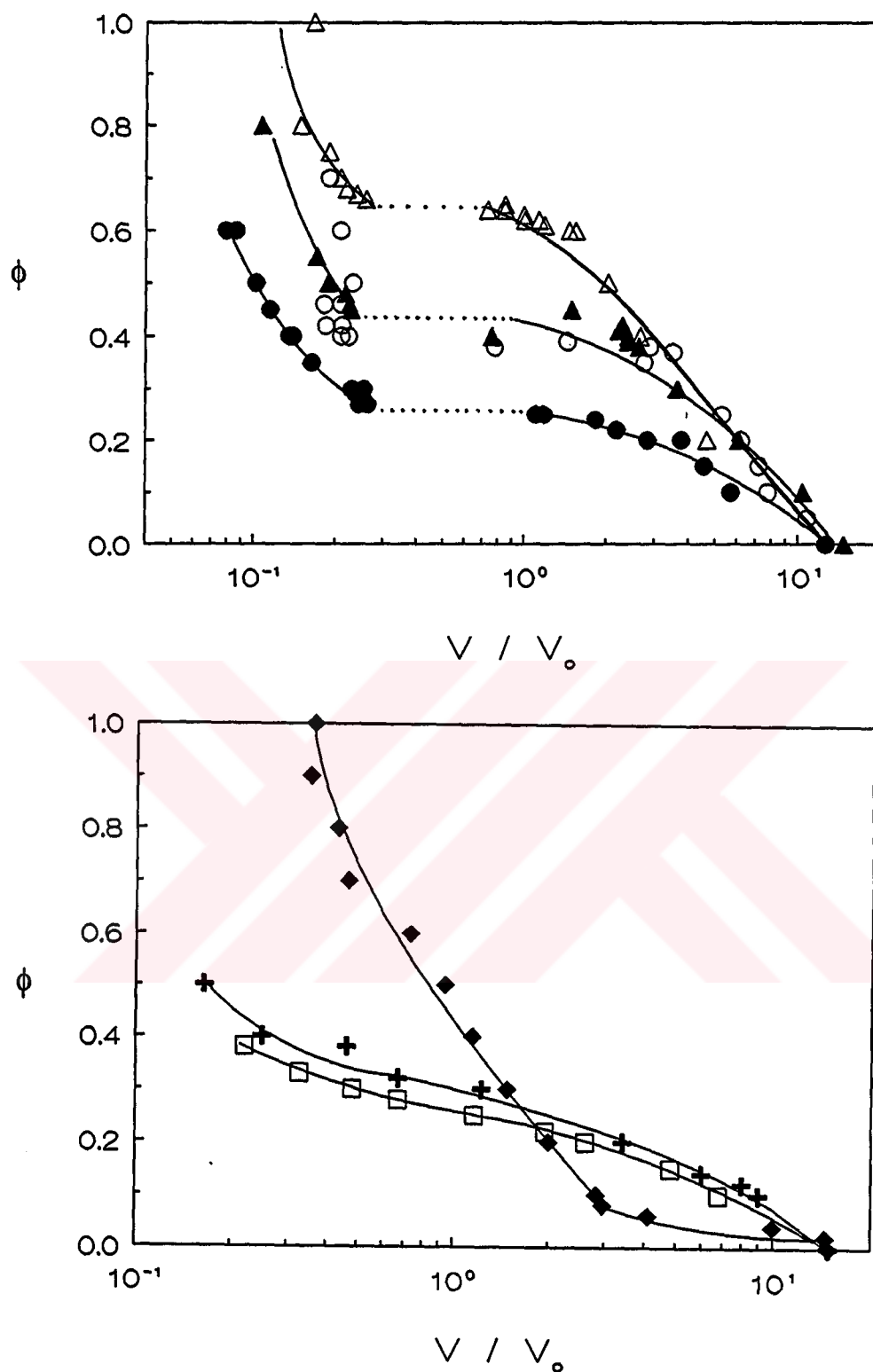


Figure 6.6. Swelling ratio V/V_0 of the ionic PAAm gel with 13 w/w% AAc content shown as functions of the concentration of PEG in the outer solution. The curves only show the trend of data. (a) PEG300 (Δ); PEG1000 ($\blacktriangle$); PEG2000 ($\circ$); and PEG6000 ($\bullet$). (b) TEG ($\blacklozenge$); PEG20000 ($+$); and PEG35000 ($\square$).

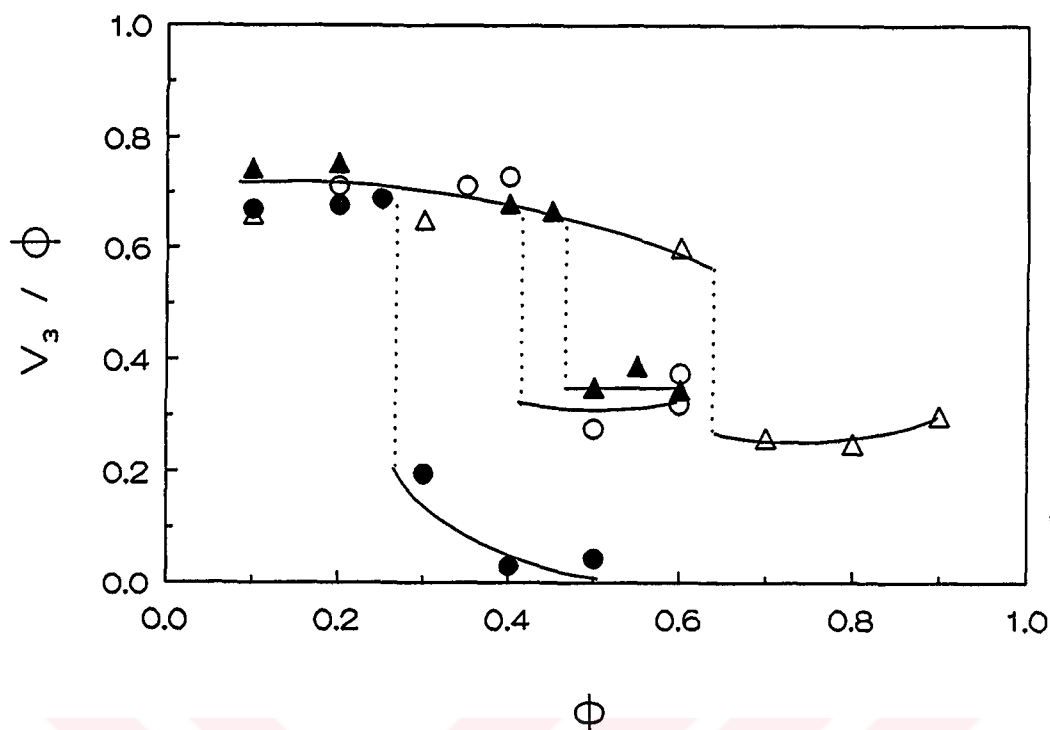


Figure 6.7. Dependence of the PEG distribution inside and outside the ionic PAAm gel with 13 w/w% AAc content, v_3/ϕ , on the PEG concentration in the solution. PEG300 (Δ); PEG1000 ($\blacktriangle$); PEG2000 ($\circ$); PEG6000 ($\bullet$). The curves show the trend of data.

6.1.3. Discussion About the Reasons of Phase Transition in Ionic Polyacrylamide Gels in Poly(ethylene glycol) Solutions

There are two possible reasons for the contraction of PAAm gels immersed in PEG solutions: (1) complex formation between the PAAm and PEG chains, and (2) osmotic deswelling of the gel in the polymer solution. In the first case, a complex between two polymers may form due to hydrogen bonding. Such a complex is expected to be much more hydrophobic than the polymer chains taken separately[76,77]. As a result, increasing PEG concentration in the solution increases the polymer content inside the gel phase so that the network becomes more hydrophobic and it collapses in water solutions. Polycarboxylic acids such as poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAAc) have long been known to form complexes with PEG under appropriate conditions of pH[78-83]. The formation of intermolecular complexes between PMAA gel and PEG is also a well

known phenomenon and results in the collapse of the gel [84]. The complexation results from cooperative hydrogen bonding between long sequences of carboxy groups and ether oxygen atoms at low pH. However, the stability of such complexes decreases sharply with the decrease of the degree of polymerization of PEG chains or with the increase of the pH of the solution. For instance, PEG with molecular weight of 7500 or lower does not form a complex with PAAc [85,86]. Moreover, since the complexation is produced only by carboxylic groups in the undissociated state, it is possible in the low pH region. As it was indicated earlier, even at $\text{pH} = 2$, there is no complexation between PAAc and PEG when the molecular weight of PEG is 1500 or lower [87]. On the other hand, at low pH, the undissociated acid groups can also interact with the amide groups to form PAAm-PAAc complexes through hydrogen bonds [88]. In the present study, the aqueous solutions of PEG exhibited a pH value not less than 6.5. Thus, it is reasonable to assume that the contraction of the gel in PEG solutions is due to the osmotic deswelling of the gel (no complex formation). That assumption is consistent with the observations of the swelling behavior of the ionic gels in PEG solutions of different pH. Figure 6.8 compares the swelling behavior of the ionic gels in PEG 600 solutions. Filled and empty circles represent the results of the swelling measurements carried out at $\text{pH} = 6.5-7$ (without addition of NaOH) and at $\text{pH} = 9$ (in the presence of NaOH), respectively. The critical value of ϕ increases and the magnitude of the collapse becomes larger as the pH of the polymer solution increases. If the complexation were the reason of the polymer collapse, increasing pH would prevent the collapse of the gel due to the excessive osmotic pressure in the swollen gel produced from the dissociation of carboxylic acid groups of the network chains. However, Figure 6.8 shows the opposite behavior.

To interpret the experimental data in the previous section, the classical Flory-Huggins theory of swelling equilibrium was used. However, Flory-Huggins theory does not account for free-volume effects or hydrogen bonding interactions, and thus cannot describe quantitatively the swelling behavior of hydrogels. Although some lattice models have been proposed recently to account for these interactions [89,90], these models are more complex mathematically than the Flory-Huggins theory and require several adjustable parameters to apply to actual systems. In this thesis the Flory-Huggins theory was adopted for a qualitative understanding of the experimental

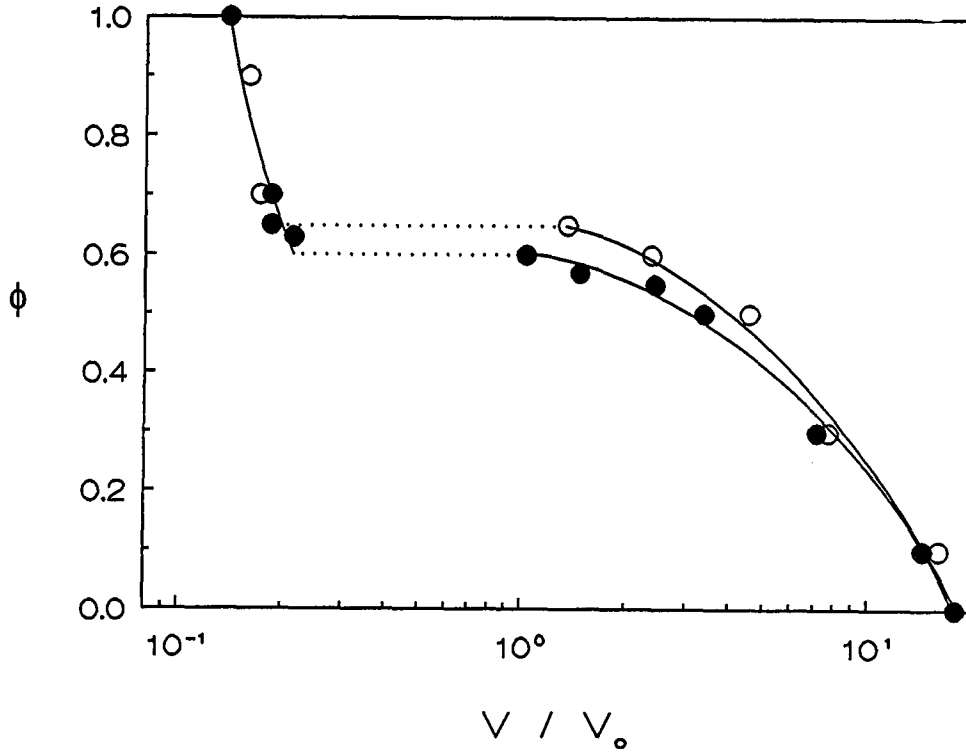


Figure 6.8. Swelling ratio V/V_0 of the ionic PAAm gel with 13 w/w% AAc content shown as functions of the concentration of PEG in the outer solution. pH of the polymer solution = 6.5-7 (●) and 9 (○).

findings. As described in section 3.2 the free energy of swollen network, ΔG , can be written as a sum; $\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i$. By differentiating the free energy with respect to the number of moles of solvent n_1 and polymer molecules n_3 , the excess chemical potentials of the solvent and the polymer in both the gel and solution phases are obtained. The equilibrium volume of the network (v_2) and the solution composition inside the network (v_3) can be found from the equality of the chemical potential inside and outside the network,

$$\Delta\mu_1^{\text{gel}} - \Delta\mu_1^{\text{sol}} = 0 \quad (6.1a)$$

$$\Delta\mu_3^{\text{gel}} - \Delta\mu_3^{\text{sol}} = 0 \quad (6.1b)$$

and the equality of osmotic pressure inside and outside the network.

$$\pi = - (\Delta\mu_1^{\text{gel}} - \Delta\mu_1^{\text{sol}}) / v_1 = 0 \quad (6.1a')$$

The system of equations represented by Equation (6.1) has been solved numerically to calculate the swelling ratio of PAAm gels in aqueous PEG solutions ($V / V_0 = v_2^0 / v_2$) and the ratio of PEG concentrations inside and outside the gel phase (v_3 / ϕ). In appendix F the related computer program was given in details.

For calculations, the values used were $v_2^0 = 0.035$ (estimated assuming additivity of the volumes of water and PAAm, $\rho = 1.42$ g/ml), $\chi_{12} = 0.48$ [91], and $\chi_{13} = 0.45$ [92]. The number of segments in a network chain N was estimated from the swelling ratio of the non-ionic gel in pure water and using Equation (3.17) for the condition $v_3 = 0$ and $\Delta\mu_1^{\text{gel}} = 0$. The value $v_2 = 0.049$ found by experiments yielded $N = 165$. N was held constant at this value in the calculations described here. It was also assumed that y is equal to the degree of polymerization of the PEG chains. The only unknown parameter χ_{23} was taken as a model parameter. The value $\chi_{23} = 0.17$, providing a best fit to the experimental swelling data obtained with non-ionic gels swollen in PEG 300 solutions, was used throughout this study. For ionic gels and for certain values of ϕ , Equation (6.1) is satisfied by three values of both v_2 and v_3 , indicating the coexistence of two gel phases with different conformations and appearance of van der Waals loop in the swelling curves. In these cases, the composition of the gels in coexisting phases was calculated by equating chemical potentials of the network chains in both gel phases.

The dotted curves in Figures 6.1-6.3 were calculated using Equation (6.1). Theoretical V / V_0 and v_3 / ϕ values are in agreement with the experimental data indicating that Equations (3.17), (3.18), (3.19) and (3.20) describe semi-quantitatively the swelling and absorption behavior of the non-ionic PAAm gels in PEG solutions. The Flory-Huggins theory predicts every trend observed by experiments. According to Equation (3.18), increase in concentration of PEG ϕ leads to decreasing chemical potential of the solvent in the outer solution. This causes a lowering the osmotic pressure in the swollen gel and to the shrinkage of the gel. The ratio v_3 / ϕ is always less than unity, i.e. the concentration of PEG chains inside the gel is always lower than in the outer solution. This is due to the loss in conformational entropy of PEG chains penetrating the gel as well as due to the repulsion between network and polymer segments represented by the value χ_{23} . This concentration difference of PEG between the inside and outside the gel leads to an additional osmotic pressure compressing the

network. This effect becomes more pronounced as the concentration or the degree of polymerization of PEG in the external solution increases. If the molecular weight of the PEG is sufficiently high, PEG does not penetrate inside the network and create strong exterior pressure.

Results of calculations for ionic gels are presented in Figure 6.9 and 6.10. The size of ionic gels in the swollen state is much larger than that of a neutral network because of the additional swelling due to the osmotic pressure of counterions. Therefore, PEG chains can penetrate the swollen ionic gels without essential loss in conformational entropy. In Figures 6.9a and 6.9b, ϕ versus V / V_0 and v_3 / ϕ plots are shown for PEG 300-water mixtures and for a series of values of f , which is proportional to the amount of ionizable group incorporated into the network. A discrete first-order phase transition is observed only if f exceeds a critical value. As f increases, the jump in V / V_0 and v_3 / ϕ moves to higher concentrations of linear polymer in the outer solution and the magnitude of the collapse becomes larger, as was found experimentally in the previous section. If f is sufficiently high, the gel remains in the swollen state over the entire range of PEG concentration and the solution compositions inside and outside the gel become practically identical. Calculated results for gels containing a fixed amount of ionic groups are presented in Figures 6.10a and 6.10b. Here, ϕ versus V / V_0 and v_3 / ϕ plots are shown for different PEG molecular weights. The discrete phase transition takes place over a small range of PEG molecular weight. Similar to the ionic-group effect, decreasing molecular weight of PEG shifts the critical concentration to higher values, in qualitative agreement with the experimental data shown in Figures 6.6 and 6.7.

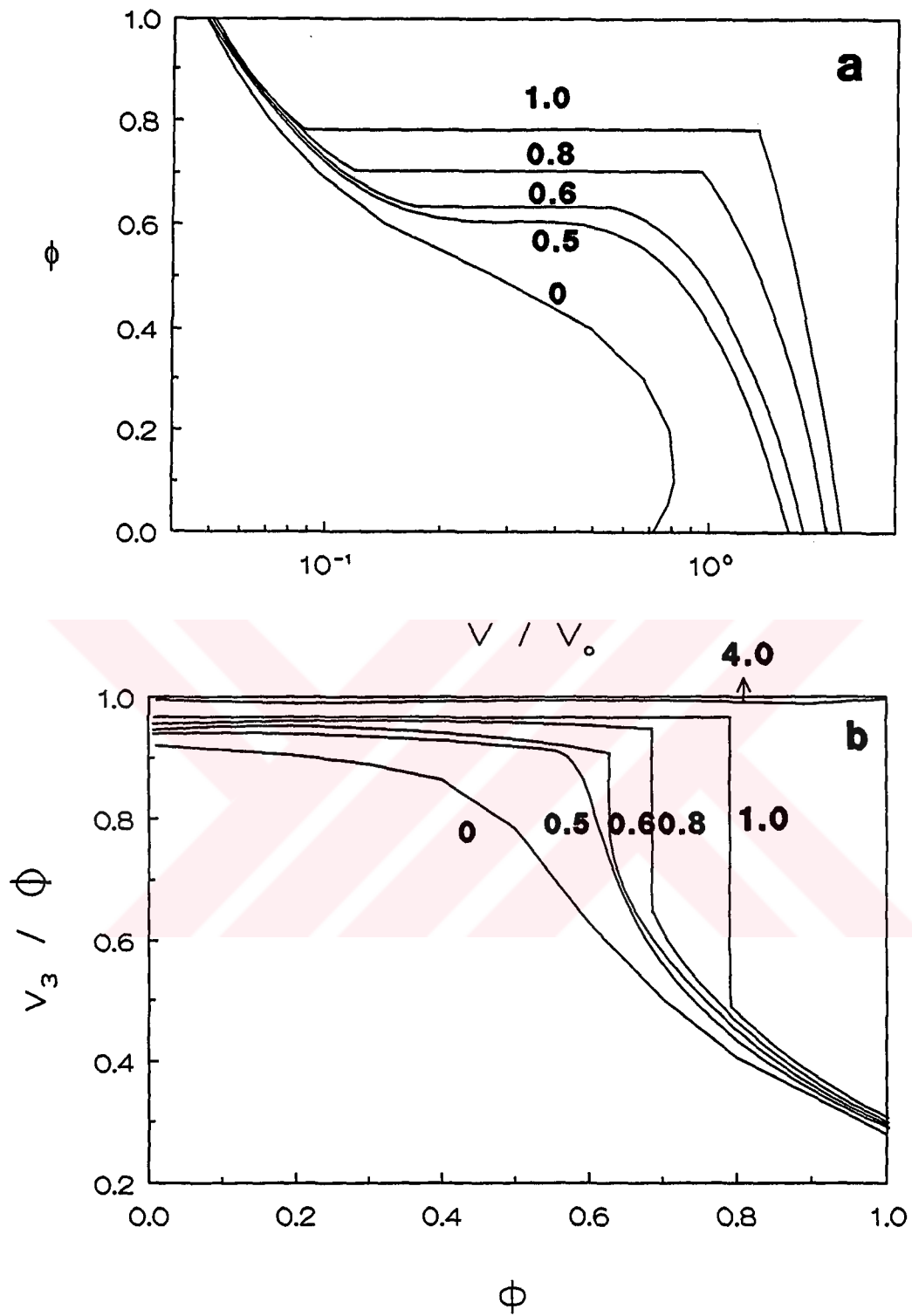


Figure 6.9. PEG 300 concentration versus swelling (a) and penetration ratio plots (b), V/V_0 and v_3/ϕ respectively, for a series of values of f . Calculations from Eqns.(3.17-3.24) for $\gamma = 6.4$.

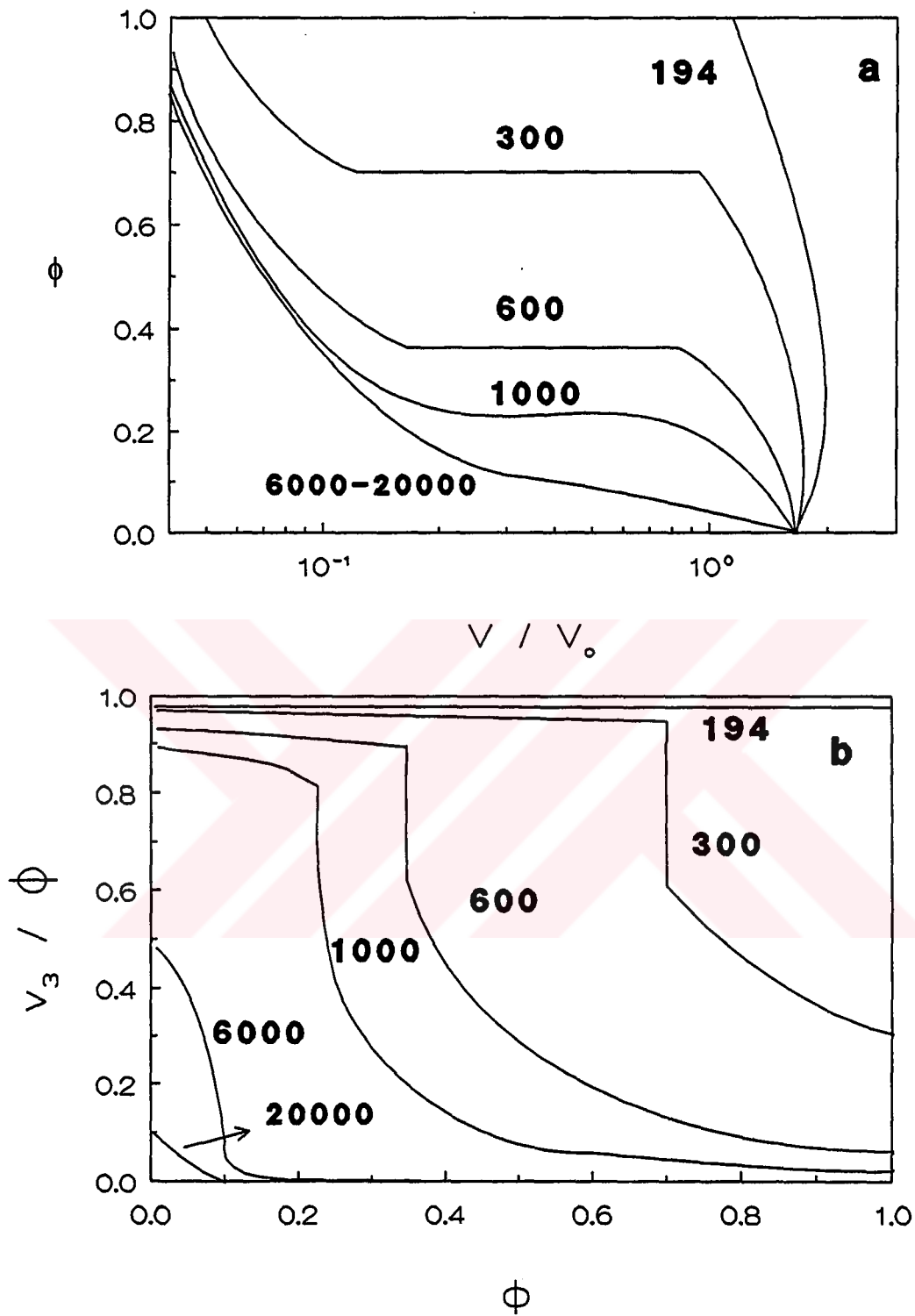


Figure 6.10. Swelling (a) and penetration ratio plots (b), V/V_0 and v_3/ϕ respectively, for an ionic PAAm gel as a functions of PEG concentrations for different PEG molecular weights. Calculations from Eqns.(3.17-3.24) for $f = 0.8$.

6.2. Phase Transition of Hydrolyzed Polyacrylamide Gels in Poly(ethylene glycol) Solutions

As pointed out in the section 6.1.3. complex formation between poly(ethylene glycol) (PEG) and poly(acrylic acid) (PAAc) chains may also be the reason for the polymer collapse. The main aim to study with hydrolyzed PAAm gels is to give an answer to the question which mechanism is operative for the collapse transition of poly(acrylamide-co-acrylic acid) gels in aqueous PEG solutions. As it is well known complexation is produced only by carboxylic acid groups in the undissociated state [84-87]. Therefore, hydrolyzed PAAm gels bearing carboxylate anions were prepared as described in section 5.3.1.2.

Hydrolysis of PAAm gels converts some of the amide groups into the carboxylate anions[40,56,93]. The fractional conversion of the amide groups depends on the time of hydrolysis. It was shown that both the time of hydrolysis, τ , and the pH of the NaOH solution have a decisive influence on the collapse behavior of PAAm gels in acetone-water mixtures. For instance, hydrolysis at a higher pH was reflected in the formation and the extent of the collapse much more distinctly ($\tau^* \sim 10$ days at pH = 12 correspond to $\tau \sim 60$ days at pH = 8-9) [91]. The maximum conversion of the amide groups is reported to be 25%; at pH = 12 this value is observed after 60 days [40].

In Figure 6.11, variation of the equilibrium swelling ratio of the gels in distilled water, V / V_0 , is shown as a function of the time of hydrolysis in aqueous NaOH solution with pH = 10.7. V / V_0 increases rapidly with rising hydrolysis time up to 8 days. This is due to the increasing number of ionic groups on the network chains with increasing hydrolysis time. Thus, since the mobile ion (Na^+) concentration within the ionic network is higher than in the surrounding solution (water), the osmotic pressure that this creates causes more water to enter the network and expand it. As the

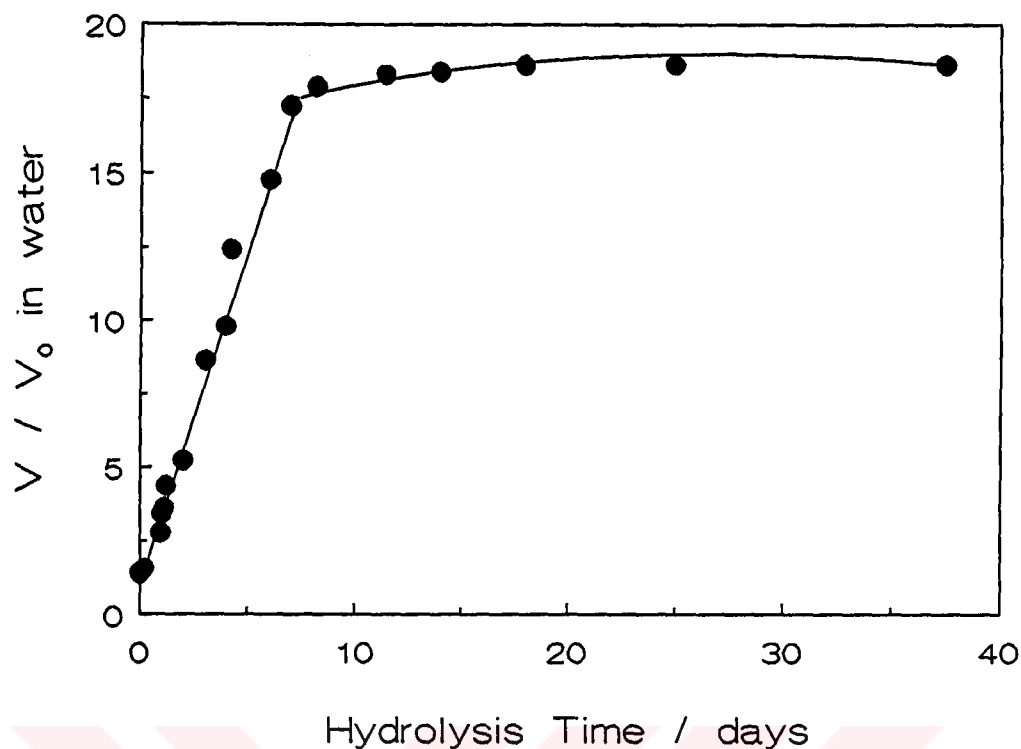


Figure 6.11. Variation of the equilibrium swelling ratio, V/V_0 , of the gels in water with the time of hydrolysis of non-ionic PAAM gels in aqueous NaOH solution (pH = 10.7).

hydrolysis time further increases, V / V_0 slightly increases and, after about 20 days, the swelling ratio becomes rather insensitive to the time of hydrolysis.

The gels isolated at different degrees of hydrolysis were then used for equilibrium swelling experiments in aqueous solutions of PEG of molecular weight of 300. Variation of the equilibrium swelling ratio of the gels, V / V_0 , with the PEG 300 concentration in the external solution is shown in Figure 6.12 and Figure 6.13 for various hydrolysis times. The hydrolysis was done at pH 10.7 (Figure 6.12) and 12 (Figure 6.13). The volume of the gel phase decreases upon increase of the PEG concentration. Starting after one day or two days of hydrolysis at pH = 12 and 10.7, respectively, this decrease becomes discontinuous. The critical value of the PEG concentration at which discrete transition takes place increases and the magnitude of the collapse becomes larger as the time of hydrolysis increases. For prolonged

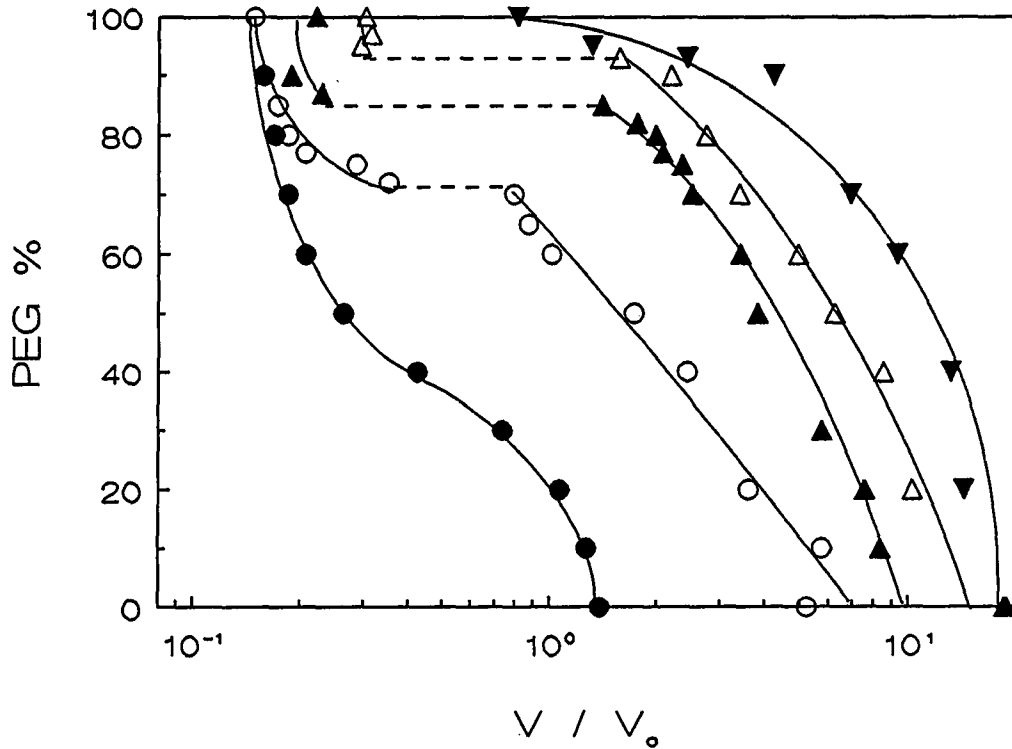


Figure 6.12. Variation of the swelling ratio, V/V_0 , of hydrolyzed PAAm gels with the concentration of PEG 300 in the outer solution. PEG concentrations are in v/v %. pH of NaOH solution used in the hydrolysis is 10.7. Hydrolysis times = 0(●); 2(o); 7(▲); 18(Δ) and 38 days(▼).

hydrolysis times the gel remain in the swollen state (Figure 6.13) or deswell only slightly (Figure 6.12) over the entire range of the external PEG concentration. As a result hydrolyzed PAAm gels also exhibit discrete volume change in response to an infinitesimal change in PEG concentration in the outer solution. If the complexation were the reason for the polymer collapse, dissociated acid groups on the network would prevent the collapse of the gel in PEG solution. For this reason we can conclude that the contraction of the gel in PEG solution is due to the osmotic deswelling of the gel (no complex formation).

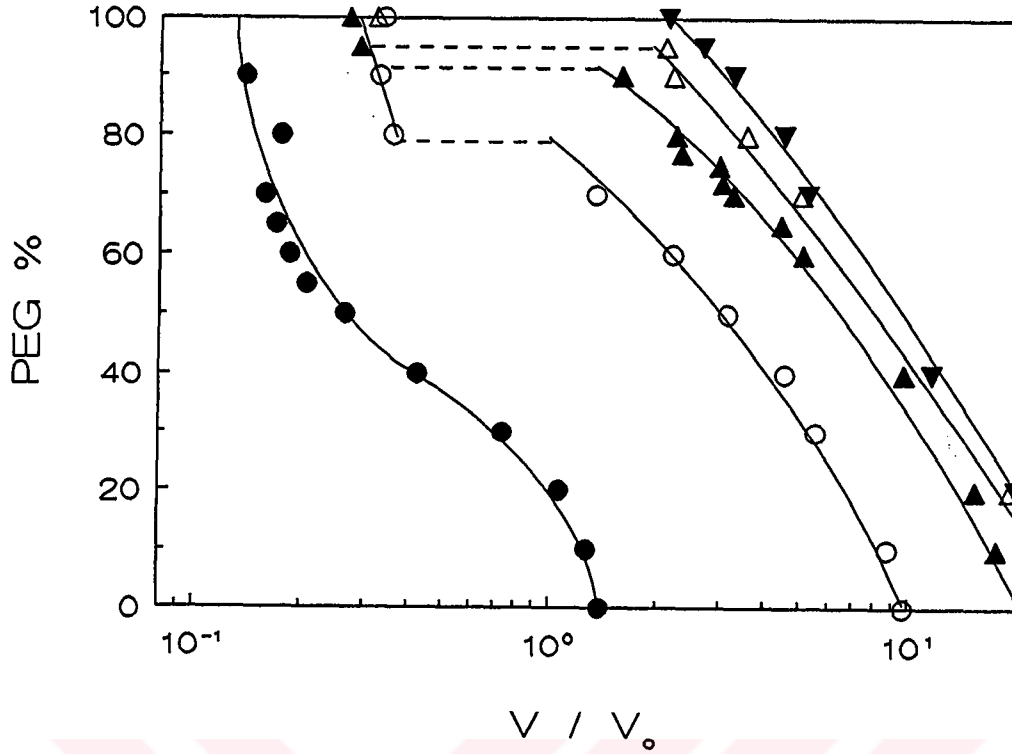


Figure 6.13. Variation of the swelling ratio, V/V_0 , of hydrolyzed PAAm gels with the concentration of PEG 300 in the outer solution. PEG concentrations are in v/v %. pH of NaOH solution used in the hydrolysis is 12.. Hydrolysis times = 0(●); 1(o); 5(▲); 9(Δ) and 16 days(▼).

6.3. Influence of the Chain Length of Ethylene Glycol Oligomers in Swelling Behavior of Polyacrylamide Gels

As you can see from Figure 6.6b and Figure 6.10a discrepancies between calculated and measured swelling behavior are apparent for tetraethylene glycol (TEG) solutions. Calculated results indicate that the PAAm gels remain in the swollen state over the whole concentration range of TEG (Figure 6.10a, the curve with $M = 194$). In contrast, experimental data show a rapid decrease of the gel volume up to 10 % TEG concentration and then the gel shrinks only slightly with increasing concentration (Figure 6.6b). Therefore, some experiments were performed to focus on the swelling behavior of the same gels in aqueous solutions of ethylene glycol oligomers with $y < 6$.

In the numerical calculations by using Flory-Huggins theory, $\chi_{12} = 0.48$ [91], $f = 0$, $v_2^0 = 0.035$, and $N = 1487$ was taken for non-ionic gels. Assuming that the

value of N does not change with the addition of acrylic acid comonomer in the monomer mixture during synthesis, the mean number of ionic units between successive junctions in a network chain, f , can also be estimated from Equation (3.17) as $f = 5.71$ for PAAm gels with 13 w/w% AAc content. This indicates that 5.71 charges exist in a network chain composed of 1487 segments. For the determination of interaction parameter between PAAm gel and ethylene glycol oligomers, χ_{23} , Equation (3.19) was applied to PAAm gels swollen in pure OEG. Thus, using the values $N = 1487$, $v_2^0 = 0.035$, $f = 0$ and the equilibrium swelling ratios of non-ionic PAAm gels in pure ethylene glycol (MEG), diethylene glycol (DEG) and tetraethylene glycol (TEG) with $y = 1, 2$ and 4 , respectively, Equation (3.19) solved for the corresponding unknown χ_{23} parameters. The equilibrium values $v_2 = 0.0303, 0.0923$ and 0.1598 yielded $\chi_{23} = 0.50, 0.27$ and 0.14 for the systems PAAm-MEG, PAAm-DEG and PAAm-TEG, respectively. Finally, χ_{13} was estimated by fitting the equilibrium swelling data of non-ionic PAAm gels in aqueous OEG solutions. The χ_{13} parameters found were $0.013, 0.066$ and 0.136 for water-MEG, water-DEG and water-TEG systems, respectively.

Figures 6.14a-6.14c shows the equilibrium degree of swelling, V/V_0 , of poly(acrylamide-co-acrylic acid) gels with different acrylic acid (AAc) content plotted as a function of the concentration of ethylene glycol oligomers (OEG) in the external solution. The number of repeat units of OEG, y , is $1, 2$, and 4 in Figures 6.14a, 6.14b and 6.14c, respectively. The filled circles represent the results of measurements for non-ionic PAAm gels, whereas the filled and empty triangles represent the measurements for ionic gels with 13 and 22 w/w% AAc contents (in the dry copolymer), respectively. The empty circles represent the results of measurements for ionic gels with 13 w/w% AAc carried out in OEG/water mixtures of $\text{pH} = 6.5-6.7$. The solid curves show the trend of data obtained for the ionic gels. The dashed and dotted curves were calculated using the Floy-Huggins theory for non-ionic and ionic gels, respectively. In aqueous solutions of monoethylene glycol (Figure 6.14a), the volume of the non-ionic gel remains almost constant over the entire range of the solvent composition. Non-ionic gels start to deswell in di- and tetraethylene glycol

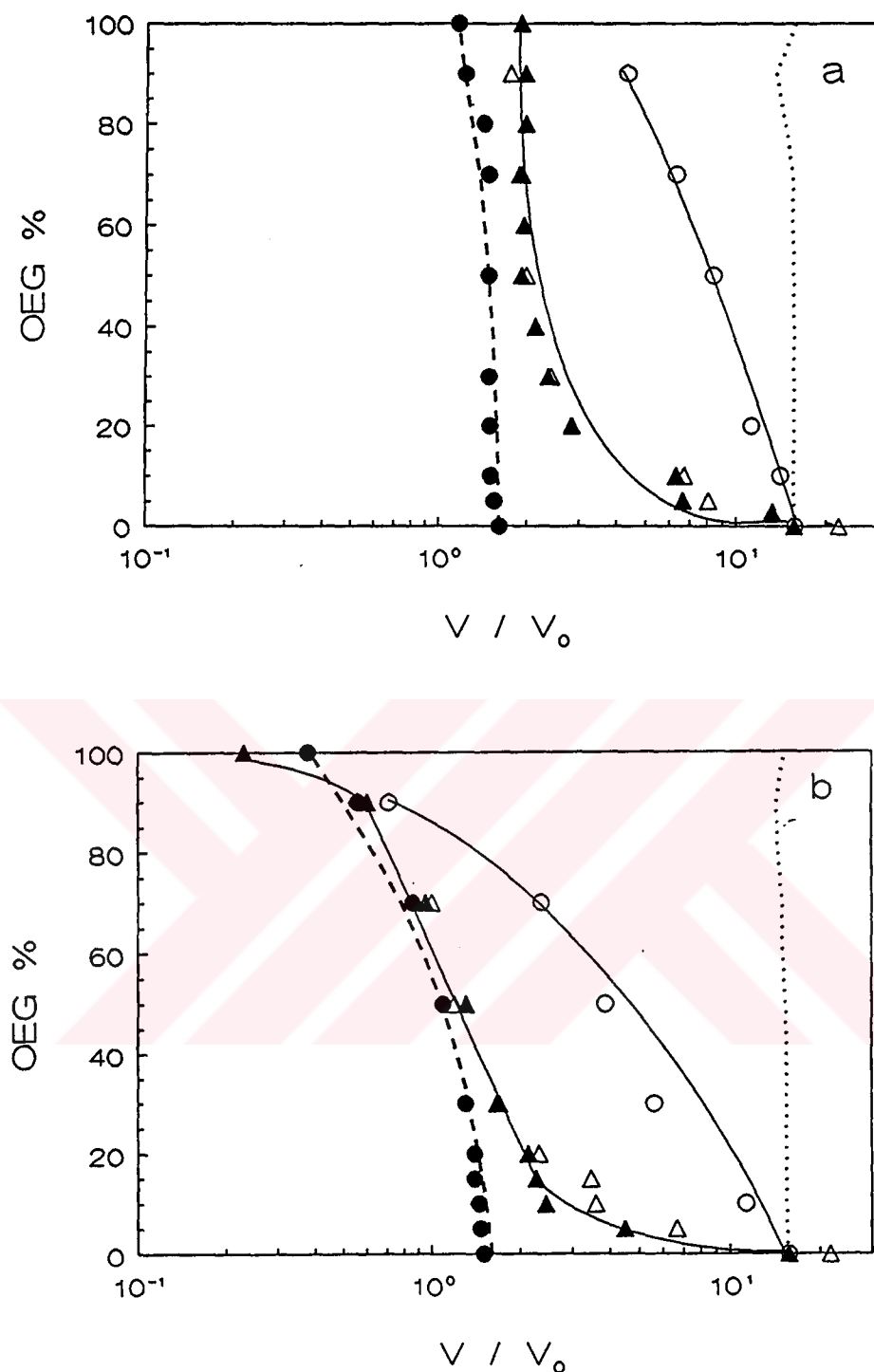


Figure 6.14. Variation of the equilibrium swelling ratio V/V_0 of poly(acrylamide-co-acrylic acid) gels with the concentration of OEG in the outer solution (v/v %). The number of repeat units in OEG $y = 1$ (a); and 2(b). AAc content in the dry copolymer = 0(●); 13(▲); and 22 w/w % (Δ). The symbol (o) represents the V/V_0 values of gels with 13 w/w % AAc content swollen in aqueous OEG solutions of pH = 6.5-6.7. The solid curves show the trend of data obtained for ionic gels. The dashed and dotted curves were calculated using FH theory for nonionic and ionic gels, respectively.

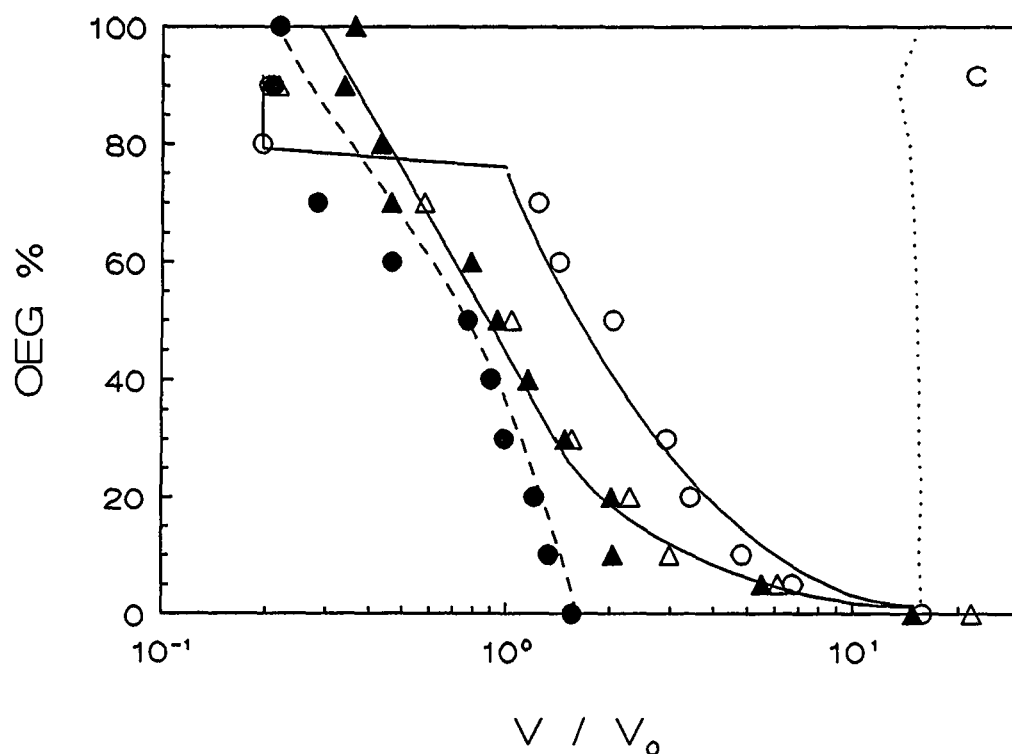


Figure 6.14c. Variation of the equilibrium swelling ratio V/V_0 of poly(acrylamide-co-acrylic acid) gels with the concentration of TEG in the outer solution (v/v %). AAC content in the dry copolymer = 0(●); 13(▲); and 22 w/w%(△). The symbol (○) represents the V/V_0 values of gels with 13 w/w% AAC content swollen in aqueous OEG solutions of pH = 6.5-6.7. The solid curves show the trend of data obtained for ionic gels. The dashed and dotted curves were calculated using FH theory for nonionic and ionic gels, respectively.

ionic gels with 13 w/w% AAC carried out in OEG/water mixtures of pH = 6.5-6.7. The solid curves show the trend of data obtained for the ionic gels. The dashed and dotted curves were calculated using the Floy-Huggins theory for non-ionic and ionic gels, respectively. In aqueous solutions of monoethylene glycol (Figure 6.14a), the volume of the non-ionic gel remains almost constant over the entire range of the solvent composition. Non-ionic gels start to deswell in di- and tetraethylene glycol solutions when their concentrations exceed about 50 %. The calculation results are in good agreement with the experimental data.

As expected, the gel with ionic constituent swells in water much more than the corresponding neutral gel due to the electrostatic repulsion between charged groups on the network chains, as well as due to the osmotic pressure of mobile ions within

the gel phase. However, as can be seen in Figures 6.14a-6.14c, the ionic gel decreases its volume sharply when a relatively small amount of OEG was added to water. At about 50 % OEG concentration, the volume of the ionic gel approaches that of the corresponding non-ionic gel. However, calculations using the Flory-Huggins theory for ionic gels (dotted curves) predicts that the volume of the gels does not change much over the whole concentration range of OEG-water mixtures. It must be noted that the aqueous solutions of OEG exhibit pH values in the range 6.2-6.7, 4.2-4.9, and 3.5-4.8 for $y = 1, 2$, and 4 , respectively. Since pH is an important parameter determining the ionization degree of gels, the experiments were repeated at fixed pH value, namely at 6.5-6.7, using titration of OEG/water mixtures with a dilute NaOH solution. The results of these measurements are also shown in Figures 4.14a-4.14c as empty circles. Although the extent of deswelling of ionic PAAm gels is reduced after adjusting the pH, the experimental data also indicate a large decrease in the equilibrium gel volume on rising the OEG concentration in the outer solution. The decrease in the gel volume is significant in TEG solutions of concentrations as high as 80%.

This interesting swelling behavior of ionic PAAm gels in OEG solutions may be due to the action of OEG as an organic solvent rather than a linear chain. The experimental results can be explained by the formation of an increasing number of ion pairs between the charges of the network and the mobile counter-ions, in the presence of water/OEG mixtures. The importance of the ion-pairing for the collapse behavior of ionic gels has been demonstrated both experimentally[94] and theoretically[95,96]. The formation of ion pairs is known to be more pronounced for solutions with a lower solvent dielectric constant ϵ . The dielectric constants, ϵ , of water, monoethylene glycol (MEG), diethylene glycol (DEG) and tetraethylene glycol (TEG) are 80, 40, 32 and 20, respectively[97]. Increasing the OEG content in aqueous solution decreases the solvent dielectric constant inside the gel and, therefore, increases the number of ion pairs. The mixtures of water with TEG have the lowest ϵ

and form more ion pairs than those with DEG or MEG. Thus, the osmotic pressure in the gels was lower in water/TEG mixtures and the degree of swelling was smaller. In the mixtures with 80 % TEG content, the number of ion pairs can be so large that, the formation of ionomer multiplets is also possible, an abrupt transition to the collapsed state becomes possible (Figure 6.14c).

In Figure 6.15, the OEG distribution inside and outside the gel, v_3 / ϕ , is shown as a function of the OEG concentration in the solution. It indicates that a large amount of OEG can penetrate into the gel phase. For ionic gels, the v_3 / ϕ ratio is about 0.8 and is essentially independent of the concentration and chain length of OEG. For non-ionic gels, the v_3 / ϕ ratio decreases with increasing OEG concentration in the outer solution.

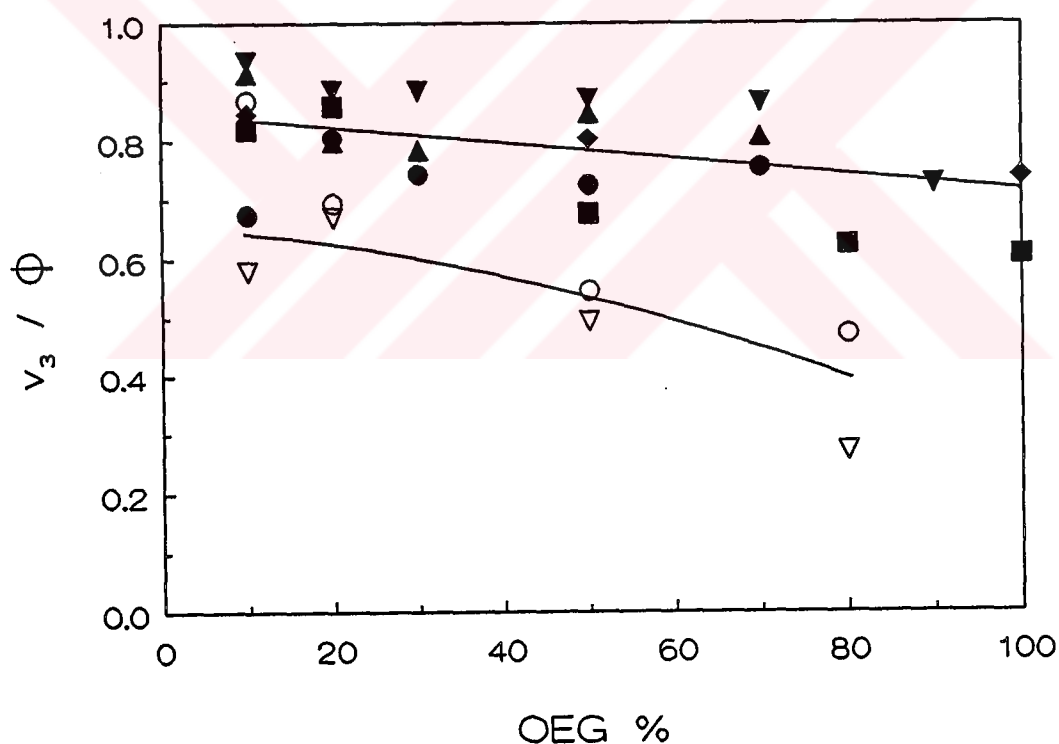


Figure 6.15. Dependence of the OEG distribution, v_3/ϕ , inside and outside the poly(acrylamide-co-acrylic acid) gel on the OEG concentration in the solution.

AAc % = 0; y = 1(o) and 4(▽)

AAc % = 13; y = 1(●); 2(▲) and 4(▼)

AAc % = 22; y = 1(◆) and 4(■)

In Figures 6.16a and 6.16b, the equilibrium swelling ratio of the gels is shown as a function of y (degree of polymerization of ethylene glycol polymers) for a fixed PEG concentration in the external solution. For the non-ionic gels (Figure 6.16a), an increase in y decreases the volume of the gel phase. This was expected due to the effect of the mixing entropy of the linear polymers. An increase in y decreases the osmotic pressure of the solution phase, so that the gel shrinks. Contrary to the non-ionic gels, the volume of the ionic gel first decreases as y increases from 1 to 4, but then it increases again rapidly up to $y = 6$ (Figure 6.16b). Further increase in y decreases the gel volume only slightly. A re-entrant swelling behavior is shown in Figure 6.16b for ionic gels. The dotted curves in the region $y = 1-6$, shown in Figure 6.16b, represent the swelling behavior of non-ionic gels for comparison. It can be seen that the volume of the ionic gel approaches that of the non-ionic gel at $y = 2-4$. The results of experiments carried out at $\text{pH} = 6.5-6.7$ are also shown in Figure 6.16b as dashed curves. These results also indicate that the addition of a small amount of OEG into water results in the destruction of the solvation structure of water molecules around carboxyl groups of the network chains due to the formation of ion pairs and so, the association of the dehydrated chains in water/OEG mixtures results in smaller volumes than those in polymer solutions of higher molecular weight.

According to the above experimental data, di- and tetraethylene glycols seem to be the most efficient deswelling agents for the ionic PAAm gels. To confirm this assumption, experiments have also been conducted using linear poly(acrylamide-co-acrylic acid) chains dissolved in OEG/water mixtures. For this purpose, linear poly(acrylamide-co-acrylic acid) of molecular weight 2×10^5 daltons, having 10 % acrylic acid units, purchased from Polyscience was used. 10 % aqueous solutions of OEG of various chain lengths were selected as solvents. The viscosities of the polymer solutions were measured in an Ubbelohde viscometer at 25°C .

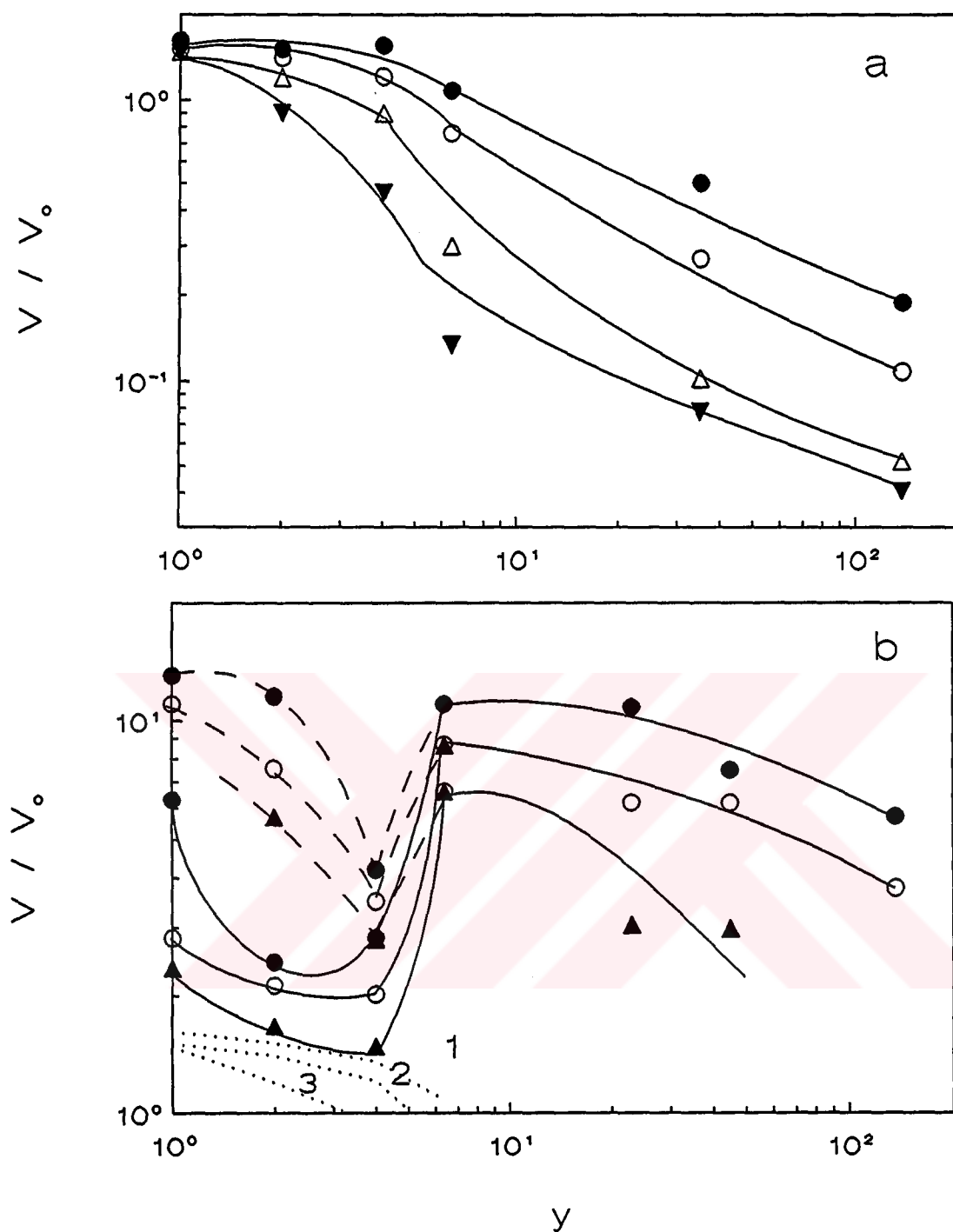


Figure 6.16. Variation of the swelling ratio V/V_0 of poly(acrylamide-co-acrylic acid) gel with the number of repeat units in ethylene glycol polymers, y . The PEG concentration in the outer solution = 10 (●); 20 (○); 30 (▲); 40 (△) and 60 v/v % (▼). AAc content in the dry copolymer is 0 and 13 w/w % in Figures 16a and 16b, respectively. The dashed curves in Figure 16b represent the swelling behavior of gels at pH = 6.5-6.7. The lower dotted curves in Figure 16b represent the swelling behavior of the nonionic gels in polymer solutions of concentrations 10 (1), 20 (2) and 30% (3).

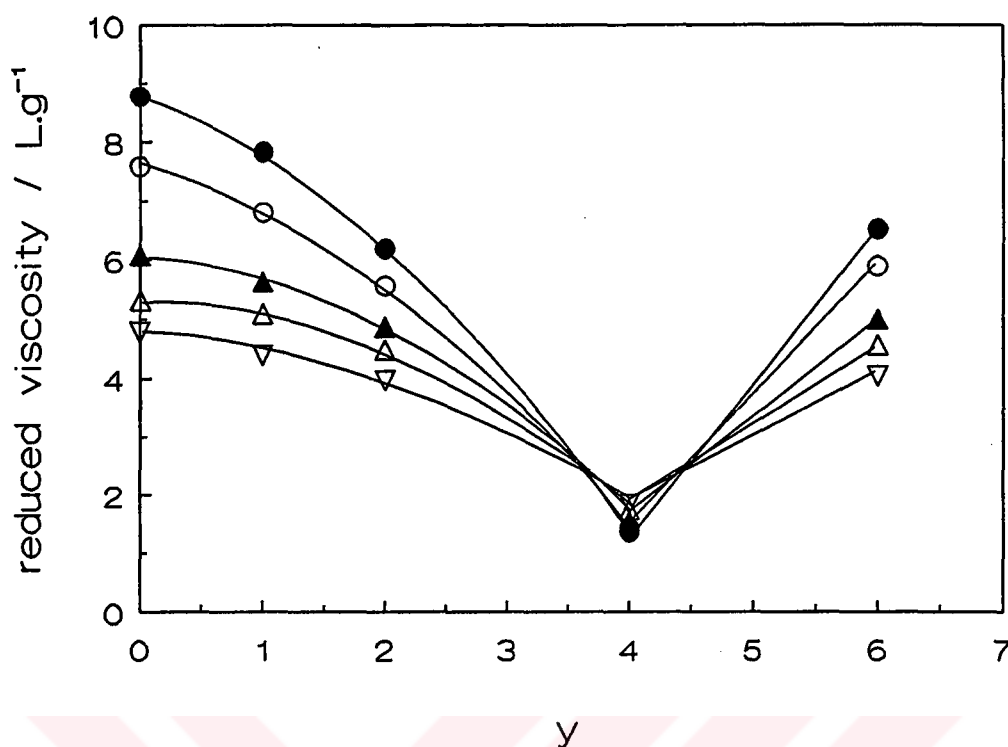


Figure 6.17. Variation of the reduced viscosity of linear poly(acrylamide-co-acrylic acid) chains in OEG-water mixtures with the number of repeat units in OEG, y . Linear PAAm-co-PAAc concentration = 1.0(●); 1.4(o); 2.0(▲); 3.0(△) and 4.0 (▽) g/L.

In Figure 6.17, reduced viscosities, η_{red} , are shown as a function of the number of repeat units of OEG, y , in the solution. The viscosity of the polymer solutions shows a minimum at $y = 4$, i.e. in TEG/water mixture. In Figure 6.18, reduced viscosity values for the above polymer were plotted against its concentration. With the exception of the TEG/water mixtures, a decrease in the reduced viscosity with increasing polymer concentration can be seen from the figure, indicating typical polyelectrolyte behavior of poly(acrylamide-co-acrylic acid) solutions. By extrapolating the plot of η_{red} vs c to zero concentration, the intrinsic viscosity of the polymer sample in the TEG/water mixture was calculated as 119.5 ml/g. Using this value and for $K = 6.31 \times 10^{-3}$, $a = 0.8$ [68], the weight-average molecular weight of the poly(acrylamide-co-acrylic acid) sample was calculated as 2.2×10^5 daltons, which is close to the value reported by the manufacturer. Thus, the chains dissolved in TEG/water mixtures behave as a non-ionic polymer. The above results, obtained with

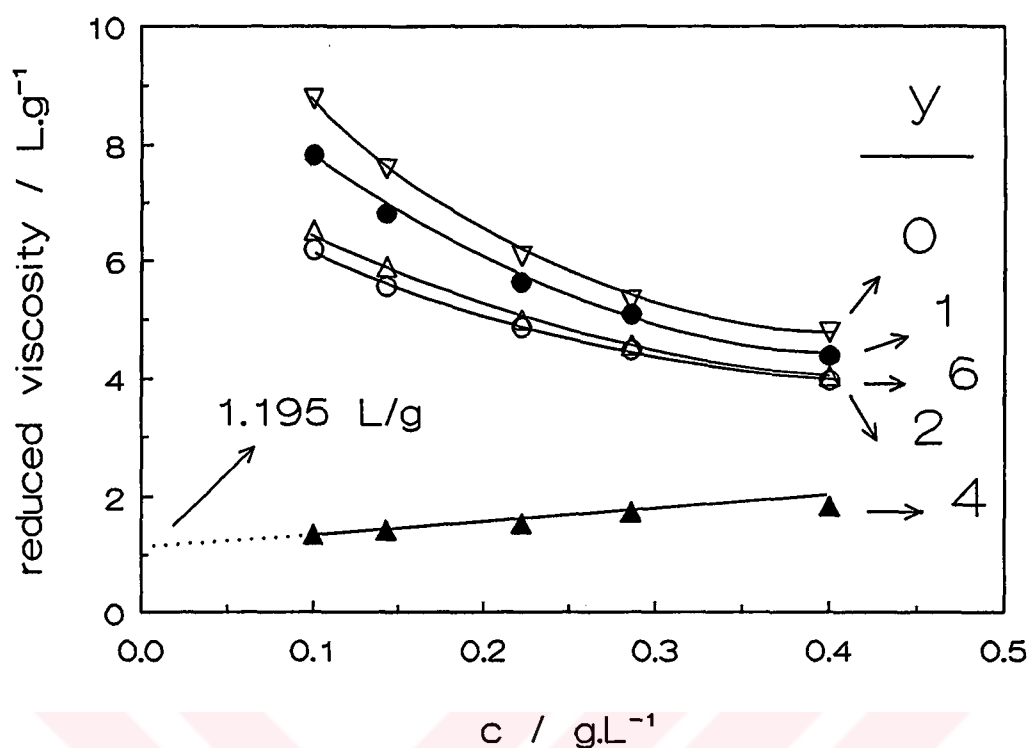


Figure 6.18. Reduced viscosity versus concentration dependences for linear poly(acrylamide-co-acrylic acid) chains dissolved in 10% aqueous solutions of OEG with different number of repeat units y . $y = 1$ ($\bullet$); 2 ($\circ$); 4 ($\blacktriangle$); 6.4 ($\triangle$) and 0 (∇).

both cross-linked and linear ionic PAAm chains, clearly show that the addition of a small amount of TEG in water screens the excess expansion of ionic polymer coils due to the ionization of the polymer chains.

6.4. Appearance of Non-Equilibrium Structures

In poly(ethylene glycol) (PEG) solutions, ionic polyacrylamide gels showed different final states. As pointed out by Dusek and recently by Khokhlov the reason of this observation is the appearance of kinetically frozen structures within the gels due to microsyneresis[98,99]. The decrease of the volume of ionic PAAm gels is shown in Figure 6.19 as a function of the contact time with pure PEG 300. Prior to the immersion of the gels in PEG 300, they were swollen in water to different degrees. Here, the gel A was directly immersed into PEG 300 after its synthesis. The gel B was partially swollen and gel C was swollen to equilibrium in water prior to the deswelling experiments. It seems that the preswollen gels deswell only slightly in PEG 300 and they cannot reach their equilibrium volume. However, the gel used after

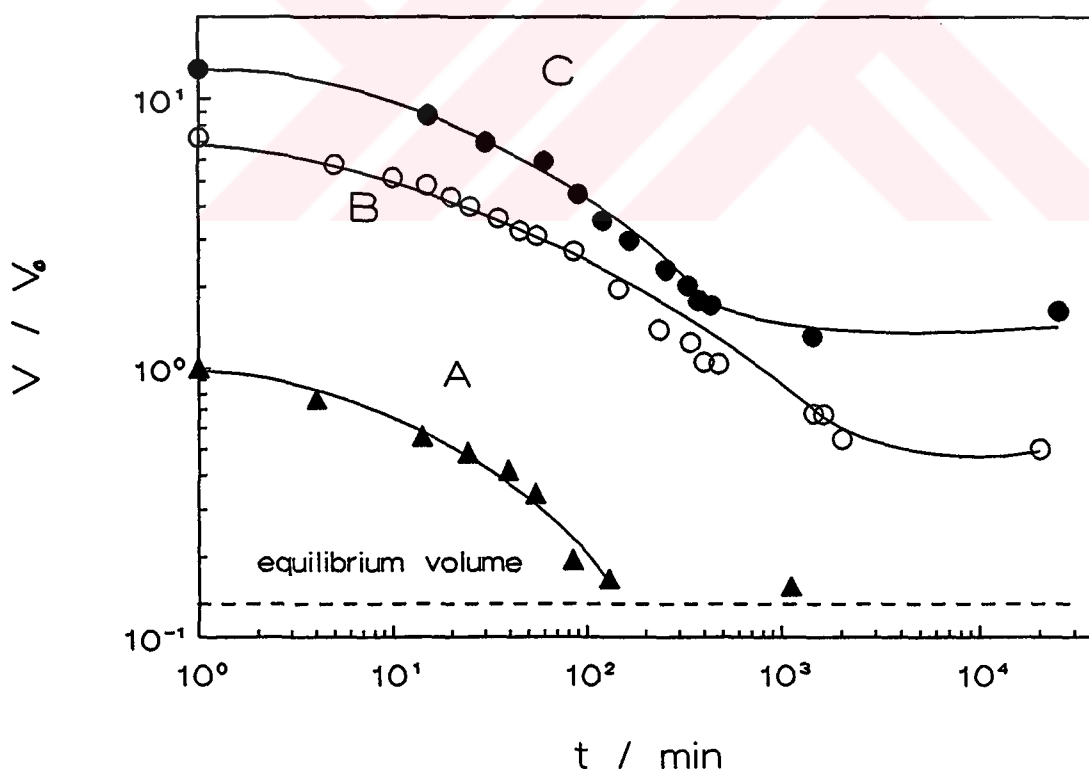


Figure 6.19. Deswelling of ionic gels with 13% AAc in pure PEG300. The gel A was immersed into PEG300 after synthesis. B and C were preswollen in water for 1 and 15 days, prior to the deswelling experiments.

synthesis reaches its equilibrium volume after about 1.5 h.

In Figure 6.20, the swelling ratio of poly(acrylamide-co-acrylic acid) gels is plotted as a function of the PEG 300 concentration in the external solution. The filled symbols belong to the gels after synthesis and the empty symbols to preswollen gel samples. For gel samples after synthesis, a first order phase transition is observed at about 70 % PEG concentration. However, if the same gel samples are swollen to equilibrium in water prior to the measurements, they remain in the swollen state over the entire PEG 300 concentration and no collapse transition was observed.

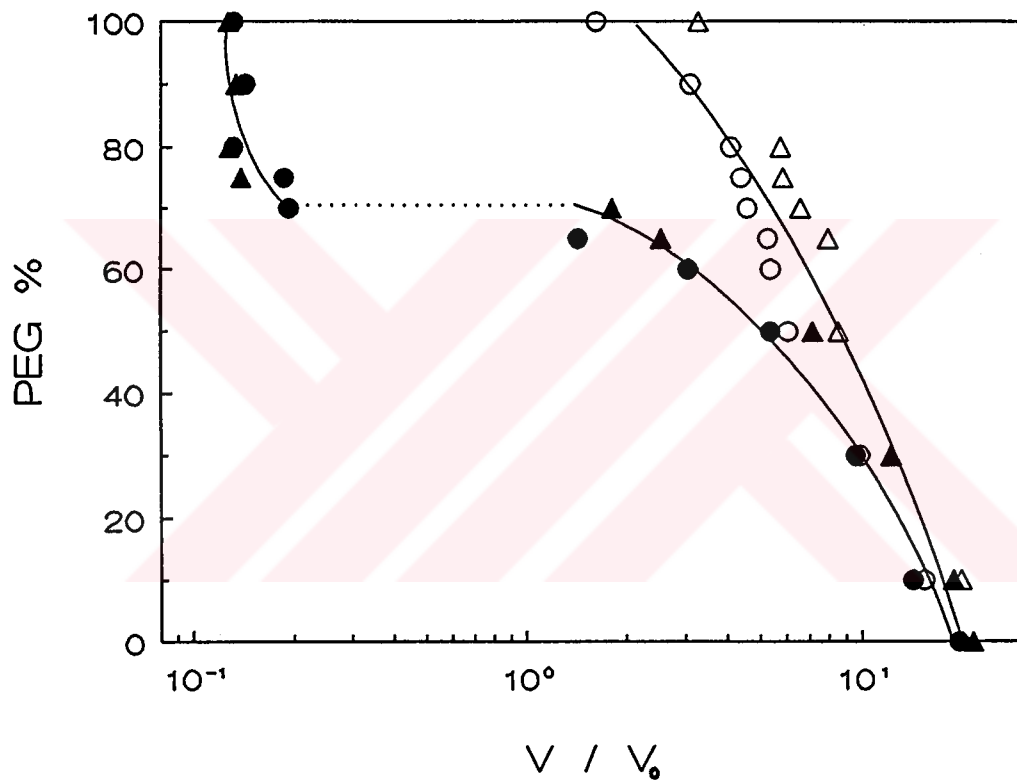


Figure 6.20. Variation of the swelling ratio V/V_0 of poly(acrylamide-co-acrylic acid) gel with the concentration of PEG(300) in the outer solution. Swelling measurements were carried out using gels after synthesis (filled symbols) and using preswollen gels (empty symbols). AAc content in the dry copolymer = 13 (•,○); and 22 w/w % (▲,△).

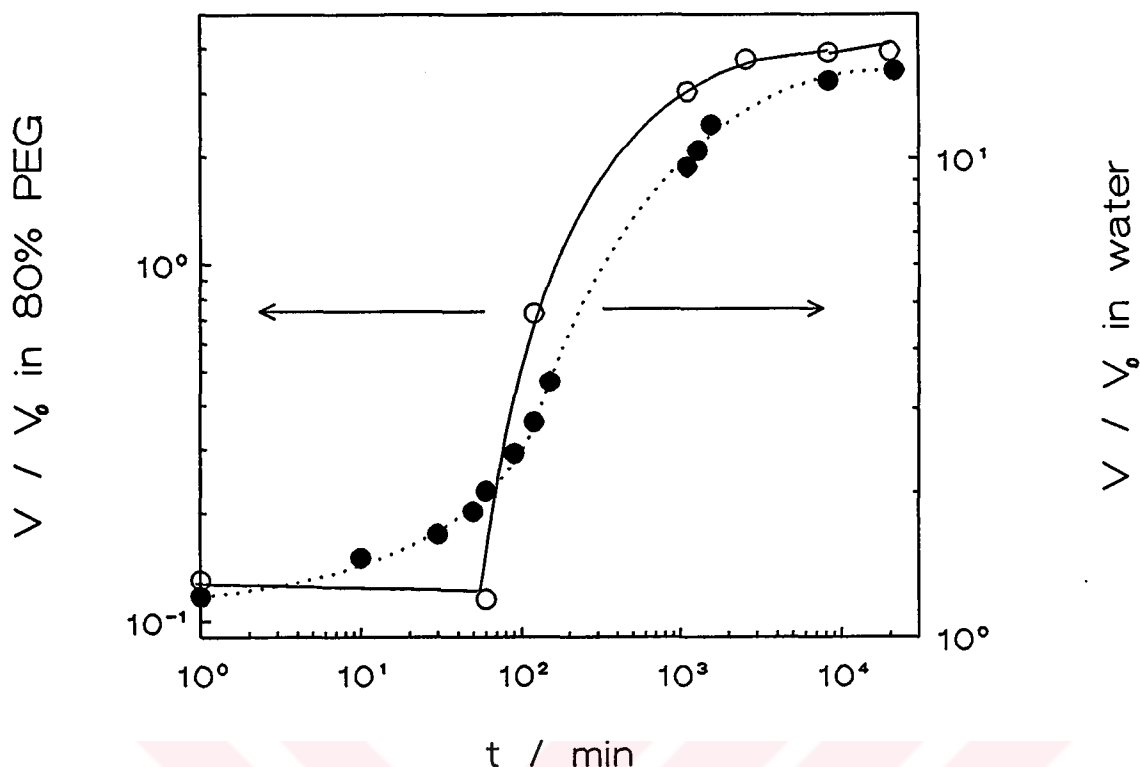


Figure 6.21. Variation of the swelling ratio V/V_0 of poly(acrylamide-co-acrylic acid) gels in PEG 300 - water mixture (80/20 v/v) with the preswelling time in water. The right axes represents the swelling ratio of the gels in water at given contact times. AAc content of the gels = 13 w/w %.

In Figure 6.21, the swelling ratio of poly(acrylamide-co-acrylic acid) gels in 80 % aqueous solution of PEG 300 is shown as a function of their preswelling time in water. The solid curve illustrates the trend of the experimental data shown as empty circles. For preswelling times less than 60 min, the gel attains its equilibrium volume in PEG solutions. However, as the preswelling time increases, the gel cannot attain its equilibrium volume in PEG solutions. The filled circles in Figure 6.21 represent the swelling ratio of the gel in water as a function of time. It seems that, as the initial volume of the gel increases, the gel fails to deswell in the PEG solution to its equilibrium volume, as is observed when deswelling is from the initial state after synthesis.

According to our results, PAAm gels attain their equilibrium volumes in PEG solutions if they are used directly after network formation process. However, highly swollen gels cannot attain their equilibrium volume in PEG solutions even after 2 months of observation. This probably due to the slow relaxation of the network

chains in the polymer-poor regions compared to the rate of removal of water molecules from the gel (microsyneresis). Thus, under such conditions the inhomogeneities within the gel remain fixed.

6.5. Swelling of Polyacrylamide Gels in Polyacrylamide Solutions

6.5.1. Non-Ionic Polyacrylamide Gels

Variation of equilibrium degree of swelling V / V_0 of PAAm gels with the volume fraction of linear PAAm in the external solution ϕ is shown in Figures 6.22a and 6.22b. The molecular weights M_w of linear PAAm's were between 5×10^6 - 6×10^4 g/mol in Figure 6.22a and between 2.5×10^4 - 1.5×10^3 g/mol in Figure 6.22b. Measurements at high polymer concentrations could not be carried out for high molecular weight PAAm's, because they were not soluble. Experimental data are shown as symbols. Filled symbols represent the results of measurements with non-ionic PAAm gels, whereas the empty symbols for PAAm-co-PAAc (ionic) gels with 13 w/w% AAc content (based on dry gel). As the PAAm concentration outside the gel phase increases, the volume of PAAm gels decreases. This decrease becomes more pronounced as the molecular weight of PAAm in the solution increases.

The solid and dashed curves shown in Figures were calculated using the Flory-Huggins theory for non-ionic and ionic gels, respectively. For calculations, polymer-solvent and network-solvent interaction parameters were taken as $\chi_{12} = \chi_{13} = 0.48$. For $M_w = 5 \times 10^6$ g/mol, since the experimental data are only available in a narrow range of polymer concentration, calculations were not performed. For all other non-ionic PAAm gel samples, calculation results for $\chi_{23} = 0$, i.e., assuming athermal interactions between polymer and network, led to poor agreement between theory and experiment. For instance in Figure 6.23, representing V/V_0 versus PAAm

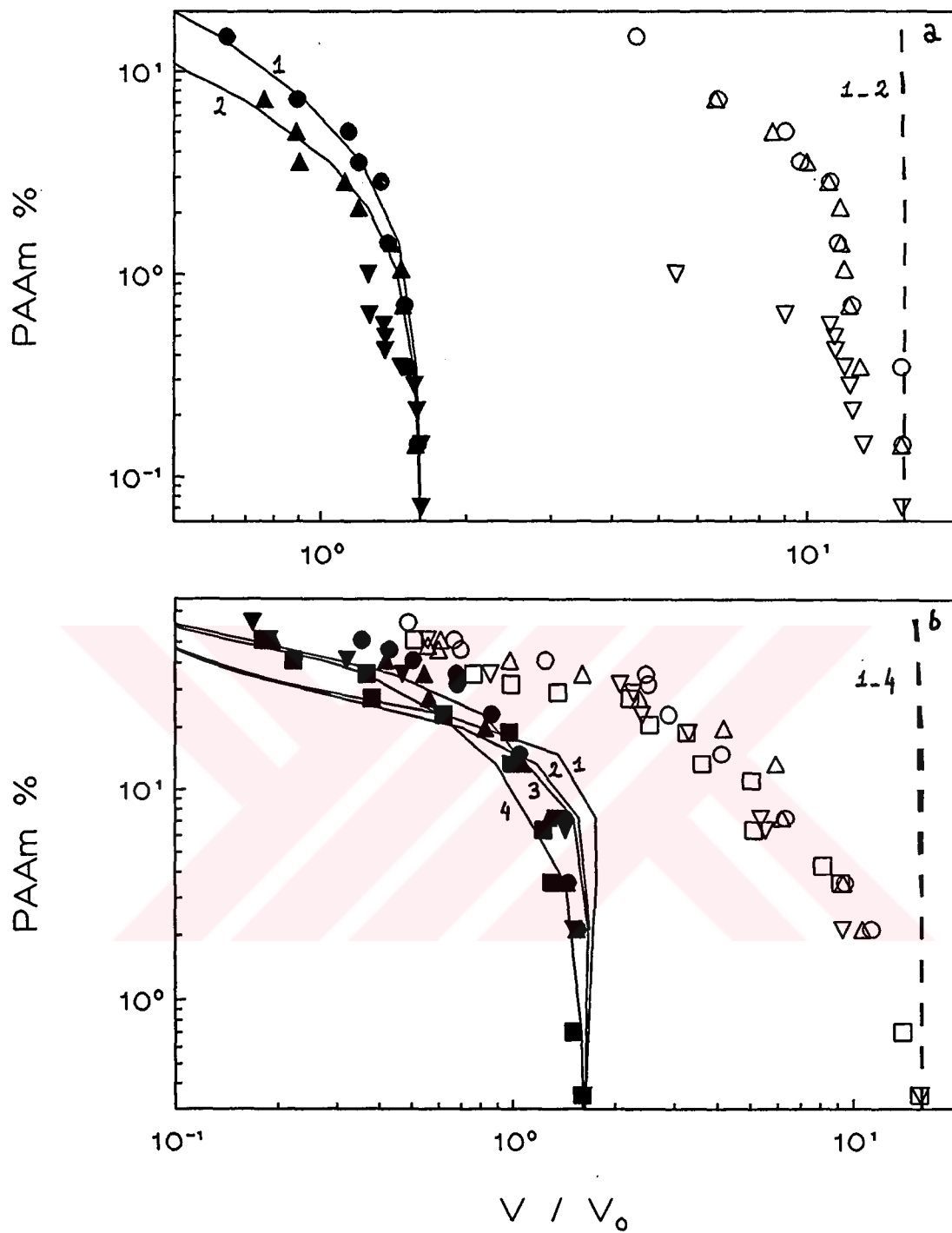


Figure 6.22. Variation of the swelling ratio V/V_0 of PAAm gels with the concentration of linear PAAm. Filled symbols represent the results of measurements with non-ionic PAAm gels, whereas the empty symbols for PAAm-co-PAAc gels. The curves were calculated using FH theory for non-ionic (solid curves) and ionic gels (dashed curves). The molecular weights, M_w , of linear PAAm's are:
a) 6×10^4 ($\bullet, \circ, 1$); 1×10^5 ($\blacktriangle, \triangle, 2$); and 5×10^6 g/mol ($\blacktriangledown, \triangledown, 3$).
b) 1.5×10^3 ($\bullet, \circ, 1$); 5×10^3 ($\blacktriangle, \triangle, 2$); 1×10^4 ($\blacktriangledown, \triangledown, 3$) and 2.5×10^4 g/mol ($\blacksquare, \square, 4$)

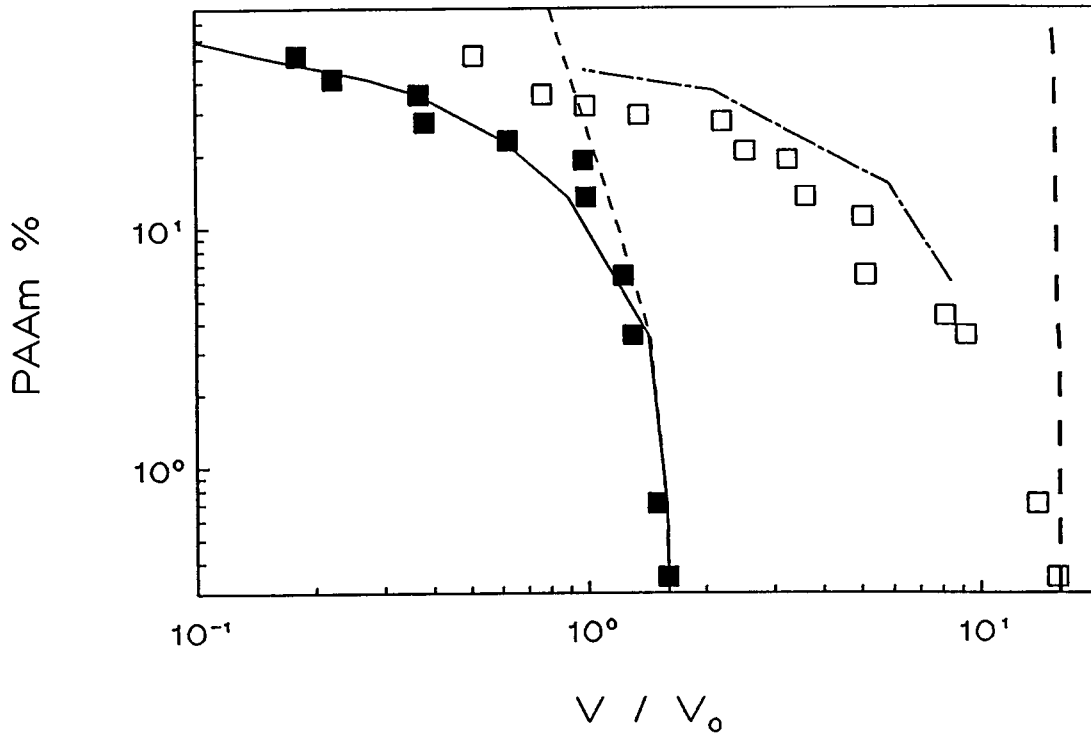


Figure 6.23. Variation of the swelling ratio V/V_0 of non-ionic (●) and ionic PAAm gels (○) with the concentration of linear PAAm in the outer solution. The molecular weight of linear PAAm is 2.5×10^4 g/mol. The solid and dashed curves were calculated for non-ionic and ionic gels, respectively for $\chi_{23} = 0.0048$. The small-dashed curve was calculated for the non-ionic gel and for $\chi_{23} = 0$. The dot-dashed curve represents the results of measurements for ionic gels carried out at 80°C .

concentration ϕ dependence for $M_w = 2.5 \times 10^4$ g/mol, the dotted curve was calculated for $\chi_{23} = 0$. The non-ionic gel deswells in PAAm solution much more than predicted using the Flory-Huggins theory for athermal interactions. The solid curve in Figure 6.23 which is a best-fit to the experimental data yields $\chi_{23} = 0.0048$. Similarly, the solid curves in Figure 6.22a and 6.22b were calculated using the least square analysis of the two swelling equations with the swelling ratio data, and yield $\chi_{23} = 0.0048, 0.0025, 0.011, 0.034$ and 0.1 for $10^{-4} M_w = 10, 6, 1, 0.5$ and 0.15 g/mol, respectively. It can be seen that, after adjusting χ_{23} parameter for each polymer molecular weight, the Flory-Huggins theory and experiment show good agreement for $M_w \geq 10000$ g/mol. For linear PAAm's with $M_w = 1500$ and 5000 g/mol, however, theory and experiment are only in fair agreement. This is probably because of the high concentration of short linear chains inside the gel phase, which increases the

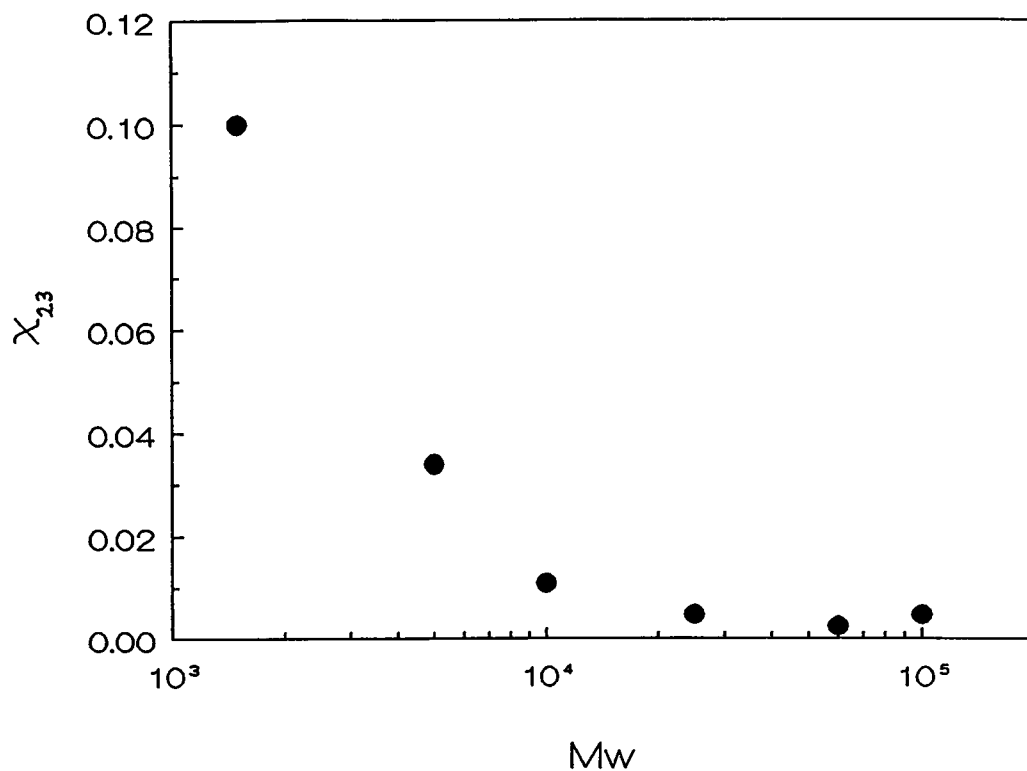


Figure 6.24. Variation of the polymer-network interaction parameter χ_{23} with the molecular weight M_w of linear PAAm.

interchain entanglements between the network and polymer chains acting as effective cross-links.

χ_{23} parameter values calculated for each set of experimental data are shown in Figure 6.24 as a function of the polymer molecular weight M_w . The smaller the molecular weights are, the larger χ_{23} is. This trend of χ_{23} is similar to that of the second virial coefficient A_2 in a binary solution, which also decreases with increasing molecular weight[100]. The molecular weight dependence of χ_{23} was also observed previously in several systems[100,101].

6.5.2. Ionic Polyacrylamide Gels

In Figures 6.22-6.23, the empty symbols represent the swelling volumes of PAAm-co-PAAc gels in aqueous PAAm solutions. The ionic gel deswells significantly as the concentration or the molecular weight of the linear polymer in the external solution increases. The swelling ratio of ionic gels approaches to that of non-ionic gels at high polymer concentrations. In contrast to the experimental results, the theory predicts almost no change in the volume of the ionic gel over the whole concentration and molecular weight ranges of PAAm.

To explain the discrepancy between theory and experiment, one has to consider the complex formation and the ion pair formation effects. A complex between AAm and AAc units due to hydrogen bonding is known to be much more hydrophobic than the polymer chains taken separately. It was reported that the stability of such complexes lowers sharply with the increase of the temperature of the solution[88,101]. The results of experiments which were carried out at 80 °C are given in Figure 6.23, denoted by dot-dashed curves. The volume of the gel phase increased only slightly as the swelling temperature increases. Thus, we can conclude that the complexation is not responsible for the contraction of ionic gels in PAAm solutions.

A more plausible explanation for the deswelling of ionic gels in polymer solution is a change in the degree of ionization of AAc units on the network chains depending on the polymer concentration. Recent studies indicate the importance of ion pairing for the collapse behavior of weakly charged polyelectrolytes[94,96]. Theoretical calculations show that the decrease in dielectric constant ϵ increases the probability of ion-pairing[96]. Since the dielectric constant $\epsilon = 80$ for water, and is about unity for PAAm, increasing content of PAAm in the gel phase decreases the effective dielectric constant of the gel. From Figure 6.25, it can be seen that the mean number of ionic units, f , in a network chain decreases with the increase in the

concentration of the linear polymer in the outer solution. This indicates the formation of ion-pairs on poly(acrylamide-co-acrylic acid) network chains as the PAAm concentration increases, leading to the deswelling of the gel.

Indeed, calculations using the Flory-Huggins theory also showed that, if f (number of fixed charges in a network chain) is taken as a fit parameter instead of χ_{23} , theory predicts the swelling data of ionic gels. The f values needed to fit the experimental data vs. ϕ plot gives a single curve, independent of the molecular weight of linear polymers. The value of f decreases from 5.7 to 0.5, i.e., more than 90 % of charged groups in the network vanish on rising the polymer concentration ϕ from 0 to 0.4.

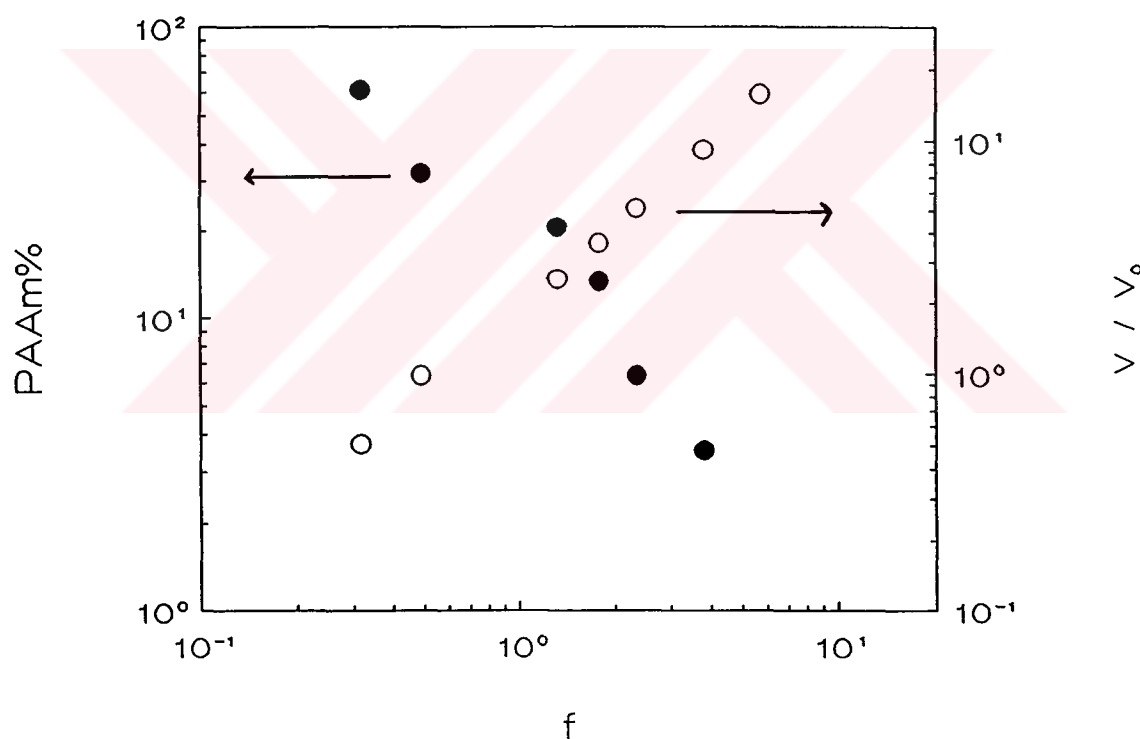


Figure 6.25. Variation of mean number of ionic units between successive junctions in a network chain, f , with the concentration of linear PAAm in the outer solution. The right axes represents the swelling ratio of the ionic gel with the change in f .

6.6. Morphology of Polyacrylamide Gels

The scanning electron microscopy (SEM) is used for study of the surface and bulk structures of network. Samples are prepared by attaching them to the specimen stub and applying a conductive surface coating. Bulk structures are observed for samples fractured in liquid nitrogen, sectioned or critical point dried.

Figure 6.26 shows the scanning electron micrographs, secondary electron images (SEI) of the polyacrylamide hydrogel network.

In Figure 6.26a fractured surface morphology of polyacrylamide gel with a magnification $\times 100$ can be seen. Higher magnification micrographs (Figure 6.26b, $\times 1500$; Figure 6.24c, $\times 5000$) show the details of (a).

As can be seen from Figure 6.26a and 6.26b SEI view shows the structure is porous with a thin, dense, surface layer.

In Figure 6.26c a large rounded porous texture is seen. This spongy bulk structure with an approximately $1\ \mu\text{m}$ pore size is a characteristic feature of hydrogel networks.

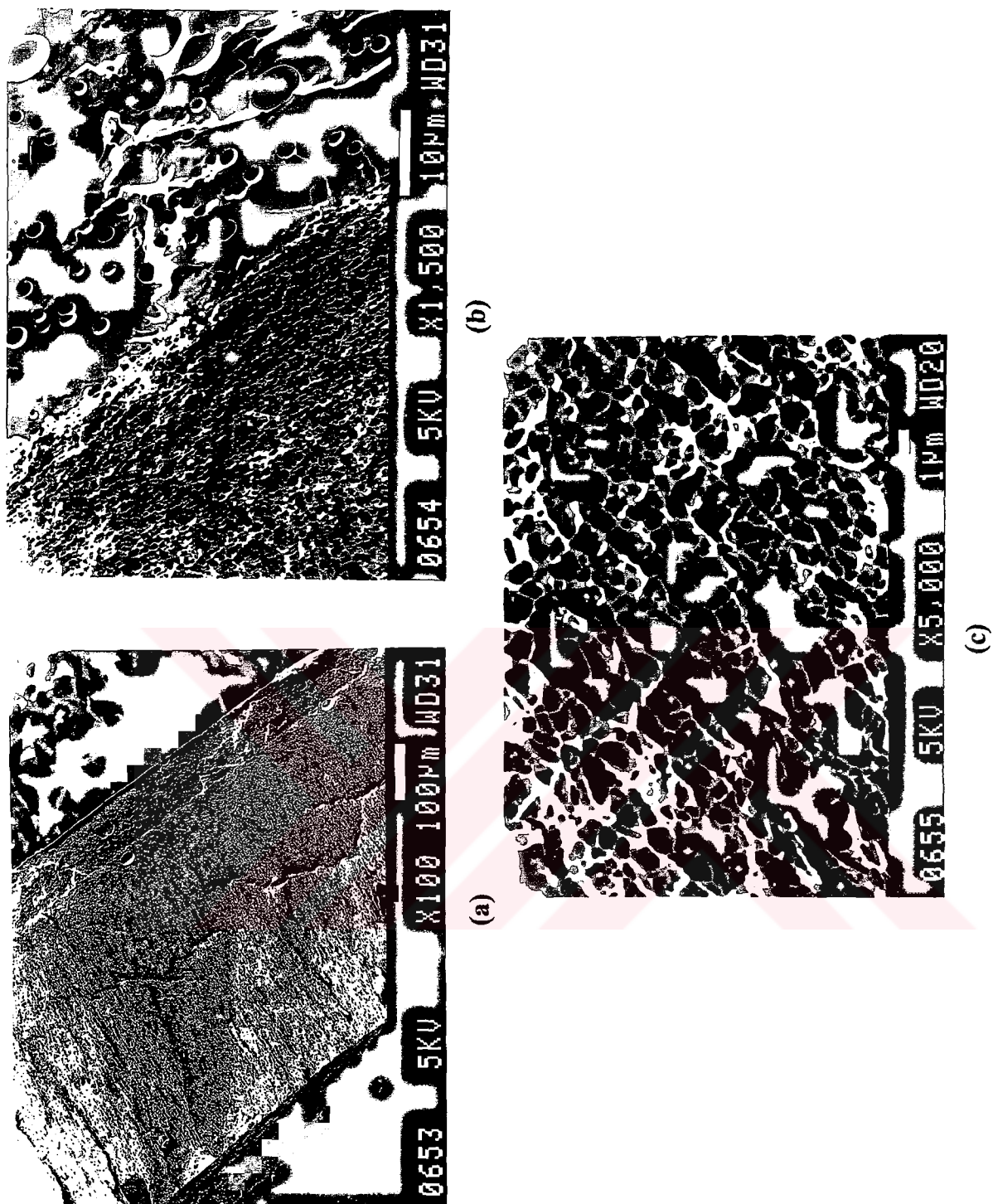


Figure 6.26. SEM micrographs of a PAAm gel.

6.7. Protein Separation Efficiency of Temperature Sensitive Poly(N-isopropyl acrylamide) Gels

In 1984, Hirokawa and Tanaka reported that poly(N-isopropyl acrylamide) (PNIPA) gels exhibit discrete and reversible volume change in response to an infinitesimal change in temperature[10]. As seen in Figure (6.27), at low temperatures the PNIPA gel is swollen, at high temperatures the gel is collapsed. At 34 °C marked with horizontal dotted line, both a swollen and a collapsed state can be observed, indicating a first-order volume transition in the gel. In the previous experiments it is shown that polymer chain with molecular weight is greater than 6000 does not penetrate into the gel phase. This feature of PNIPA gels were used in the separation of protein from their dilute solution. The effect of synthesis conditions on the structure and separation efficiency of the PNIPA gel was investigated.

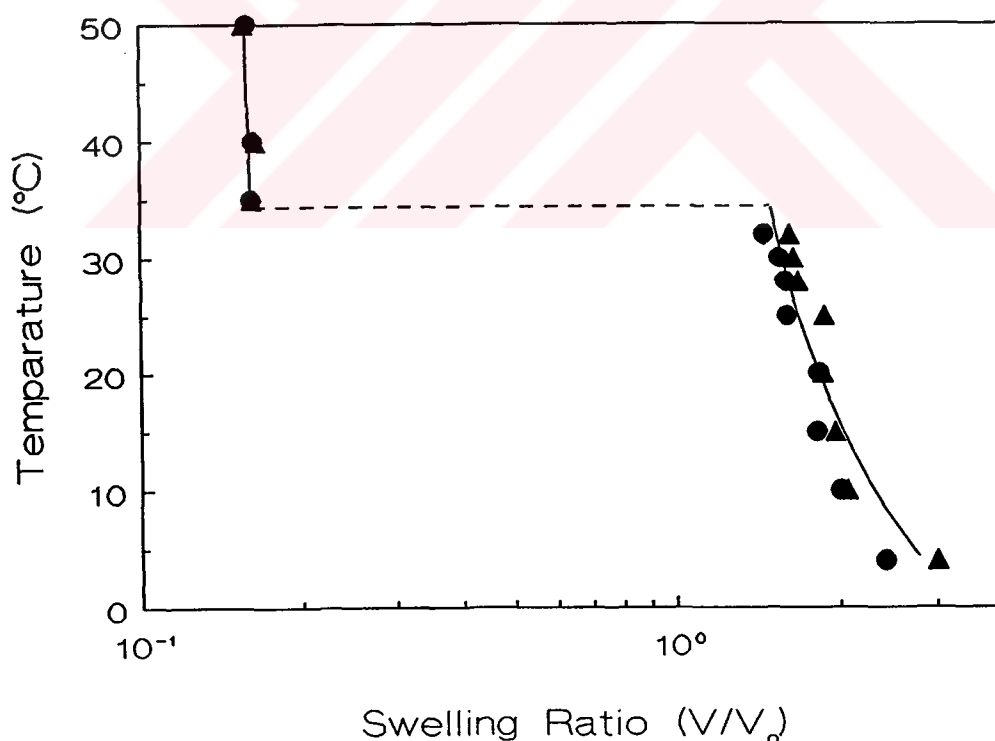


Figure 6.27. Variation of the equilibrium swelling ratio, V/V_0 , of PNIPA gels in water with the swelling temperature. MBA = 1.6(●) and 2.5 wt% (▲).

6.7.1. Solution Polymerization

PNIPA gels were prepared by free radical cross-linking copolymerization of N-isopropyl acrylamide (NIPA) and N,N'-methylenebis(acrylamide) (MBA) monomers. Visual observations showed that the gel prepared at 18°C or lower were transparent, whereas those formed at higher temperatures, i.e., at 25 °C were opaque. At low temperatures, polymerization solvent water remains in the gel phase throughout the polymerization, resulting in the formation of expanded homogeneous networks. At high temperatures, water separates out of the network phase due to the polymer-solvent incompatibilities resulting in heterogeneous structures.

The effect of the gel preparation temperature on the swelling ratio of the PNIPA gels, V/V_0 , is shown in Figure 6.28. The gel samples were prepared at 2 wt% MBA concentration but at different temperatures between 4 and 34 °C. The swelling measurements were carried out at room temperature ($23^{\circ}\text{C} \pm 1$) in water. For the transparent gels, the equilibrium swelling ratio increases only slightly with increasing gel preparation temperature. However, for heterogeneous gels, V/V_0 strongly depends on the preparation temperature and it drastically increases with increasing temperature of the polymerization mixture. Furthermore, the gels prepared at temperatures higher than 30°C exhibited a loose structure, indicating a very low degree of effective cross-linkages within these gels. At lower temperatures, the diluent water present during the network formation process remains in the gel throughout the polymerization. As the temperature is increased, the diluent starts to separate out of the network. Thus, the polymerization system tends to separate into polymer-rich and polymer-poor regions. Due to the high concentration of pendant vinyl groups in polymer-rich regions, one may expect enhanced rates of cross-linking and multiple cross-linking reactions, which would lead to the formation of highly cross-linked, microgel-like regions in the final gels[102-104]. On the other hand, the

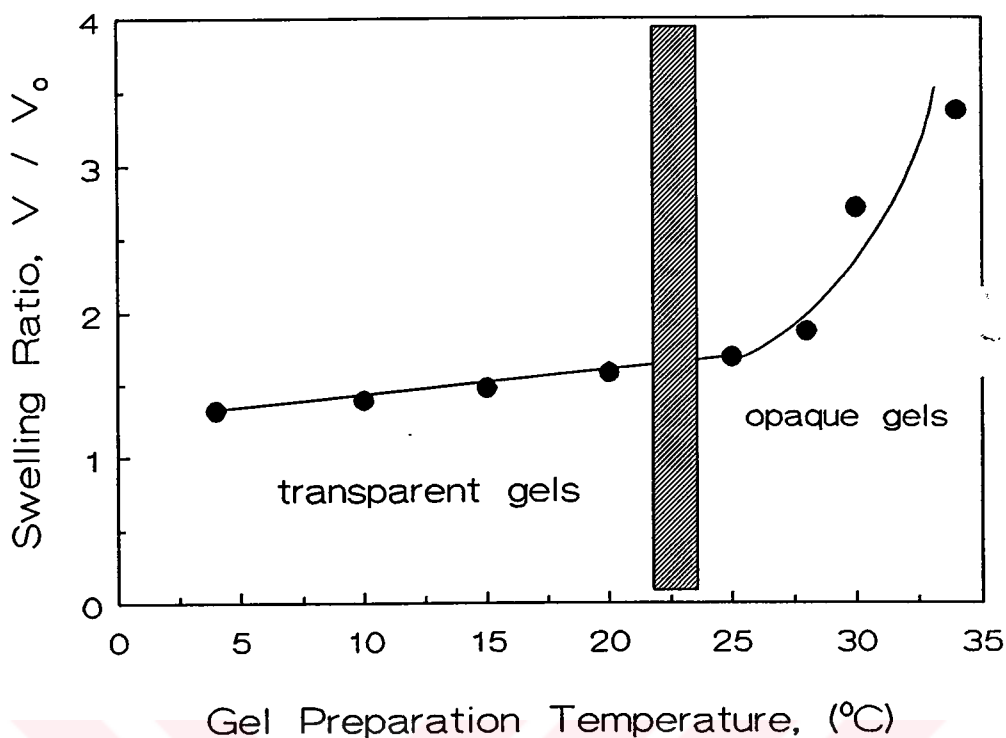


Figure 6.28. Variation of the swelling ratio of the PNIPA gels, V/V_0 , with the polymerization temperature. MBA = 2 wt%. The shaded area represents the transition region from homogeneous to heterogeneous gels.

polymer-poor regions become slightly cross-linked due to the high degree of dilution. According to this picture, the highly cross-linked regions may contribute to the rubber elasticity of the final gels as single junction points. Increasing temperature will increase the extent of phase separation and also, the concentration difference between the gel and diluent phases. As a result, the compactness of the microgels will increase but the connections between the microgels become weaker and weaker as the temperature increases, which would lead to increased degree of swelling of heterogeneous PNIPA gels on raising temperature.

Another factor determining the equilibrium swelling ratio of the gels is the amount of the cross-linker MBA used in their synthesis. In Figure 6.29, the equilibrium swelling ratio of PNIPA gels, V/V_0 , is plotted against the MBA concentration. Here, the gel preparation temperature was fixed at 25°C. The filled and empty circles represent the results of swelling measurements carried out at 4°C

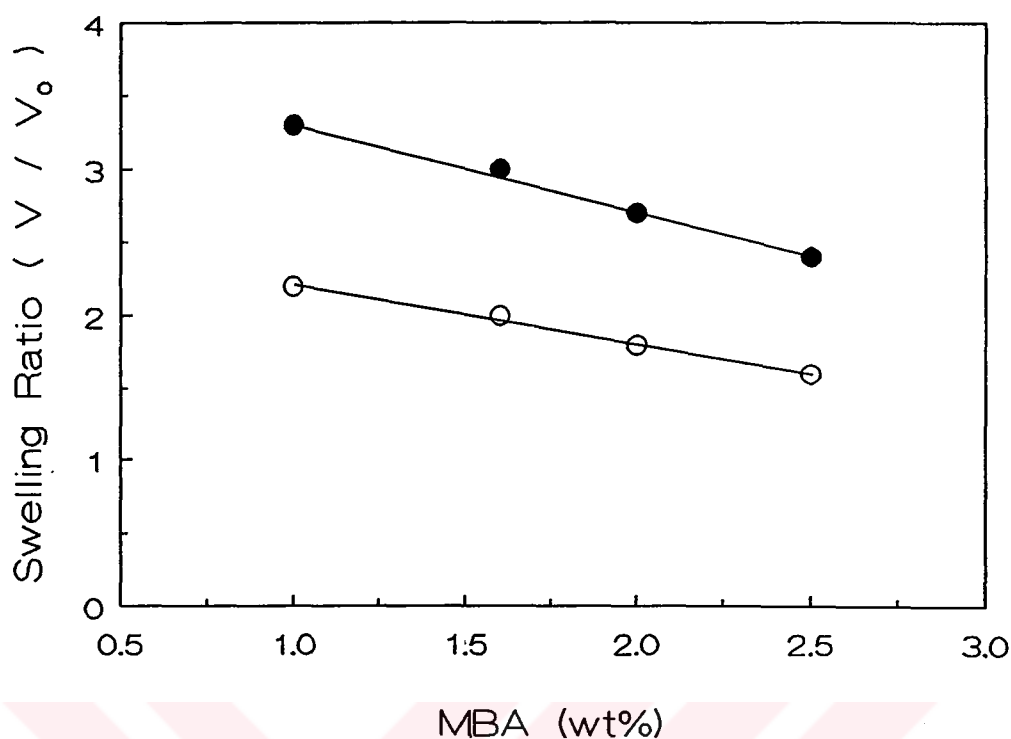


Figure 6.29. Variation of the equilibrium swelling ratio of PNIPA gels, with the crosslinker (MBA) content. Swelling measurements were performed at 4°C (●) and 23°C±1 (○). The gel preparation temperature = 25°C.

and at room temperature (23°C±1), respectively. The equilibrium swelling ratio decreases as the MBA content increases due to the increasing cross-linking density of the networks. Furthermore, the gel swells much more at low temperatures due to the decrease of the polymer-network interaction parameter χ_{12} of PNIPA-water system. From Figures 6.28 and 6.29, it may be concluded that high swelling ratios can be achieved at low swelling temperatures using loosely cross-linked PNIPA gels prepared at temperatures as high as 35°C.

Variation of swelling ratio of PNIPA gels immersed in aqueous solutions of bovine serum albumin (BSA) with the swelling time is shown in Figure 6.30. Prior to the swelling experiments, the equilibrium swollen gels in water after synthesis were collapsed by incubating them for 60 min at 55°C. The BSA concentration in the external solution was varied between 0 and 0.1 g / L. The gel volume increases first abruptly up to 2 h and then slightly increases with increasing swelling time. The gel attains its equilibrium volume in water after about 70 h. The results indicate that the

gel reaches 30% of its equilibrium volume within 2 h. This value is important for application of PNIPA gels as extraction solvent because it determines the time interval of the extraction process.

Figure 6.31 shows the separation efficiencies η^* of bovine serum albumin (BSA), penicillin G acylase (PGA) and 6-aminopenicillanic acid (6-APA) molecules by gel extraction with PNIPA gels plotted against the cross-linker content of the gels prepared at $23^\circ\text{C}\pm 1$. The filled and empty symbols represent the results of experiments carried out using BSA and PGA solutions, respectively. It is seen that about 80% of both BSA and PGA molecules do not penetrate inside the network. The loss of 20% may be attributed to the adsorption of protein molecules on the surface of the gel samples. Experiments carried out at two different temperatures,

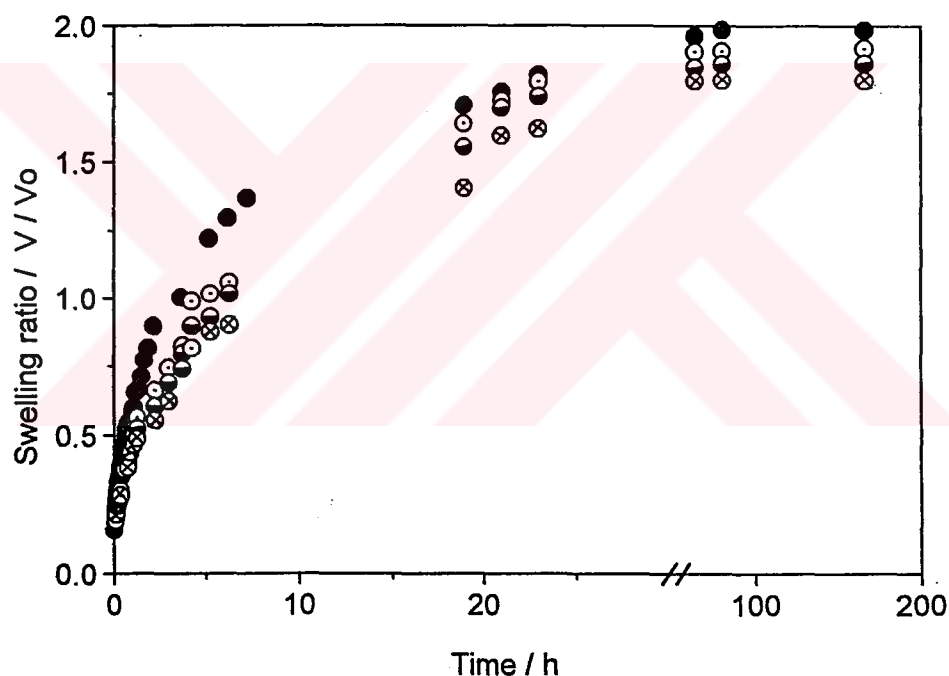


Figure 6.30. Variation of the swelling ratio V/V_0 of PNIPA gels immersed in BSA solutions with the swelling time. BSA concentration in the external solution = 0 ($\bullet$), 0.125 ($\odot$), 0.50 ($\bullet$) and 1.0 mg/10mL ($\otimes$). MBA content of the gel = 1.6 %. Preparation temperature = $23^\circ\text{C}\pm 1$. Swelling temperature = 25°C .

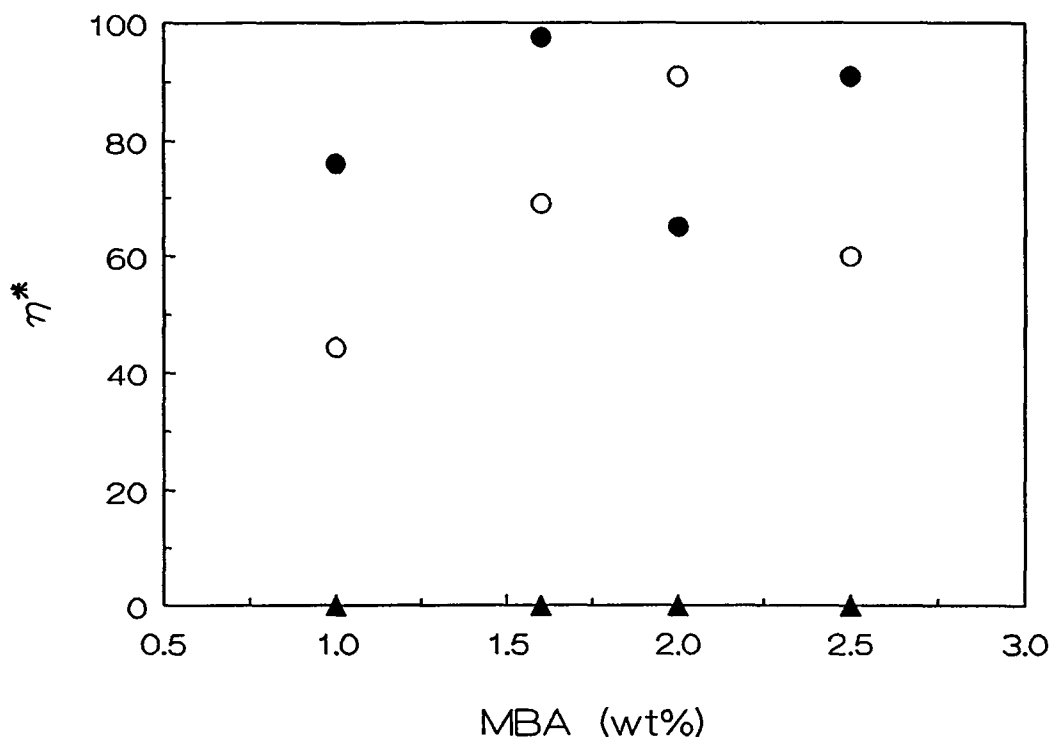


Figure 6.31. Effect of the crosslinker (MBA) content of PNIPA gels on the separation efficiency η^* of BSA ($\bullet$), PGA ($\circ$) and 6-APA ($\blacktriangle$) from dilute solutions. Gel preparation temperature = $23^\circ\text{C} \pm 1$.

namely at 4 and $23^\circ\text{C} \pm 1$, showed that the efficiency of the extraction process is largely insensitive to the extraction temperature. Compared to the protein molecules, the separation efficiency of 6-APA is zero, indicating that the concentration of 6-APA inside the gel phase is equal to that in the outer solution. Since the molecular weights of BSA and PGA are high (66000 g/mol and 90000 g/mol, respectively), they cannot penetrate the gel phase due to the loss in conformation entropy of the protein molecules as well as due to the repulsion between network and protein chains. However, as the molecular weight of the solute decreases as in the case of 6-APA (218 g/mol), the amount of molecules penetrating into the gel increases, i.e., the separation efficiency decreases. These results are in accord with our previous observation carried out with poly(acrylamide-co-acrylic acid) gels swollen in aqueous solutions of poly(ethylene glycol) of different molecular weights.

Figure 6.32 shows the variation of the separation efficiency η^* of PGA with the preparation temperature of PNIPA gels of 2 wt% MBA content. η^* is about 80% for homogeneous gels, i.e., for gels prepared below 25°C . However, for

heterogeneous gels formed at higher temperatures, η^* decreases abruptly due to the simultaneously increase of the gel's swelling ratio (Figure 6.28), which facilitates the penetration of PGA molecules inside the gel phase.

6.7.2. Inverse Suspension Polymerization

PNIPA gel beads prepared by inverse suspension polymerization were used for swelling and separation experiments. Rigid, transparent and spherical beads were obtained without using an external emulsifier and therefore, they are free from impurities affecting the separation process. The polymerization reaction was carried out at 100 rpm stirring rate and the beads obtained were in the size range of 0.125-2.8 mm in the swollen states. Figure 6.33 shows a typical size distribution of PNIPA beads with 2 wt% MBA content prepared at 100 rpm. The bar graph indicates that about 70% of the microspheres were in the range of 0.8-1.4 mm. A representative optical micrograph of the particles is shown in Figure 6.34.

The influence of the preparation technique of PNIPA gels with 2 wt% MBA content on their swelling properties is shown in Table 6.1. Here, the equilibrium swelling ratios are given in terms of the water absorption capacity, which is defined as the volume of water in equilibrium swollen gel per gram of dry gel. The gels were prepared under the same experimental conditions; the differences are only in the preparation technique used.

Table 6.1 clearly indicates that the gels A, which were prepared by inverse suspension polymerization technique, swell in water much more than the gels B which were obtained by solution polymerization. Furthermore, contrary to the gels B, the water absorption capacity of the gels A decreases as the gel preparation temperature increases. This inverse relation between the preparation temperature and equilibrium swelling ratio of the gel beads as well as their higher swelling ratios compared to the gels formed in solution can be accounted for the characteristics of inverse suspension

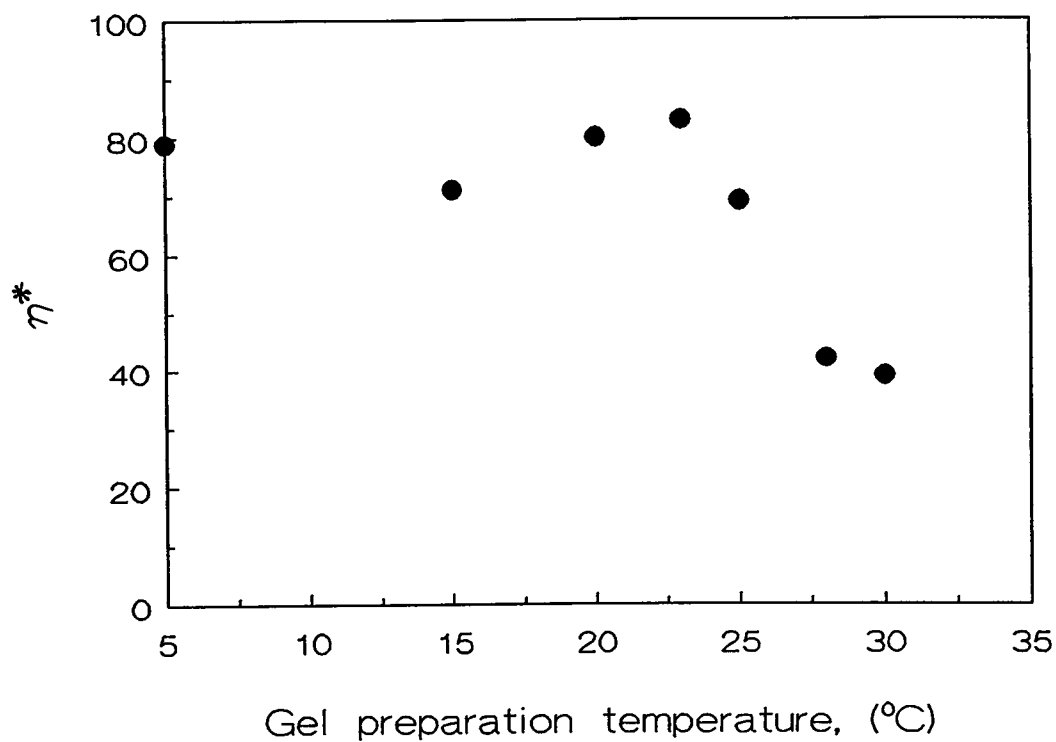


Figure 6.32. Variation of the separation efficiency η^* of PGA with the gel preparation temperature. Swelling experiments were performed at 4°C. MBA content of the PNIPA gel = 2 wt%.

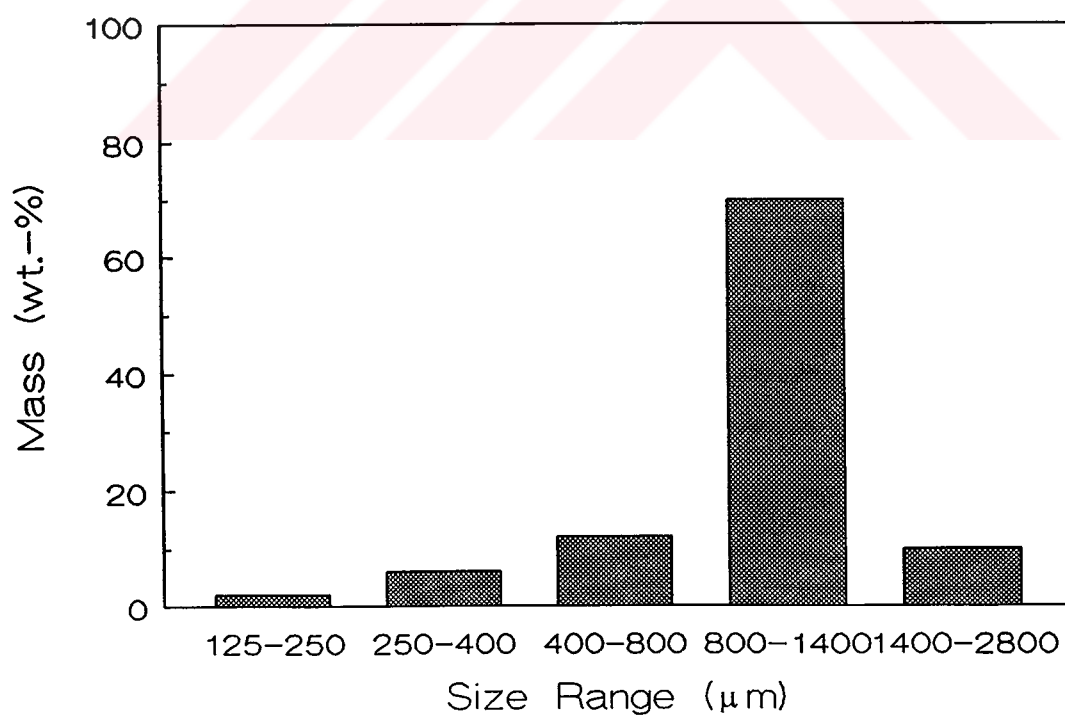


Figure 6.33. Size distribution of PNIPA beads with 2 wt% MBA content.



Figure 6.34. A representative optical micrograph of PNIPA gel beads obtained by inverse suspension polymerization technique. Magnification = 40x

Table 6.1. The influence of the preparation technique of PNIPA gels on their swelling properties. MBA = 2 wt%. Gels A were prepared by inverse suspension polymerization technique, whereas gels B were obtained by solution polymerization.

Preparation Temperature (°C)	Water absorption capacity (ml of water in swollen gel / g of dry gel)			
	at 4°C		at 23°C±1	
	A	B	A	B
4	37	24	33	15.5
10	34	27	31	16.5
25	32	28	25	22

polymerization technique. One possible explanation is the solubility of the monomers in the continuous phase, which decreases the monomer concentration in the droplets and so, increases the number of elastically inactive links within the final gel beads.

When the swelling rates of the gels A and B were compared, polymer gels in the form of beads absorb water more rapidly than the gels prepared by solution polymerization. For example, 1 g of the gel beads in dried state absorbs 20 ml of water in 10 min, whereas the same amount of gel in the form of rods absorbs only 3 ml of water in the same time interval. The higher water absorption capacity and rapid swelling feature of PNIPA gel beads make them the first choice as a separation agent in extraction experiments.

In the second column of Table 6.2, the separation efficiency η^* of PGA by PNIPA gel beads of sizes 0.25-0.40 mm is given for various gel preparation temperatures. When the polymer beads were used in the separation processes, the protein separation efficiency is less than 17%. This lower efficiency is probably due to the increase of the surface area of the gel when it is in the form of spherical beads, which increases the amount of adsorbed solute molecules on the bead surfaces. To overcome this problem, the gel beads of sizes 0.25-0.40 mm were immersed in BSA solutions of concentration 1 mg BSA / ml and they were left for 24 h prior to the separation experiments. In this way their surfaces were coated by protein molecules prior to the experiments. In the third column of Table 6.2, η^* values are collected for

Table 6.2. PGA separation efficiency η^* at 4°C using PNIPA gel beads of sizes 0.25-0.40 mm. MBA = 2 wt%.

Gel Preparation Temperature (°C)	η^*	
	Uncoated Beads	Coated Beads
4	4	28
10	11	47
25	17	74

coated PNIPA gel beads prepared at three different temperatures. It is seen that the separation efficiency η^* increases up to 74%.

The effect of the particle size of the coated gel beads on the separation efficiency η^* is seen in Table 6.3. η^* increases as the particle size of the coated beads increases. η^* approaches to 100% when the size of the PNIPA beads is larger than 0.8 mm.

Table 6.3. PGA separation efficiency η^* at 4°C using coated PNIPA gel beads of various sizes. MBA = 2 wt%. Gel Prep. Temp = 23°C±1.

Bead Size (mm)	η^*
0.25-0.40	69
0.40-0.80	72
0.80-1.40	99
1.40-2.80	100

6.8. Coil-Globule Transition of Poly(methyl methacrylate)

According to the polymer solution thermodynamics, polymer chains in solution show various dimensions depending on the solvent quality. In poor solvent below the θ temperature, the mean force acting between the segments of a polymer chain becomes attractive. The attraction leads to a shrinkage of the polymer coil below its size under the θ condition, and the degree of shrinkage should increase as the temperature is lowered. As the coil shrinks, its segment density increases and the chain is collapsed. This change in the state of a polymer chain from the open coil to the globular particle is called the coil-globule transition[52].

The coil-globule transition observed for polyacrylamide molecules in acetone-water mixtures by varying the composition[105], a covalently cross-linked polyacrylamide network had been known to collapse reversibly in the mixtures. In addition several experimental studies of this transition have been reported mainly using polystyrene solution systems[41, 43, 45, 53-54]. The greatest difficulty of these studies is that quite high molecular weight and well-fractionated samples and dilute enough solutions are necessary.

On the otherhand, poly(N-isopropyl acrylamide) chains in water show unique thermal behavior, that is, a phase change occurs reversibly at some temperature independent of molecular weights and concentrations. Moreover, it has been observed that hydrogels of this polymer show a volume phase transition and this has attracted great attention because of its technological, mechanical and scientific importance[106].

In order to support our understanding the underlying theory on the volume-phase transitions of hydrogels induced by varying the solvent composition and temperature, it is of importance to investigate the solution and thermal behavior of linear polymer around the phase-change temperature. Since the extensively studied polystyrene-cyclohexane system shows limited contraction, we studied the coil-globule transition of two different molecular weight PMMA samples ($M_w = 2.55 \times 10^6$ g/mol for PMMA-1 and $M_w = 4.73 \times 10^6$ g/mol for PMMA-2) in their θ solvent (*tert*-butyl alcohol + water) by viscosity measurements.

As it was pointed out in section 4.3. in details, Birshtein and Pryamitsyn indicated that the Flory equation for α cannot be extended to the globule state because of the different segment distributions about the center of mass in expanded and contracted coils. Therefore, in this section we investigated the transition of a Gaussian chain to a compact globule, in the light of Birshtein and Pryamitsyn's theory.

The experimental results of specific viscosities in *tert*-butyl alcohol + water mixture for two poly(methy methacrylate) samples are reported in Table 6.4 and 6.5. Since the viscosity measurements were carried out at very low concentrations (2.55×10^{-5} g/ml), it is assumed that the measured values of specific viscosities are identical to intrinsic viscosities. Nakata recently has found that the second virial coefficient, A_2 , vanishes at 41.5°C so that this temperature can be taken as θ temperature for PMMA ($M_w = 2.38 \times 10^6$ g/mol) in mixed solvent system [71].

Figure 6.35 shows the temperature dependence of intrinsic viscosities for these two PMMA samples in *tert*-butyl alcohol + water solution at above and below of theta temperature. For PMMA-1 a gradual transition was observed up to 16°C. At lower temperatures it was not possible to obtain reproducible results. After performing viscosity measurements at 16°C, the solution was heated to 55°C and shock cooled to 21°C. The same specific viscosity results were obtained for these runs at 21.05 and 20.00°C. The viscosity measurements were replicated using the same PMMA-1 solution and the results were given in Table 6.4.

The α_η^3 values of PMMA-samples were plotted against temperature in Figure 6.36. For comparison, the α^2 values of PMMA reported by Nakata[71] were included in this figure. The viscosity expansion factors, α_η^3 , were reduced gradually 86-87% of their θ state dimension. That means, a true collapse experiment was realized in this PMMA-*tert*-butyl alcohol + water system.

In order to compare the observed behavior with the theory α^2 values were calculated by using Equation (4.20) and (4.21). The related computer programs were given in Appendix G. The theoretical data were plotted in Figure 6.37 against the temperature. Literature values of light scattering data[71] were also included in this figure.

To evaluate the parameters B and C given in Equation (4.20), $(\alpha^3 - \alpha)/(1 - \alpha^3)$ values were plotted against $\tau N^{1/2} / (1 - \alpha^3)$ in Figure 6.38, for contraction of PMMA

Table 6.4. Specific Viscosities of Poly(methyl methacrylate) ($M_w = 2.55 \times 10^6$ g/mol in *tert*-BuOH + water mixture). $C = 2.55 \times 10^{-5}$ g / ml

Temp (°C)	$10^3 \eta_{sp}$	α_{η}^3 (η_{sp} / η_{sp}^0)	α^2 ($\alpha_{\eta}^3 = \alpha^{2.43}$)	$\tau M_w^{1/2}$	$\alpha^3 \tau M_w^{1/2}$
70.00	15.257	1.119	1.161	---	---
65.00	14.922	1.173	1.140	---	---
59.90	15.382	1.209	1.169	---	---
55.30	14.564	1.145	1.118	---	---
50.00	14.290	1.123	1.100	---	---
45.10	13.587	1.068	1.055	---	---
43.00	13.340	1.048	1.040	---	---
42.05	13.054	1.026	1.021	---	---
41.50	12.725	1.000	1.000	0	0
41.00	11.644	0.915	0.930	2.537	2.274
40.10	10.486	0.824	0.853	7.11	5.595
37.90	9.161	0.720	0.763	18.27	12.18
35.05	7.290	0.573	0.632	32.73	16.46
34.10	6.680	0.525	0.588	37.55	16.95
32.15	5.552	0.436	0.505	47.45	17.04
30.00	4.526	0.356	0.427	58.36	16.29
28.00	3.411	0.268	0.338	68.51	13.49
25.10	2.547	0.200	0.266	83.23	11.42
22.10	2.256	0.177	0.241	98.46	11.63
21.05	2.032	0.160	0.221	103.79	10.71
20.00	2.081	0.164	0.225	109.12	11.65
19.10	2.019	0.159	0.220	113.68	11.71
18.00	1.943	0.153	0.213	119.26	11.72
17.00	1.872	0.147	0.207	124.34	11.67
16.00	1.770	0.139	0.197	129.41	11.33
21.05*	1.931	0.152	0.212	103.74	10.12
20.00*	2.026	0.159	0.220	109.11	11.29
41.00 ⁺	12.385	0.973	0.978	2.54	2.45
40.10 ⁺	11.218	0.882	0.902	7.11	6.08
37.90 ⁺	9.263	0.728	0.770	18.27	12.34
36.00 ⁺	7.815	0.614	0.670	27.91	15.29
20.00 ⁺	2.021	0.159	0.220	109.11	11.25
18.00 ⁺	1.948	0.153	0.213	119.26	11.72
16.00 ⁺	1.849	0.145	0.205	129.41	12.27

* Shock cooling from 55°C; ⁺ Repeat experiments with a new solution.

Table 6.5. Specific Viscosities of PMMA ($M_w = 4.73 \times 10^6$ g/mol) in *tert*-BuOH + water mixture. $C = 2.54 \times 10^{-5}$ g/mol

Temp (°C)	$10^3 \eta_{sp}$	α_η^3 (η_{sp} / η_{sp}^0)	α_η^2 ($\alpha_\eta^3 = \alpha_\eta^{2.43}$)	$\tau M_w^{1/2}$	$\alpha^3 \tau M_w^{1/2}$
70.00	17.967	1.332	1.266	---	---
65.15	18.133	1.344	1.276	---	---
59.90	17.811	1.320	1.257	---	---
55.10	17.321	1.284	1.228	---	---
50.00	16.793	1.244	1.198	---	---
45.10	15.819	1.173	1.140	---	---
43.00	14.681	1.088	1.072	---	---
42.00	14.163	1.050	1.041	---	---
41.50	13.490	1.000	1.000	0	0
41.00	12.099	0.897	0.914	3.456	3.021
40.00	10.859	0.805	0.836	10.37	7.931
38.00	9.125	0.676	0.725	24.19	14.93
37.00	8.716	0.646	0.698	31.10	18.14
36.00	8.081	0.599	0.656	38.02	20.19
35.00	6.953	0.515	0.580	44.93	19.82
34.00	6.002	0.445	0.514	51.84	19.08
32.00	4.875	0.361	0.433	65.66	18.69
30.00	3.832	0.284	0.355	79.49	16.46
28.00	2.677	0.199	0.264	93.31	12.66
25.10	2.145	0.159	0.220	113.36	11.71
22.00	1.919	0.142	0.200	134.78	12.06
21.00	1.805	0.134	0.191	141.69	11.98
20.00	1.749	0.130	0.186	148.61	11.92

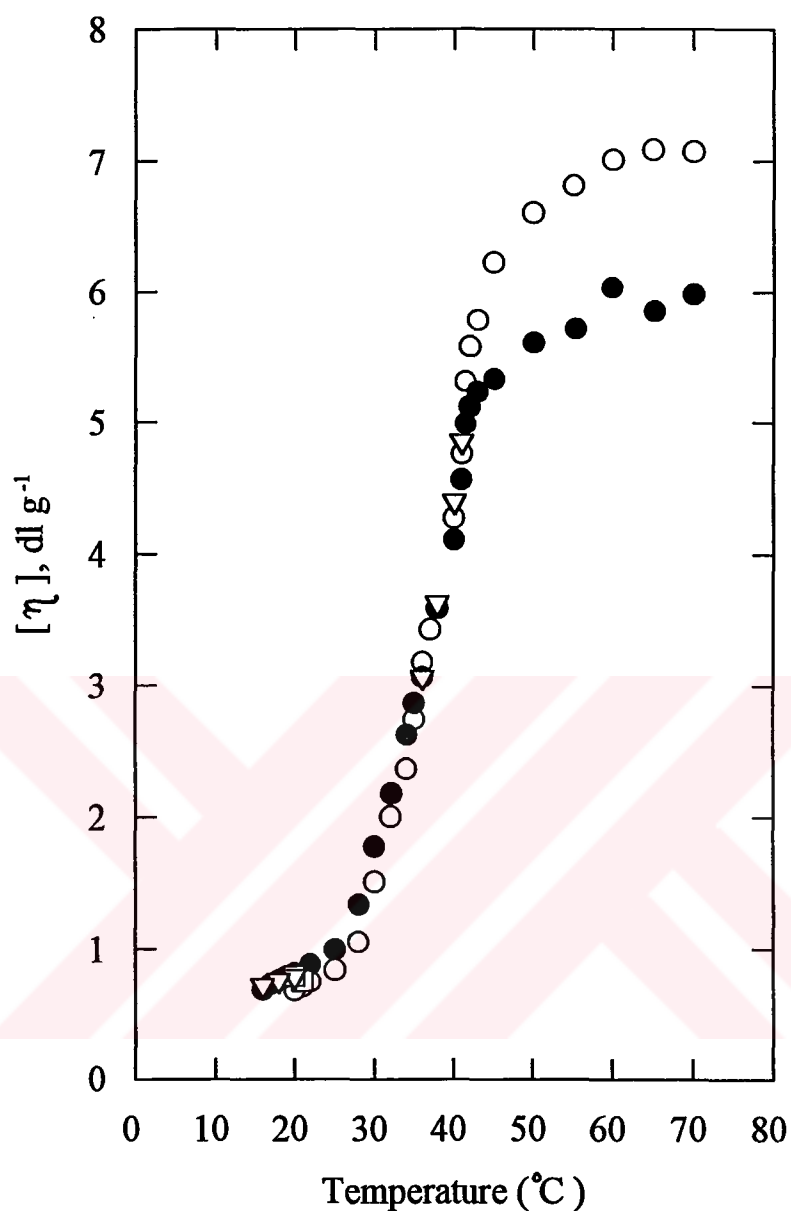


Figure 6.35. Intrinsic viscosity $[\eta]$ versus temperature for poly(methyl methacrylate) in *tert*-butyl alcohol + water mixture. The intrinsic viscosities for: (o) $M_w = 4.73 \times 10^6$; (•) $M_w = 2.55 \times 10^6$ (□) $M_w = 2.55 \times 10^6$ “shock cooling experiments”; (▼) $M_w = 2.55 \times 10^6$ “repeat experiments with a new solution”.

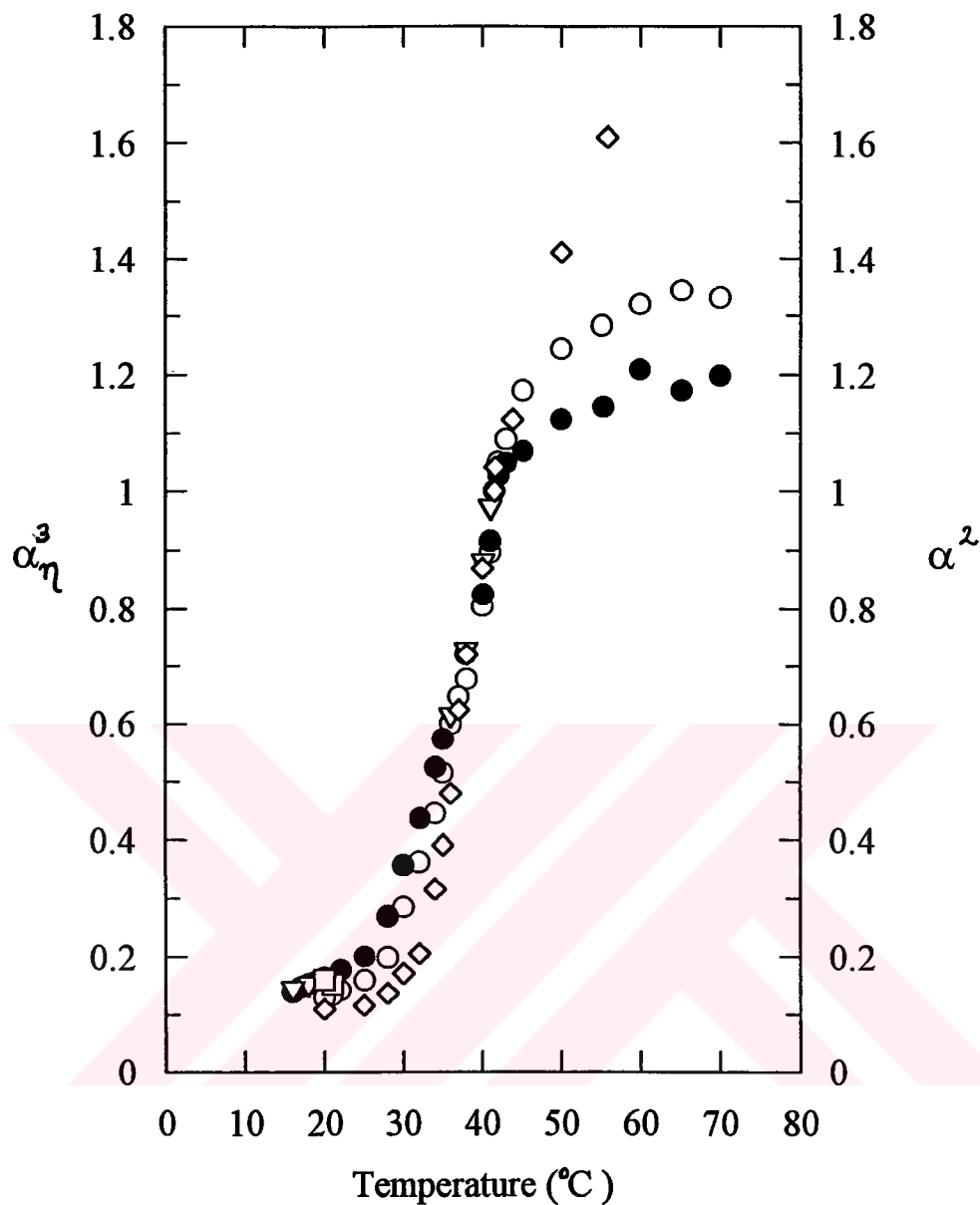


Figure 6.36. Plot of expansion factor, α_η^3 , versus temperature for PMMA in *tert*-butyl alcohol + water mixture. For comparison, α^2 values obtained from Ref.71 were included and denoted by $\diamond$.
 (o) $M_w = 4.73 \times 10^6$; ($\bullet$) $M_w = 2.55 \times 10^6$;
 ($\square$) $M_w = 2.55 \times 10^6$ “shock cooling experiments”;
 (∇) $M_w = 2.55 \times 10^6$ “repeat experiments with a new solution”.

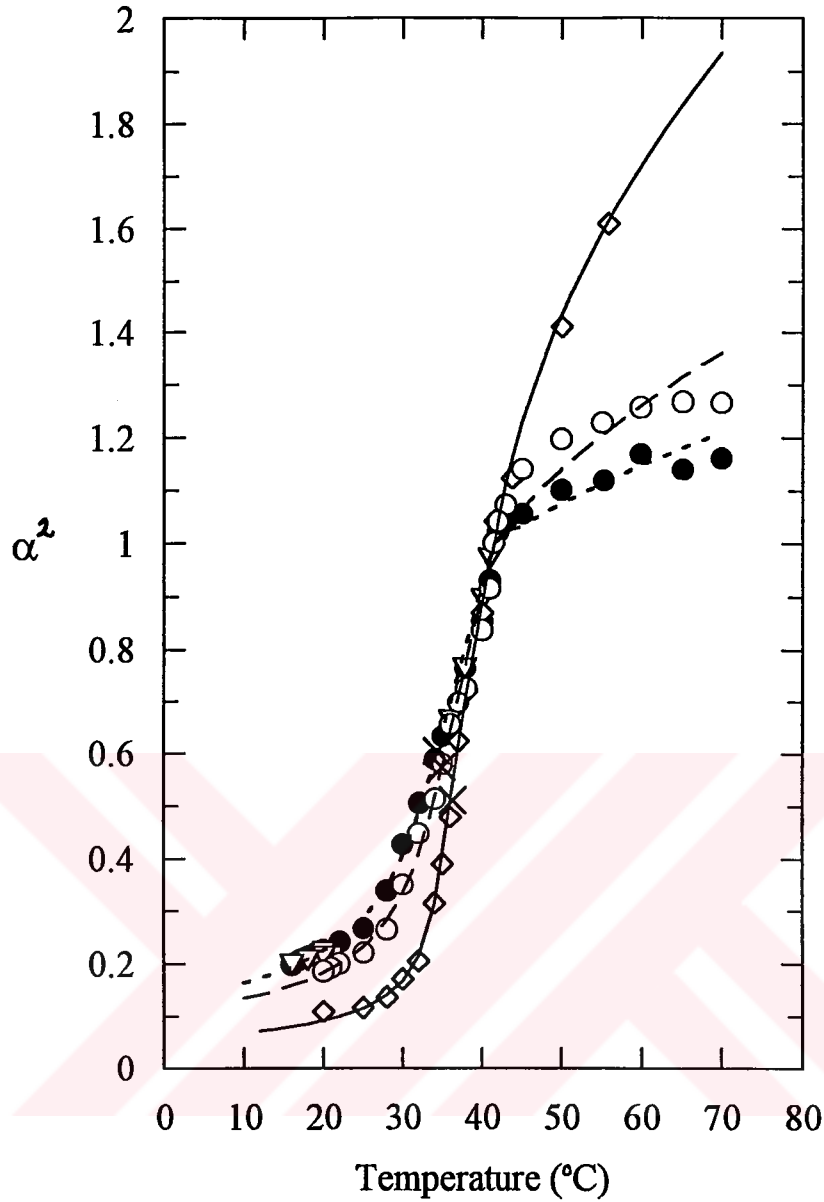


Figure 6.37. Comparison of theoretical and experimental values of the expansion factor, α^2 . Theoretical curves calculated from Eqn.(4.20) for $T < \theta$ and Eqn.(4.21) for $T > \theta$ and denoted by broken lines. For experimental points, the ordinate denotes $\alpha^2 = \alpha_\eta^{6/2.43}$ (see Eqn.(4.12)). The crosses indicate coil-globule transition points.
 (o) $M_w = 4.73 \times 10^6$; (•) $M_w = 2.55 \times 10^6$;
 (□) $M_w = 2.55 \times 10^6$ "shock cooling experiments";
 (▽) $M_w = 2.55 \times 10^6$ "repeat experiments with a new solution"
 (◇) Ref.71.

chains ($\alpha < 1$) below the θ temperature. The calculation of the number of Kuhn segments in PMMA chain was given in Appendix H. From the slopes and intercepts of linear plots B and C values were calculated and given in Table 6.6.

Parameter B in Equation (4.21) was evaluated plotting $(\alpha^5 - \alpha^3)$ values against $N^{1/2} \tau$ in Figure 6.39 for expansion of PMMA chains ($\alpha > 1$) above the θ temperature. The calculated B values were also included in Table 6.6. Figure 6.39 shows that the radius expansion factors indicate much bigger expansions compare with viscosity expansions.

It may be seen from Table 6.6 that both B and C values for contraction and B value for expansion are depend on molecular weight of the PMMA chains. The values of these parameters are also depend on experimental method used to study the dimension of polymeric chains. This diversity between theory and experiments was also observed for polystyrene-cyclohexane system[107].

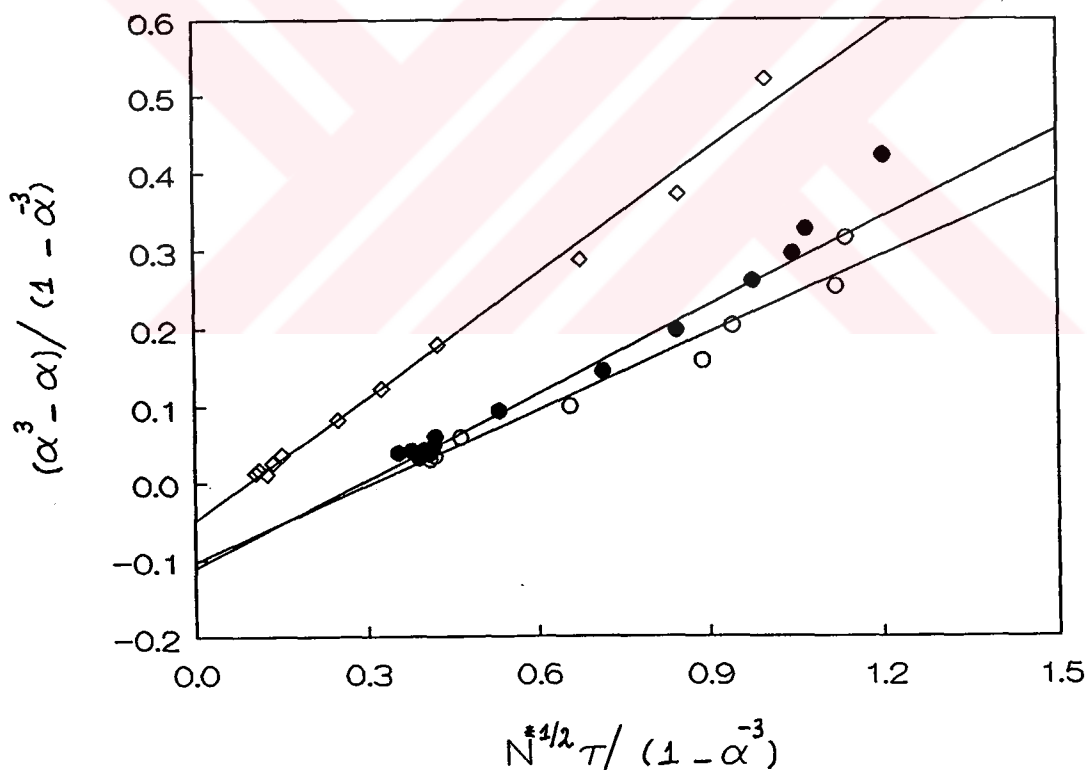


Figure 6.38. A plot of $(\alpha^3 - \alpha)/(1 - \alpha^3)$ versus $\tau N^{1/2} / (1 - \alpha^3)$ for random coil-globule transition of PMMA. (○) $M_w = 4.73 \times 10^6$; (●) $M_w = 2.55 \times 10^6$; (◇) Ref. 71.

Table 6.6. The values of parameters of B and C for PMMA-*tert*-butyl alcohol + water system

	$M_w = 2.55 \times 10^6$	$M_w = 4.73 \times 10^6$	$M_w = 2.38 \times 10^6$
	$(\tau < 0)$		
B	0.377	0.295	0.506
C	0.110	0.085	0.044 ^a
(C/B) ^b	9.23	9.15	2.75 ^a
	$(\tau > 0)$		
B	0.061	0.092	0.569 ^a

^a Ref.71, ^b Reported ratios were obtained multiplying the (C/B) values by $(M_w/N^*)^{1/2}$ values.

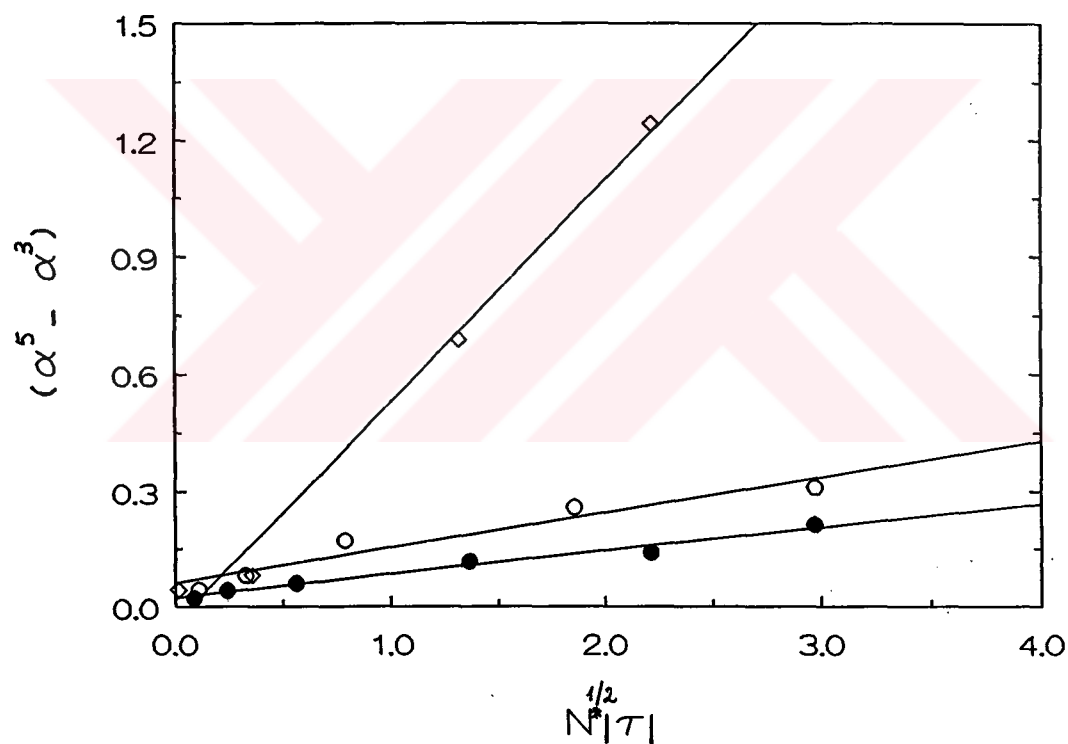


Figure 6.39. A plot of $(\alpha^5 - \alpha^3)$ versus $N^{*1/2} |\tau|$ for expansion of PMMA.
 (o) $M_w = 4.73 \times 10^6$; (•) $M_w = 2.55 \times 10^6$; (◊) Ref.71.

In Figure 6.40, universal curves of scaled expansion factor, $\alpha^3 |\tau| M_w^{1/2}$, were plotted against scaled reduced temperature, $|\tau| M_w^{1/2}$, to observe the transition to globule state. These points represent the experimental data. The light scattering data was included to compare the results of experimental methods[71]. The curves give the calculation due to Equation (4.20). The horizontal lines at the right indicate asymptotic values $\alpha^3 |\tau| M_w^{1/2} = (C / B)$. The curves approach the asymptotic limit for $|\tau| M_w^{1/2} > 90$.

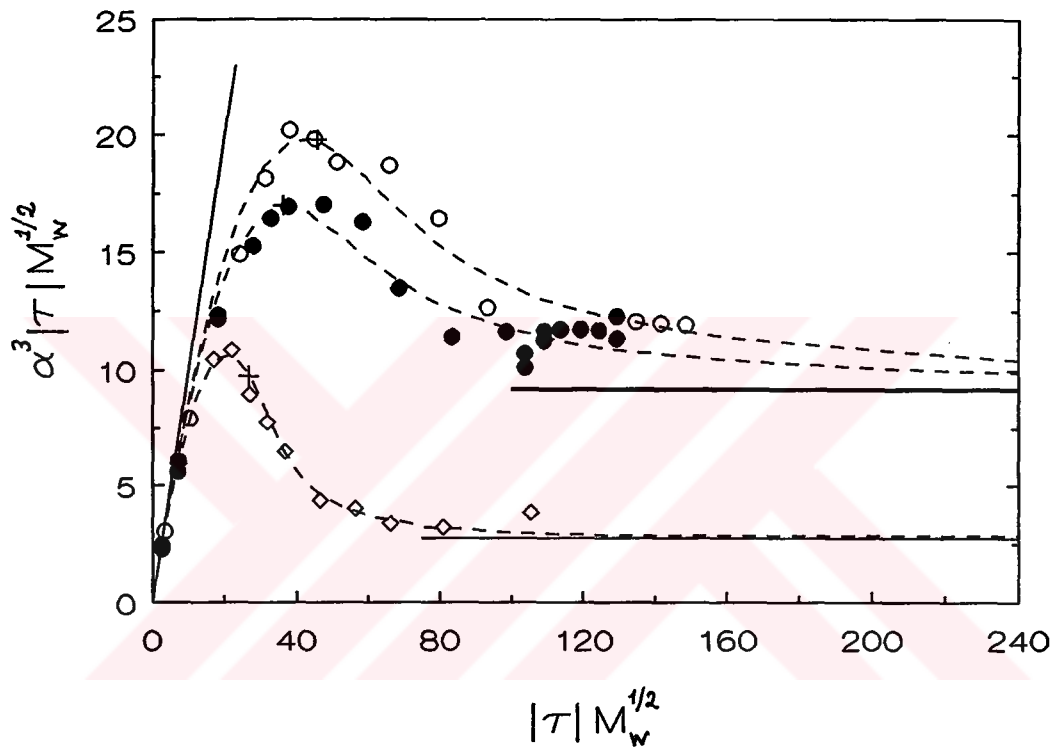


Figure 6.40. Plot of scaled expansion factor $\alpha^3 |\tau| M_w^{1/2}$ of intrinsic viscosity as a function of scaled reduced temperature $|\tau| M_w^{1/2}$. The solid and the hollow circles are for viscosity data of PMMA-1 and PMMA-2, respectively. The hollow diamonds denote the dynamic light scattering data obtained from Ref.71. The broken lines are for Eqn.(4.20). The horizontal lines indicate the asymptotic limits. The crosses indicate crossover points.

The inflection points of the curves in Figure 6.37 represent critical conditions and indicate coil-globule transition points. α^2 values were obtained by considering $\frac{d^2T}{d\alpha^2}=0$. The evaluated values of α^2 were 0.604 and 0.574 for PMMA-1 and 2 respectively. The reported light scattering value was 0.511[71]. Corresponding $|\tau| M_w^{1/2}$ values were 36.2, 45.5 and 26.7 respectively. The crossover points were also shown in Figure 6.40.

The radius of single amorphous poly(methyl methacrylate) molecules for PMMA-1 and PMMA-2 samples were calculated using the density of amorphous PMMA as 1.191 g cm^{-3} and were given in Table (6.7). The radius calculated using Equations (4.4) and (4.5) were also given in Table (6.7). The calculated radii of PMMA-1 and PMMA-2 samples from hydrodynamic volumes were not identical to the amorphous solid molecules. That means collapsed globules still contains considerable amounts of solvent molecules.

Using the values, $\alpha_s^2 = 0.331$ [71], $\alpha_\eta^2 = 0.5171$ (16°C) and $\langle R_g^2 \rangle_\theta^{1/2} / \langle R_h^2 \rangle_\theta^{1/2} = 1.25$ [108], and the following well known relation

$$\frac{\alpha_s^2}{\alpha_\eta^2} = \frac{\langle R_g^2 \rangle}{\langle R_h^2 \rangle} \times \frac{\langle R_h^2 \rangle_\theta}{\langle R_g^2 \rangle_\theta} \quad (6.1)$$

we can calculate the ratio, $R_g / R_h = 0.798$ which is in agreement with $(3/5)^{1/2} = 0.774$.

The mean square radius of gyration reported by Nakata for a PMMA sample having approximately identical molecular weight ($2.38 \times 10^6 \text{ g/mol}$) in the same θ solvent system at 20°C is found to be $\langle s^2 \rangle = 0.16 \times 10^{-11} \text{ cm}^2$ [71]; As it is well known, the following relation holds for polymeric chains,

$$\langle r^2 \rangle / \langle s^2 \rangle = 6 \quad (6.2)$$

The calculated ratio for the collapsed globule of PMMA is as follows: $(304 \times 10^{-8})^2 / 1.6 \times 10^{-12} = 5.8$.

For the PMMA samples used in this work, tacticity determined from ^1H NMR (Table 5.2) indicates the presence of higher percent syndiotriads compare with an atactic free radical poly(methyl methacrylate)[71].

Table 6.7. Dimensions of PMMA molecules

	radius of an amorphous solid molecule	radius calculated from hydrodynamic volume Eqns.(4.4) and (4.5)
PMMA-1	95 Å°	304 Å° (16°C)
PMMA-2	116 Å°	295 Å° (20°C)

CONCLUSIONS AND RECOMMENDATIONS

The conclusion that can be drawn from the experimental findings of this work can be summarized as follows:

Polyacrylamide gels were prepared by free-radical cross-linking copolymerization of acrylic acid with N,N'-methylenebis(acrylamide) in aqueous solution. Acrylic acid was used as the ionizable comonomer.

Non-ionic polyacrylamide (PAAm) gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) exhibit a continuous volume change upon continuous increase of the PEG concentration in the external solution. The volume change becomes discontinuous when ionizable groups are incorporated into the network. As the proportion of ionizable groups increases, or, as the molecular weight of PEG decreases, the critical concentration of PEG required for a discontinuous volume collapse rises. The distribution of PEG inside and outside the gel phase changes with gel volume; it also exhibits a discontinuous change at the phase transition.

The addition of a small amount of ethylene glycol oligomers (OEG) with number of repeat units $y = 2-4$ in the aqueous solution leads to the contraction of both linear and cross-linked poly(acrylamide-co-acrylic acid) chains. These results present clear evidence for the screening effect of OEG on the ionic groups of the polymer chains. Linear and network chains of ionic PAAm in 10% TEG-water mixtures behave like nonionic polymers.

The immersion of swollen ionic PAAm gels in PEG solutions leads to the formation of nonequilibrium structures. These structures become more stable as the initial swelling degree of the gels increases.

Hydrolyzed polyacrylamide gels immersed in aqueous solutions of PEG of molecular weight 300 exhibit a discontinuous volume change upon continuous increase of the PEG concentration in the external solution. As the time of hydrolysis increases, that is, as the proportion of the ionic groups on the network chains increases, the critical concentration of PEG required for a discontinuous volume

change rises and also, the magnitude of the volume collapse becomes larger. Experimental results indicate that the gel collapse in PEG solution is due to the osmotic deswelling of the ionic gel rather than due to the complex formation between polyacrylamide and poly(ethylene glycol) chains.

The volume of PAAm gels in aqueous solutions of linear PAAm decreases as the concentration or the molecular weight of linear polymer in the external solution increases. It is shown that this swelling behavior of non-ionic gels is correctly predicted by the classical Flory-Huggins (FH) theory. The polymer-polymer interaction parameter χ_{23} decreases as the molecular weight of PAAm solutions increases. The swelling behavior of PAAm-co-PAAc gels in PAAm solutions deviates from the predictions of FH theory. This is probably due to the change of the ionization degree of AAc units depending on the polymer concentration in the external solution.

Cross-linked poly(N-isopropyl acrylamide) (PNIPA) gels with different cross-link densities in the form of rods and beads were prepared by free radical cross-linking copolymerization. Solution and inverse suspension polymerization techniques were used for the gel synthesis. It can be concluded that the polymerization technique used significantly affects the properties of PNIPA gels. The swelling capacity of the gels further increases when they are prepared in the form of beads by using inverse suspension polymerization technique. The separation efficiency η of BSA and PGA by gel extraction with PNIPA gels formed in solution was found to be about 80%. If the same gels were prepared by inverse suspension polymerization technique, η decreases up to 4-17%. However, after coating the gel beads by protein molecules prior to the separation experiments, separation efficiency values of 100% were reached using gel beads of sizes larger than 0.8 mm.

Coil-globule transition of poly(methyl methacrylate) has been studied in the mixed solvent *tert*-butyl alcohol+water system. Two polymeric samples having molecular weights $M_w = 2.55 \times 10^6$ and $M_w = 4.73 \times 10^6$ were used. The viscosity expansion factors, α_η^3 , were reduced gradually 86-87% of their θ -state dimension. That means, a true collapse experiment was realized in this PMMA-*tert*-butyl alcohol+water system.

The present investigation concerns the preparation of polyacrylamide gels and their swelling properties in linear poly(ethylene glycol) solutions. For future studies, experiments may be performed to prepare hydrophilic polyurethane networks that contain poly(ethylene glycol) units. The swelling behavior of this polyurethane hydrogels may be investigated in linear polyacrylamide solutions.

On the other hand, coil-globule transition of highly syndiotactic poly(methyl methacrylate) may be examined by viscosimetry and light scattering measurements.



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Appendix A

The Calculations of Soluble Fractions of Gels

For a PAAm gel soluble fractions can be calculated as follows:

Final weight of the precipitate after vacuum drying	:	0.0008 g
--	---	----------

Final weight of extracted sample after vacuum drying	:	0.833 g
---	---	---------

$$\text{Soluble fraction (\%)} = \frac{0.0008}{0.8330} \times 100$$

$$\cong 0.1 \%$$



Appendix B

The Calculations of Swelling Data

For a polyacrylamide gel, swelling data from the gravimetric analysis was the following:

Dry weight of the sample : 0.0383 g

Swollen weight of the sample
in water : 1.2429 g

$$q_w = \frac{\text{swollen weight}}{\text{dry weight}} = \frac{1.2429}{0.0383} = 32.452 \quad (\text{B.1})$$

$$q_v = \text{swelling ratio} = \frac{1}{v_{2m}} \quad (\text{B.2})$$

$$q_v = 1 + \frac{(q_w - 1) \rho}{d_1} \quad (\text{B.3})$$

$$\rho_{\text{PAAm}} = 1.42 \text{ g / cm}^3 [93], \quad d_{\text{water}} = 1.0 \text{ g / cm}^3$$

$$q_v = 1 + \frac{(32.452 - 1) 1.42}{1.0} = 45.662$$

$$v_{2m} = \frac{1}{q_v} = 0.0219$$

$$\frac{V}{V_0} = \frac{v_2^0}{v_{2m}} \quad (\text{B.4})$$

$$v_2^0 = 0.035$$

$$\frac{V}{V_0} = \frac{0.0350}{0.0219} = 1.60$$

The swelling measurements were also carried out with volumetric method. The data for polyacrylamide gel taken from digital caliper as follows:

D_0 = initial diameter of the gel after synthesis

D = swelling equilibrium diameter of the gel

$D_0 = 5.80$ mm

$D = 6.81$ mm

$$\frac{V}{V_0} = \left(\frac{D}{D_0} \right)^3 = \left(\frac{6.81}{5.80} \right)^3 = 1.62$$



Appendix C

The Calculations of Linear Polymer Distribution Inside and Outside The Gel Phase

A calibration curve was prepared for PEG 300 and a relation between concentration of aqueous PEG 300 solution and its refractive index was found and given as follows:

$$n^{20} = 1.33406 + 0.001357 c \quad (C.1)$$

n^{20} = refractive index at 20.0 °C

c = concentration of aqueous PEG 300 solution (% w/v)

PEG 300 distribution inside and outside the polyacrylamide gel phase, v_3 / ϕ (Figure 6.3), can be calculated as follows:

The volume fraction of PEG 300
in the outer solution :

$$\phi = 0.2$$

The refractive index of 10 ml of
solution used in extraction experiment :

$$n^{20} = 1.3374$$

$$c \text{ (\% w/v)} = \frac{1.3374 - 1.33406}{0.001357}$$

$$= 2.46 \%$$

The amount of extracted PEG 300
from 10 ml of solution

$$= \frac{2.46}{100} \times 10$$

$$= 0.246 \text{ g}$$

$$m_{\text{swollen gel}} = 1.7180 \text{ g}$$

$$m_{\text{dry gel}} = 0.1157 \text{ g}$$

$$m_{\text{water}} = m_{\text{swollen gel}} - m_{\text{dry gel}}$$

$$= 1.7180 - 0.1157$$

$$= 1.6023 \text{ g}$$

(C.2)

$$\rho_{\text{PAAm}} = 1.42 \text{ g / cm}^3 [93], \quad d_{\text{water}} = 1.0 \text{ g / cm}^3, \quad d_{\text{PEG}} = 1.1 \text{ g / cm}^3$$

$$V_{\text{swollen gel}} = \frac{m_{\text{dry gel}}}{\rho_{\text{PAAm}}} + \frac{m_{\text{water}}}{d_{\text{water}}} \quad (\text{C.3})$$

$$= \frac{0.1157}{1.42} + \frac{1.6023}{1.00}$$

$$= 1.6838 \text{ ml}$$

The volume of fraction PEG in 1.6838 ml of swollen polyacrylamide gel was:

$$v_3 = \frac{0.246 / 1.1}{1.6838} = 0.1328$$

$$v_3 / \phi = \frac{0.1328}{0.2} = 0.664$$



Appendix D

The Calculations of Protein Separation Efficiency

Protein separation efficiency of N-isopropyl acrylamide gel, η^* (Figure 6.31), can be calculated as follows:

$$\eta^* = \frac{\text{actual increase in raffinate concentration}}{\text{expected increase in raffinate concentration}} \times 100 \quad (\text{D.1})$$

(from the altered solution volume)

$$= \frac{\frac{m_{\text{final}}}{V_{\text{final}}} - \frac{m_{\text{initial}}}{V_{\text{initial}}}}{\frac{m_{\text{initial}}}{V_{\text{final}}} - \frac{m_{\text{initial}}}{V_{\text{initial}}}} \times 100 \quad (\text{D.2})$$

$$= \frac{c - c_0}{c_0 \left(\frac{V_0^*}{V^*} - 1 \right)} \times 100 \quad (\text{D.3})$$

Initial concentration of BSA	= 0.125 mg / ml
Initial solution volume	= 2 ml
Initial weight of gel	= 1.031 g
Temperature	= 23°C±1
Incubation time	= 90 min
Remaining solution volume	= 0.9746 ml

Remaining solution concentration was determined from ultraviolet spectroscopy by measuring optical density of the solution at 415 nm.

Remaining solution concentration = 0.2539 g /ml

$$\eta^* = \frac{0.2539 - 0.125}{0.125 \left(\frac{2}{0.9746} - 1 \right)} \times 100 = 98\% \quad (\text{Figure 6.31})$$



Appendix E

**The Calculation of the Volume Fraction of the Network After Synthesis, v_2^0 ,
The Average Molecular Weight Between Junctions, M_c ,
The Number of Segments in a Network Chain, N ,
The Mean Number of Ionic Units Between Successive Junctions, f ,
and
The Interaction Parameter Between Polymer Network and Linear Polymer, χ_{23} ,
Values of Polymer Gels**

Calculation of v_2^0 :

The volume fraction of the network after preparation, v_2^0 , was given as follows:

$$v_2^0 = \frac{\text{volume of the dry network}}{\text{volume of the network after synthesis}} \quad (\text{E.1})$$

$$v_2^0 = \frac{V_{\text{dry}}}{V_{\text{initial}}} = \frac{m_{\text{dry}} / \rho}{V_{\text{initial}}} \quad (\text{E.2})$$

For the PAAm gel which were prepared according to procedure described in section 5.3.1.1, the v_2^0 can be calculated as follows:

$$\rho_{\text{PAAm}} = 1.42 \text{ g / ml } [93]$$

$$v_2^0 = \frac{5 \text{ g} / 1.42 \text{ g/ml}}{100 \text{ ml}} = 0.035$$

Calculation of M_c and N :

The average molecular weight between junctions, M_c and the number of segments in a network chain, N , were given as follows:

$$M_c = - \frac{\rho v_1 (v_2^{0/3} v_{2m}^{1/3} - v_{2m}/2)}{\ln(1 - v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2} \quad (E.3)$$

$$N = \frac{M_c}{\rho v_1} \quad (E.4)$$

where ρ is the density of polymer gel, v_1 is the molar volume of solvent, v_2^0 is the volume fraction of network after synthesis, v_{2m} is the volume fraction of network in the equilibrium swollen gel and χ_{12} is the network-solvent interaction parameter.

For the non-ionic PAAm gel swollen in water, the M_c and N values were calculated as follows: (section 6.3)

$$\begin{aligned} \rho_{\text{PAAm}} &= 1.42 \text{ g/ml} \quad [93] \\ v_2^0 &= 0.035 \\ \chi_{12} &= 0.48 \\ v_{2m} &= 0.0216 \\ v_1 &= 18 \text{ ml/mol} \end{aligned}$$

$$M_c = - \frac{1.42 \times 18 \times (0.035^{2/3} \times 0.0216^{1/3} - 0.0216/2)}{\ln(1 - 0.0216) + 0.0216 + 0.48 \times 0.0216^2}$$

$$= 38000$$

$$N = \frac{38000}{1.42 \times 18} = 1487$$

Calculation of f:

The thermodynamic equilibrium condition for an ionic network swollen in pure solvent may be written as:

$$\ln(1-v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2 + N^{-1} (v_2^{0^{2/3}} v_{2m}^{1/3} - v_{2m}/2) - N^{-1} v_{2m} f = 0 \quad (E.5)$$

where v_{2m} is the volume fraction of network in the equilibrium swollen gel, v_2^0 is the volume fraction of the network after synthesis, χ_{12} is the interaction parameter between the network and solvent, N is the mean number of segments and f is the mean number of ionic units between successive junctions.

For PAAm gel, assuming that the value N does not change with the addition of acrylic acid (AAc) comonomer in the monomer mixture during synthesis, the mean number of ionic units in a network chain can be estimated. (Section 6.3)

$$\chi_{12} = 0.48$$

$$N = 1487$$

$$v_2^0 = 0.035$$

$$v_{2m} = 0.00223 \quad (\text{the equilibrium } v_{2m} \text{ value found by swelling experiments for PAAm gels (13 w/w \% AAc content) in water})$$

$$f = \frac{\ln(1-v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2 + N^{-1} (v_2^{0^{2/3}} v_{2m}^{1/3} - v_{2m}/2)}{N^{-1} v_{2m}}$$

$$f = \frac{\ln(1-0.00223) + 0.00223 + 0.48 \times 0.00223^2 + \frac{1487^{-1} (0.035^{2/3} \times 0.00223^{1/3} - 0.00223/2)}{1487^{-1} \times 0.00223}}{1487^{-1} \times 0.00223}$$

$$f = 5.71$$

Calculation of χ_{23} parameters:

Thermodynamic equilibrium condition for an ionic PAAm gel swollen in a linear polymer melt may be written as:

$$\begin{aligned} \frac{1}{y} \ln(1 - v_{2m}) + \frac{1}{y} v_{2m} + \chi_{23} v_{2m}^2 + N^{-1} (v_2^{0/3} v_{2m}^{1/3} - v_{2m} / 2) \\ - N^{-1} v_{2m} f = 0 \end{aligned} \quad (E.6)$$

where y is the number of segments in the linear polymer and χ_{23} is the interaction parameter between polymer network and linear polymer. Thus, using the values $N = 1487$, $v_2^0 = 0.035$, $f = 0$ and the equilibrium swelling ratio of nonionic PAAm gel in pure polymer, Equation (E.6) can be solved for the corresponding unknown χ_{23} parameter.

For the PAAm-TEG system the χ_{23} parameter can be calculated as follows:
(Section 6.3)

$$\begin{aligned} y &= 4 \text{ for TEG} \\ v_{2m} &= 0.1598 \end{aligned}$$

$$\begin{aligned} \chi_{23} &= \frac{\frac{1}{4} \ln(1 - 0.1598) + \frac{1}{4} 0.1598 + 1487^{-1} (0.035^{2/3} \times 0.1598^{1/3} - 0.1598 / 2) - 1487^{-1} \times 0.1598 \times 5.71}{0.1598^2} \\ &= 0.14 \end{aligned}$$



Appendix F

Computer Program for Theoretical Calculation of Swelling Behavior of Polymer Gels in Linear Polymer Solutions

Calculation of v_2 and v_3 for the polymer network immersed in a linear polymer solution:

```

DIM SS (15000), NN (15000), E9 (15000)
CLS
RO = 1.42 : '          Density
VS = 18 : '           Molar Volume
Y = 350 : '           Degree of Polymerization
MC = 38000 : '        Molecular Weight Between Successive Junctions, Mc
V20 = 0.035 : '       Vol. Fraction of Network After Synthesis
F = 5.71 :           Number of Ionic Units Between Successive Junctions

PSI = 0.1 : '         Volume Fraction of Linear Polymer in Solution
KAI13 = 0.48'         Interaction Parameter
KAI12 = 0.48'
KAI23 = 0

V3 = 0.501#
20 V3 = V3 + 0.00001#

DEF FNF1 (X) = (RO / MC) * VS * ( V20^(2 / 3) * X^(1 / 3) - X / 2 )
              + LOG (( 1 - X - V3) / ( 1 - PSI )) + X + V3 - PSI - ( V3 - PSI ) / Y
              + KAI12 * X^2 + KAI13 * ( V3^2 - PSI^2 ) + ( KAI12 + KAI13
              - KAI23 ) * X * V3 - ( X * F * RO * VS / MC )

DEF FNF2 (X) = - LOG (( 1 - X - V3 ) / ( 1 - PSI )) + ( 1 / Y )
              * LOG ( V3 / PSI )
              + 2 * KAI13 * ( PSI - V3 ) + ( KAI23 - KAI13 - KAI12 ) * X

BAS = 0.00001# : BITT = 0.015 : HASSAS = 0.000001#
50 BASY1 = FNF1 ( BAS ) : BITTY2 = FNF1 ( BITT )
  IF SGN ( BASY1 ) = - SGN ( BITTY2 ) THEN 200
  UZUN = ( BITT - BAS ) / 10
  FOR BASAMAK = 1 TO 9 : BASY9 = FNF1 ( BAS + BASAMAK * UZUN )

  IF SGN ( BASY9 ) = SGN ( BASY1 ) THEN 100
  BITT = BAS + BASAMAK * UZUN : GOTO 200

100 NEXT BASAMAK
  BITT = BITT + 0.1 : GOTO 50

200 BASY1 = FNF1 ( BAS )
  BITTY2 = FNF1 ( BITT )
  IF ABS ( BITT - BAS ) < ABS ( HASSAS ) THEN V21 = 0.5 *
    ( BAS + BITT ) : GOTO 300

ORTA = 0.5 * ( BAS + BITT )
ORTAY3 = FNF1 ( ORTA )

```

```
IF SGN ( ORTAY3 ) = SGN ( BASY1 ) THEN BAS = ORTA : GOTO 200
BITT = ORTA : GOTO 200
```

```
300 PRINT V21,
```

```
BAS = 0.000001# : BITT = 0.002136
```

```
350 BASY1 = FNF2 ( BAS ) : BITTY2 = FNF2 ( BITT )
IF SGN ( BASY1 ) = - SGN ( BITTY2 ) THEN 500
UZUN = ( BITT - BAS ) / 2
FOR BASAMAK = 1 TO 9 : BASY9 = FNF2 ( BAS + BASAMAK * UZUN )
```

```
IF SGN ( BASY9 ) = SGN ( BASY1 ) THEN 400
BITT = BAS + BASAMAK * UZUN : GOTO 500
```

```
400 NEXT BASAMAK
BITT = BITT + 0.1 : GOTO 350
```

```
500 BASY1 = FNF2 ( BAS )
BITTY2 = FNF2 ( BITT )
IF ABS ( BITT - BAS ) < ABS ( HASSAS )
    THEN V22 = 0.5 * ( BAS + BITT ) : GOTO 600
ORTA = 0.5 * ( BAS + BITT )
ORTA3 = FNF2 ( ORTA )
IF ABS ( BITT - BAS ) < ABS ( HASSAS )
    THEN V22 = 0.5 * ( BAS + BITT ) : GOTO 600
ORTA = 0.5 * ( BAS + BITT )
ORTAY3 = FNF2 ( ORTA )
IF SGN ( ORTAY3 ) = SGN ( BASY1 ) THEN BAS = ORTA : GOTO 500
BITT = ORTA : GOTO 500
```

```
600 PRINT V22, ABS ( V21 - V22 ), V3
IF ABS ( V21 - V22 ) > HASSAS / 10 THEN GOTO 20
PRINT "V3 ="; V3, "V21 ="; V21, "V22 ="; V22
END
```

Calculation of v_2 for the presence of a linear polymer:

```
CLS
RO = 1.42: '
VS = 18: '
MC = 38000: '
V20 = 0.035: '
F = 5.71
Y = 70
KAI23 = 0.0183
Density
Molar Volume
Mc
Interaction Parameter

DEF FNF1 ( X ) = ( RO / MC ) * VS * ( V20 ^ ( 2 / 3 ) * X ^ ( 1 / 3 ) - X / 2 )
+ ( 1 / Y ) * LOG ( 1 - X ) + X / Y + KAI23 * X ^ 2
- X * F * RO * VS / MC

FOR X = 0.000003# TO 1 STEP 0.0001#
PRINT X, FNF1 ( X )
NEXT
END
```

Calculation of v_2 for the absence of a linear polymer:

```
CLS
RO = 1.42: '
VS = 18: '
MC = 38000: '
V20 = 0.035
F = 0
KAI12 = 0.57
KAI13 = 0
Density
Molar Volume
Mc
Interaction Parameter

DEF FNF1 ( X ) = ( RO / MC ) * VS * ( V20 ^ ( 2 / 3 ) * X ^ ( 1 / 3 ) - X / 2 )
+ LOG ( 1 - X ) + X + ( KAI12 + KAI 13 * X ) * X ^ 2
- X * F * RO * VS / MC

FOR X = 0.0001 TO 1 STEP 0.0001
PRINT X, FNF1 ( X )
NEXT
END
```



Appendix G

**Computer Program for Theoretical Calculation of Molecular Expansion Factor,
 α , Using Birshtein and Pryamitsyn Equation**

Calculation of molecular expansion factor, α , below θ temperature:

```
CLS
N! = 57.53: '           Kuhn Segment
C = 0.087358
B = 0.354756
TETA! = 314.66: '       Theta Temperature,  $\theta$ 

FOR T! = 263.16 TO 314 STEP 0.5
TOT! = ( T! - TETA! ) / TETA!
ALF! = 0.1: '           Expansion Factor,  $\alpha$ 
SON! = 10
MIK! = 0.1
DO WHILE MIK! > 0.0001
SON! = ALF! ^ 6 - ALF! ^ 4 + ( C! - B! * N! * TOT! ) * ALF! ^ 3 - C!
IF SON! > 0 THEN
DO WHILE SON! > 0!
SON! = ALF! ^ 6 - ALF! ^ 4 + ( C! - B! * N! * TOT! ) * ALF! ^ 3 - C!
ALF! = ALF! + MIK!
LOOP
ELSE
DO WHILE SON! < 0
SON! = ALF! ^ 6 - ALF! ^ 4 + ( C! - B! * N! * TOT! ) * ALF! ^ 3 - C!
ALF! = ALF! + MIK!
LOOP
END IF
ALF! = ALF! - 2 * MIK!
MIK! = MIK! / 10
SON! = 10
LOOP
PRINT T!, ALF!, ALF! ^ 2
NEXT T!
END
```

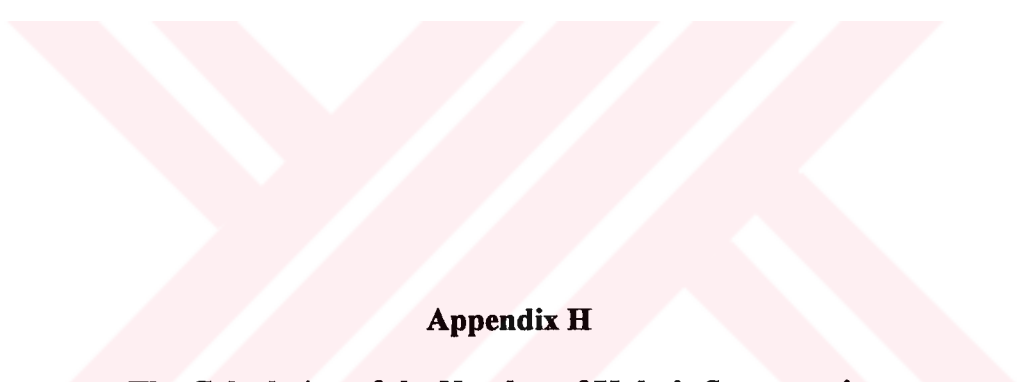
Calculation of molecular expansion factor, α , above θ temperature:

```

CLS
N! = 48.78: '           Kuhn Segment
B = 0.488
TETA! = 314.66: '       Theta Temperature,  $\theta$ 

FOR T! = 314.16 TO 343.16 STEP 1
TOT! = ( T! - TETA! ) / TETA!
ALF! = 0.1: '           Expansion Factor,  $\alpha$ 
SON! = 10
MIK! = 0.1
DO WHILE MIK! > 0.0001
SON! = ALF! ^ 5 - ALF! ^ 3 - ( B! * N! * TOT! )
IF SON! > 0 THEN
DO WHILE SON! > 0!
SON! = ALF! ^ 5 - ALF! ^ 3 - ( B! * N! * TOT! )
ALF! = ALF! + MIK!
LOOP
ELSE
DO WHILE SON! < 0
SON! = ALF! ^ 5 - ALF! ^ 3 - ( B! * N! * TOT! )
ALF! = ALF! + MIK!
LOOP
ELSE
END IF
ALF! = ALF! - 2 * MIK!
MIK! = MIK! / 5
SON! = 10
LOOP
PRINT T!, ALF!, ALF! ^ 2
NEXT T!
END

```



Appendix H

The Calculation of the Number of Kuhn's Segments in a Poly(methyl methacrylate) Chain

The number of Kuhn's segments, N^* , in a polymer chain can be written as follows:

$$N^* = \frac{x}{p} \quad (\text{H.1})$$

where x is the degree of polymerization of the polymer chain and p is the number of units in a Kuhn segment.

For the poly(methyl methacrylate) (PMMA) chain, the number of Kuhn's segment was calculated as follows:

The molecular weight of the monomer = 100 g/mol

$p = 10$ for PMMA

$M_w = 2.55 \times 10^6$ g/mol

$$N^* = \frac{\frac{2.55 \times 10^6}{100}}{10} = 2550$$

BIOGRAPHY

Nilhan Kayaman was born in Istanbul in 1970. She graduated from Marmara University, Faculty of Education, Department of Chemistry Teaching in 1992.

She attended as a M.Sc. student to the Institute of Science and Technology of Istanbul Technical University and obtain M.Sc. degree in Chemistry in 1994.

She was registered as a Ph.D. student to the Institute of Science and Technology of Istanbul Technical University in 1994.

She has been working as a researcher in Chemistry Department at TUBITAK Marmara Research Center since 1994. She was awarded with a grant by TUBITAK BAYG during her studies on M.Sc. thesis. She was the top student in the honor list both in B.Sc. and M.Sc. She is the co-author of seven research papers in international scientific journals and also has a patent (TR 96/ 00295).

