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**SWELLING PROPERTIES AND ELASTIC BEHAVIOR OF
TEMPERATURE SENSITIVE IONIC POLY (N-T-
BUTYLACRYLAMIDE-co-ACRYLAMIDE) HYDROGELS**

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**SICAKLIĞA DUYARLI İYONİK POLİ (N-T-
BUTİLAKRİLAMİD-co-AKRİLAMİD)
HİDROJELLERİNİN ŞİŞME ÖZELLİKLERİ VE
ELASTİK DAVRANIŞLARI**

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LIST OF SYMBOLS

n_1, n_2	: Number of solvent and polymer molecules
n_o	: Total number of lattice sites
x	: Number of segments of a polymer chain
V_1	: Molar volume of solvent
i	: Number of chains added to the lattice
z	: Coordination number of the lattice
Ω	: Total number of conformations
v_1, v_2	: Volume fractions of solvent and polymer molecule
ΔS_m	: Entropy change of mixing
w_{ij}	: Energy of the formation of a contact between a pair of segments of molecules i and j
ΔH_m	: Enthalpy change of mixing
χ	: Polymer-solvent interaction parameter
k	: Boltzman's constant
T	: Absolute temperature (K)
ΔG_m	: Free energy change of mixing
p	: Probability of a one end of the chain located within a small element
s	: Entropy of the chain
λ	: Deformation ratio (deformed length/initial length)
$\lambda_1, \lambda_2, \lambda_3$	: Macroscopic deformation ratios of the network chains
r_o	: End to end distance of an individual chain in the unstrained state
r	: End to end distance after deformation
ΔS_{el}	: Entropy change during deformation
$\overline{r_o^2}$	: Mean-square end-to-end distance of the chains
ΔG_{el}	: Free energy change during deformation
v_2^0	: Volume fraction of the crosslinked polymer after the gel preparation
ΔG	: Free energy change during swelling
V_o, V	: Gel volumes after the gel preparation and after swelling
μ_1, μ_1^o	: Chemical potentials of solvents inside and outside the gel
v_2	: Volume fraction of crosslinked polymer in the gel
v_e	: Number of chains per unit volume of the network
ρ	: Polymer density
$\overline{M_c}$	: Molecular weight of the network chains
π_i	: Osmotic pressure due to the concentration difference
f	: Mole fraction of ionic segments in the network chains
ΔA_{el}	: Helmholtz free energy

W	: Work of deformation
ν	: Concentration of the network chains.
R	: Gas constant
qF	: Mass swelling ratio after the gel preparation (mass of gel after preparation /mass of dry gel)
D, D_o	: Diameter of the hydrogels after equilibrium swelling and after preparation
q_v	: Volume swelling ratio
g	: Gravitational acceleration
l_o, l	: Initial undeformed and deformed lengths
A	: Cross-sectional area of the specimen
c	: Initial monomer concentration
G_o	: Elastic modulus of gel after preparation
G	: Elastic modulus of gel
$M_{c,chem}$	: Chemical molecular weight of the network chains
X	: Crosslinker ratio
M_r	: Molecular weight of polymer repeated units.



SUMMARY

SWELLING PROPERTIES AND ELASTIC BEHAVIOR OF TEMPERATURE SENSITIVE IONIC POLY(N-t-BUTYLACRYLAMIDE-co-ACRYLAMIDE) HYDROGELS

Intensive studies have been reported in the literature on poly(N-isopropylacrylamide) (PNIPA) hydrogels. However, there is no study on hydrogels based on (N-t-butylacrylamide) (TBA) and acrylamide (AAm) monomers.

In this study, a series of temperature sensitive hydrogels based on (TBA-co-AAm) at a TBA mole fraction of 0.60 in the monomer mixture was synthesized at a fixed crosslinker ratio and monomer concentration but at various ionic group contents. 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was used as the ionic comonomer during the hydrogel preparation. These hydrogels were subjected to swelling and mechanical measurements. The swelling properties of the hydrogels were investigated in the following solvents or solvents mixtures: water, methanol-water, ethanol-water and dimethylsulfoxide (DMSO)-water. The swelling degrees of the hydrogels in water were also measured as a function of temperature. The temperature was increased gradually in order to observe various Lower Critical Solution Temperatures (LCST).

The elastic moduli of the hydrogels after preparation were measured. The results were used to calculate the molecular weight of the network chains M_c . The elastic moduli of the hydrogels were also measured at various swelling degrees as well as at equilibrium swelling.

It was observed that the hydrogels exhibit reentrant conformational transitions in methanol-water, ethanol-water and DMSO-water mixtures. As the composition of the solvent mixture was continuously varied, the hydrogels first collapsed and then reswelled. It was also shown that the t-butyl groups are responsible for such reentrant phase transitions. It was found that the elastic modulus of hydrogels after the gel preparation increases with increasing the ionic group content of the hydrogels. As the

swelling ratio decreases the elastic modulus of the hydrogels increases rapidly. Finally, the swelling measurements showed that, (TBA-co-AAm) based hydrogels exhibit smooth and continuous volume transition upon increasing the temperature of water.



ÖZET

SICAKLIĞA DUYARLI İYONİK POLİ(N-T-BUTİLAKRİLAMİD-co- AKRİLAMİD) HİDROJELLERİNİN ŞİŞME ÖZELLİKLERİ VE ELASTİK DAVRANIŞLARI

Poly (N-isopropilakrilamid) (PNİPA) jelleriyle ilgili yoğun çalışmalar yayınlanmıştır. Ancak, (N-t-Butilakrilamid) (TBA) ve Akrilamid (AAm) monomer esaslı jellerle ilgili hiçbir çalışma yapılmamıştır.

Bu çalışmada, monomer karışımında 0.60 TBA mol oranında, (TBA-co-AAm) esaslı sıcaklığa duyarlı bir seri hidrojel, sabit çapraz bağlayıcı oranı ve monomer konsantrasyonu fakat farklı iyonik grup içeriklerinde sentezlendi. 2-akrilamido-2-metilpropan sülfonik asit sodyum tuzu (AMPS) hidrojellerin hazırlanmasında iyonik komonomer olarak kullanıldı. Hidrojeller, şişme ve mekanik ölçümlere tabi tutuldu. Hidrojellerin şişme özellikleri, aşağıdaki çözücü veya çözücü karışımlarında incelendi: Su, metanol-su, etanol-su, dimetilsülfoksid(DMSO)-su. Hidrojellerin şişme dereceleri su sıcaklığının bir fonksiyonu olarak ta ölçüldü. Çeşitli kritik geçiş sıcaklıkları gözlemlemek için sıcaklık kademeli olarak arttırıldı.

Hidrojellerin sentez sonrası elastik modulleri ölçüldü. Sonuçlar çapraz bağlı zincirlerin molekül ağırlığının hesaplanmasında kullanıldı. Aynı zamanda hidrojellerin çeşitli şişme derecelerindeki ve denge durumundaki elastik modulleri de ölçüldü.

Hidrojellerin, metanol-su, etanol-su ve DMSO-su karışımlarında reentrant konformasyonel geçişler gösterdiği bulundu. Çözücü karışımının kompozisyonu sürekli olarak arttırıldığına jeller önce büzüldü sonra yeniden şişti. Bu tür bir reentrant geçişe t-butil gruplarının neden olduğu da gösterildi. Hidrojellerin sentez sonrası elastik modülünün hidrojellerin iyonik grub içeriğiyle arttığı da bulundu. Şişme oranı azaldıkça hidrojellerin elastik modülü hızlı arttı. Son olarak, şişme ölçümleri, (TBA-co-AAm) bazlı hidrojellerin sıcaklığın artmasına bağlı olarak suda yumuşak ve sürekli bir hacim geçişi yaptıklarını gösterdi.

1. INTRODUCTION

A gel is a crosslinked polymer network swollen in a liquid medium. The polymer network serves as a matrix to hold the liquid together. The swelling behavior of gel is induced by the interaction between the gel network and the liquid [1]. Figure 1.1 shows schematic representation of a swollen gel. The liquid inside the gel prevents the polymer network from collapsing into a compact mass, whereas the network prevents the liquid from flowing away. In dried state, gels are solid materials. The properties of gels, such as their equilibrium swelling ratio and elasticity are known to depend on their network structure. An interesting aspect of gels is that a gel contains a “single polymer molecule” [2]. The term single polymer molecule means that all the monomer units in gel are connected to each other and form one big molecule on a

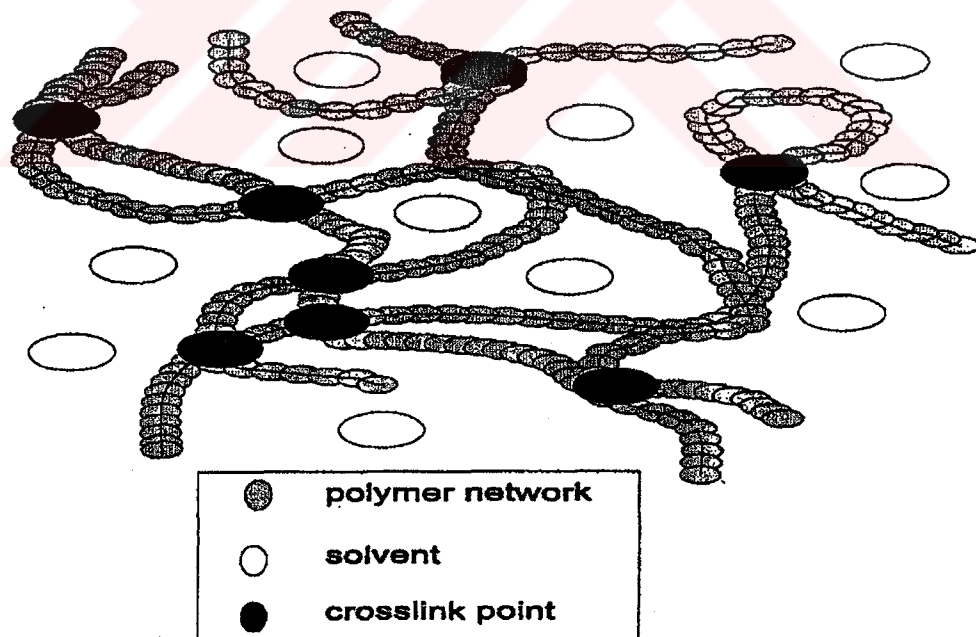


Figure 1.1 A schematic representation of a swollen gel.

macroscopic scale. Polymer gels can be prepared by chemical or physical crosslinking processes. Most of the gels are prepared by chemical crosslink process induced by free radicals, called free-radical crosslinking polymerization. Here, a mixture of a monovinyl monomer and a divinyl monomer (crosslinker) is copolymerized in the presence of free-radical initiators. In order to increase swelling capacity of gels, an ionic monomer is also included in the monomer mixture.

The gels play a vital role in the fields of medicine, foods, chemical, agricultural and other industries [3]. Softness, elasticity, and the capacity to store a fluid make gels unique materials. Highly swollen gels have a wide range of applications as absorbents and superabsorbents. In recent years, attention has turned to the swelling and collapse phenomena that are observed when a hydrogel is brought into contact with a solvent [4].

Hydrogels received considerable attention for use as specific sorbents and support carriers in biomedical engineering because of their low toxicity and high biocompatibility. Certain hydrogels called stimuli sensitive hydrogels change their volume in response to external signals such as temperature, pH and solvent composition. Temperature sensitive hydrogels 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 around the gel. Most of the temperature sensitive hydrogels studied over the last 50 years have been synthetic polymers based on N-isopropylacrylamide (NIPA). Poly(N-isopropylacrylamide) (PNIPA) gel is a well-known temperature sensitive gel exhibiting swelling or deswelling transition at its Lower Critical Solution Temperature (LCST), approximately 34 °C in water [5,6].

The volume phase transition is one of the most important phenomena of gels which has rendered soft materials technologically useful [7]. Study of the volume phase transition of gels can be traced back to the theoretical work by Dusek and Patterson in 1968 [8]. Their theoretical considerations show that a gel undergoes either a continuous volume change or a first-order discontinuous phase transition depending on the proportion of ionizable groups incorporated in the polymer network. Gel phase transition has been widely studied since the first observation of gel collapse by Tanaka [9]. It has been well demonstrated that small changes in the external conditions can bring about drastic changes in the state of the gel. Up to 1000-fold

changes in volume can take place [10]. Gel transition is a gas-liquid type condensation phase transition and results from a competition between attraction and repulsion of polymer segment and polymer rubber elasticity [11]. For example, gels of some polymers undergo a discontinuous volume change upon changes in external stimuli, such as temperature [9], type of surfactant [12], salt concentration [13], light [14], solvent composition [9,15], pH [16], electric field [17], ionic composition [18]. Most of the phase transitions studied experimentally are in aqueous systems [19].

Some gels have been synthesized that undergo the phase transition twice as the solvent composition is monotonically varied. In such cases, the gel shrinks once and then swells again as the solvent composition is changed continuously. The transition in gels from swollen to the collapsed state and then again to the swollen state as the external condition varied continuously is called reentrant phase transition. The reentrant phase transitions has been observed in PNIPA gels immersed in solvent mixtures such as water-dimethylsulfoxide (DMSO) [20, 21], water-methanol [20], and water-ethanol [22] or poly(ethylene glycol) (PEG) solutions [23].

The aim of this study is to investigate the swelling properties and the elastic behavior of temperature sensitive hydrogels based on N-t-butylacrylamide (TBA) and acrylamide (AAm). Although much has been reported in the literature on PNIPA gels, no work can be found on gels based on TBA monomer and TBA and AAm monomers. Here, the synthesis conditions of hydrogels based on TBA and AAm monomers in a mole ratio of 60/40 are described. The hydrogels were prepared by free radical copolymerization of TBA and AAm with N,N-ethylene(bis)acrylamide (BAAm) crosslinker in t-butanol-water mixture (1:1). 2-acrylamido-2-methylpropane sulfonic acid sodium salt AMPS was used as the ionic comonomer of TBA. The elastic behavior of gels at various swelling degrees as well as the swelling properties in solvents and in solvent mixtures at various temperatures was determined. As will be shown below, several interesting phenomena such as the temperature sensitivity and reentrant conformational transitions were observed.

2. SWELLING OF HYDROGELS

Polymeric gels absorb large quantities of suitable solvents without dissolving. As more and more solvent is absorbed by the polymer network, the network expands progressively. During the swelling process, the network chains are forced to attain more elongated conformation. As a result, like pulling a spring from both ends, a decrease in chain configurational entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies the swelling.

The equilibrium swelling theory developed by Flory and Rehner treats simple polymer networks in the presence of small molecules. The theory considers forces arising from three sources:

1. The entropy change caused by mixing of polymer and solvent. The entropy change from this source is positive and favors swelling.
2. The entropy change due to the reduction in the number of possible chain conformations on swelling. The entropy change from this source is negative and opposes swelling.
3. The heat of mixing of polymer and solvent, which may be positive, negative or zero. Usually, it is slightly positive and opposing mixing.

In the following paragraphs, these forces are explained separately.

2.1 Entropy of Mixing in Polymer Solutions

The polymer solutions show deviation from ideal solution behavior because of the wide difference in molecular size between the two components. Flory and Huggins independently found expressions for the total number of configurations of a mixture formed from n_1 solvent and n_2 polymer molecules. They estimated the number of ways in which n_1 solvent molecules and n_2 macromolecular chains could be placed on a lattice. Each polymer chain is represented by x segments, with the molar

volume of the segment equal to the solvent molecule V_1 . The total number of lattice sites n_o can thus be given as:

$$n_o = (n_1 + xn_2) \quad (2.1)$$

According to the Flory-Huggins theory, polymer molecules are added one by one to the lattice before adding the solvent molecules and simultaneously, the number of possible arrangements are calculated for each segment of the chain. For example, the total number of possible conformations for the $(i+1)$ th polymer molecule in the lattice ν_{i+1} is obtained:

$$\nu_{i+1} = \left\{ \frac{(n_o - xi)!}{[n_o - x(i+1)]!} \right\} \left[\frac{z-1}{n_o} \right]^{x-1} \quad (2.2)$$

where i is the number of chains added to the lattice and z is the coordination number of the lattice. The total number of distinguishable spatial arrangements of placing the n_2 polymer molecules on n_o sites is given by:

$$\Omega_{12} = \frac{1}{n_2!} \prod_{i=1}^{n_2-1} \nu_{i+1} \quad (2.3)$$

The number of ways Ω_2 by which chains can be placed on xn_2 sites is obtained by setting $n_1 = 0$ in Equation (2.3).

The configurational entropy of mixing is;

$$\Delta S_m = k \ln \frac{\Omega}{\Omega_2} = -k [n_1 \ln \nu_1 + n_2 \ln \nu_2] \quad (2.4)$$

where k is the Boltzman's constant, ν_1 and ν_2 are the volume fractions of solvent and polymer, i.e.,

$$\nu_1 = \frac{n_1}{n_1 + xn_2}, \quad \nu_2 = \frac{xn_2}{n_1 + xn_2} \quad (2.5)$$

2.2 Enthalpy and Free Energy of Mixing in Polymer Solutions

Solvent-solvent (1-1), solvent-segment (1-2) and segment-segment (2-2) are the three types of contacts in polymer solutions. The energy change for the formation of a polymer-solvent pair from solvent-solvent and polymer-polymer pairs is given as:

$$\Delta w_{12} = w_{12} - 1/2(w_{11} + w_{22}) \quad (2.6)$$

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

The expression for the enthalpy of mixing was then written [24]:

$$\Delta H_m = z n_1 v_2 \Delta w_{12} \quad (2.7)$$

To eliminate the coordination number z and the energy parameter Δw_{12} from the above equation, Flory (or polymer-solvent) interaction parameter χ was introduced:

$$\chi = \frac{z \Delta w_{12}}{kT} \quad (2.8)$$

The expression for the enthalpy of mixing can then rewritten by combining equations (2.7) and (2.8):

$$\Delta H_m = kT \chi n_1 v_2 \quad (2.9)$$

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

The Flory-Huggins expression for the Gibbs free energy of mixing is simply obtained by combining Equations (2.4) and (2.9):

$$\Delta G_m = kT [n_1 \ln v_1 + n_2 \ln v_2 + n_1 \chi v_2] \quad (2.10)$$

2.3. Elastic Deformation of the Network Chains

2.3.1 Statistical properties of long chain molecules

The statistical form of long-chain molecules may be illustrated by considering an idealized model of the polymethylene or paraffinic type of a chain $(CH_2)_n$ in which the angle between successive bonds (i.e. the valence angle) is fixed but complete freedom of rotation of any given bond with respect to adjacent bonds in the chains is allowed. This is illustrated in Figure 2.1 in which the first two bonds C_1C_2 and C_2C_3 are represented as lying in the plane of the paper.

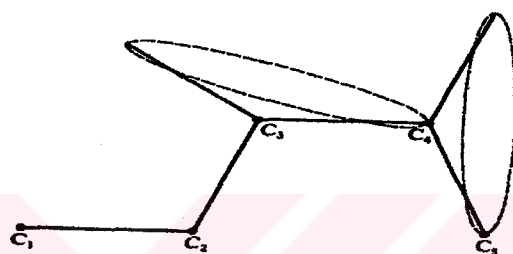


Figure 2.1 Rotation about bonds in paraffin-type molecule [25].

The third bond, C_3C_4 will in general not lie in this plane but will rotate in a random manner about the bond C_2C_3 as axis. Similarly C_4C_5 will rotate about C_3C_4 , and so on. The chain will thus take up an irregular or randomly kinked form in which the distance between the ends is very much less than that corresponding

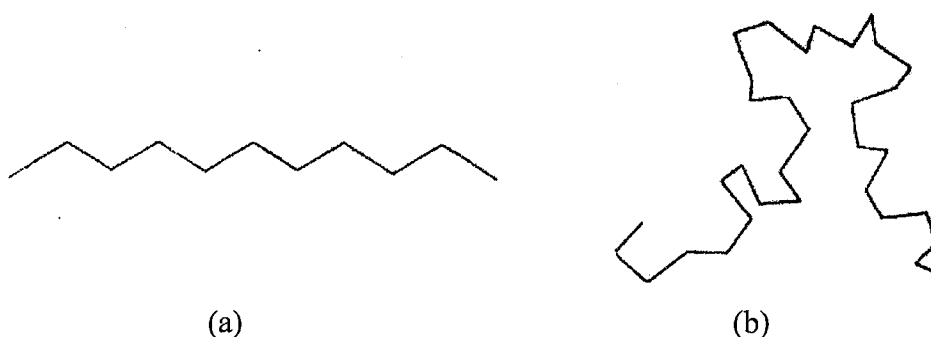


Figure 2.2 (a) Planar zigzag; (b) randomly kinked chain

to the outstretched or planar zigzag form (Figure 2.2). The actual conformation will be subject to continual fluctuation due to thermal agitation and hence cannot be defined explicitly, but it is possible to specify some of the properties of the system in statistical terms, or in terms of certain average values.

An idealized model for the development of the statistical theory consists of a chain of n links of equal lengths, l , in which the direction in space of any link is entirely random and bears no relation to the of any other link in the chain. Such a randomly jointed chain automatically excludes valence angle or other restrictions on the freedom of motion of neighboring links.

In order to define the statistical properties of the randomly jointed chain, one end (A) is assumed to be fixed at the origin of a Cartesian coordinate system Ox, Oy, Oz and the other end (B) moves in a random manner throughout the available space (Figure 2.3). However, although the motion is random, all positions of (B) are not equally probable. For any particular position p , having coordinates (x, y, z) , there will be an associated probability that the end (B) shall be located within a small volume element ($dx dy dz = d\tau$).

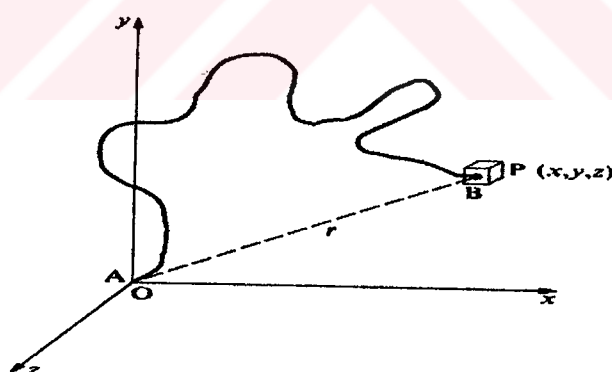


Figure 2.3 The statistically kinked chain. Specification of probability that the end should fall in volume element $d\tau(=dx dy dz)$ [25].

The derivation of this probability requires the evaluation of the relative numbers of configurations or conformations of the chain which are consistent with different positions of the point p , the probability of any particular position being taken as proportional to the corresponding number of conformations. The solution of this problem, given by Kuhn [26, 27], Guth and Mark [28] is presented as:

$$p(x, y, z)dx dy dz = \frac{b^3}{\pi^{3/2}} \exp(-b^2(x^2 + y^2 + z^2))dx dy dz \quad (2.11)$$

where b is a constant and it is given by the following equation:

$$b^2 = 3/2nl^2 \quad (2.12)$$

and x, y, z are the components of the vector r , i.e.,

$$r^2 = x^2 + y^2 + z^2 \quad (2.13)$$

This formula gives the probability that the components of the vector r representing the end-to-end distance for the chain shall lie within the intervals x to $x + dx$, y to $y + dy$, and z to $z + dz$, respectively. This probability is expressed as the product of the probability function $p(x, y, z)$ and the size of the volume element considered, which in this case is $dx dy dz (=d\tau)$.

2.3.2 The entropy of a single chain

According to the general principles of statistical thermodynamics, as developed by Boltzmann, the entropy will be proportional to the logarithm of the number of conformations available to the system, i.e., to the logarithm of the number of possible conformations corresponding to any specified state. Thus, since the number of conformations available to a polymer chain is proportional to the probability density given by Equation (2.11) the entropy s of the chain is therefore given by:

$$s = k(\ln p(x, y, z)d\tau) \quad (2.14)$$

Substitution of the expression (2.11) for $p(x,y,z)$ thus yields:

$$s = c - kb^2r^2 \quad (2.15)$$

where c is an arbitrary constant which includes the volume element $d\tau$. Equation (2.15) shows that the entropy has its maximum value when the ends of the chain are coincident ($r = 0$) and it decreases continuously with increasing distance between the ends.

2.3.3 The elasticity of a molecular network

The statistical theory of rubber elasticity is based on the concept of a network polymer as an assembly of long-chain molecules linked together at a relatively small number of points so as to form an irregular three-dimensional network. The statistical treatment of a network is similar in principle to the treatment of the single chain. It is required first to calculate the entropy of the whole assembly of chains as a function of the macroscopic state of strain in sample and from this to derive the free energy of work or deformation.

The following presentation of the theory is based essentially on the original theory of Kuhn. It makes use of the following assumptions:

1. The network contains ν chains. A chain is being defined as a set of segments between successive points of crosslinkages.
2. The mean square end-to-end distance for the whole assembly of chains in the unstrained state is the same as for a corresponding set of free chains.
3. There is no volume change on deformation. This assumption is well justified on the bases of experiments, which show the volume change on deformation is negligible at low deformation ratios.
4. The junction points between chains move on deformation as if they were embedded in an elastic continuum (Affine deformation assumption).
5. The entropy of the network is the sum of the entropies of the individual chains.

2.3.4 Entropy and free energy changes during deformation

Under an external strain, a unit cube (Figure 2.4) is transformed into a rectangular parallelepiped having three unequal edge lengths λ_1, λ_2 , and λ_3 . These extension ratios may be either greater than 1, corresponding to a stretched, or less than 1, corresponding to a compression, provided that the condition for constancy of volume (assumption 3 above), namely:

$$\lambda_1 \lambda_2 \lambda_3 = 1 \quad (2.16)$$

is satisfied.

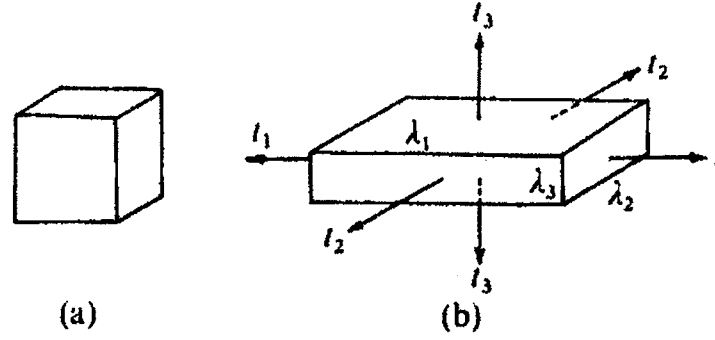


Figure 2.4 Pure homogenous strain (a) the unstrained state; (b) the strained state [25].

As seen in Figure 2.5, an individual chain in the unstrained state has an end to end distance r_o , with components (x_o, y_o, z_o) . After deformation, the vector r_o becomes r and the components become (x, y, z) . Then, the affine deformation assumption leads to the following equations:

$$x = \lambda_1 x_o, \quad y = \lambda_2 y_o, \quad z = \lambda_3 z_o \quad (2.17)$$

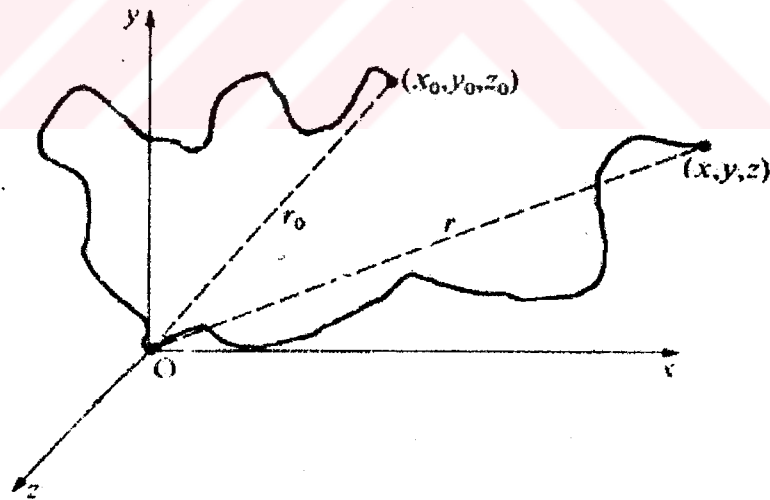


Figure 2.5 The affine deformation of a chain [25].

The entropy of the chain in the original (unstrained) state, as given by the equation (2.15), will be:

$$s_o = c - kb^2 r_o^2 = c - kb^2 (x_o^2 + y_o^2 + z_o^2) \quad (2.18)$$

The entropy of the same chain in the strained state is obtained by substituting the values of (x, y, z) for (x_0, y_0, z_0) , i.e.,

$$s = c - kb^2(\lambda_1^2 x_o^2 + \lambda_2^2 y_o^2 + \lambda_3^2 z_o^2) \quad (2.19)$$

The entropy change during deformation Δs_{el} will therefore be:

$$\Delta s_{el} = s - s_o = -kb^2 \{ (\lambda_1^2 - 1)x_o^2 + (\lambda_2^2 - 1)y_o^2 + (\lambda_3^2 - 1)z_o^2 \} \quad (2.20)$$

The total entropy for all the ν chains of the network is obtained by summation of the expression (2.20) for all the chains:

$$\Delta S_{el} = \sum_{i=1}^{\nu} \Delta s = -kb^2 \left\{ (\lambda_1^2 - 1) \sum_{i=1}^{\nu} x_o^2 + (\lambda_2^2 - 1) \sum_{i=1}^{\nu} y_o^2 + (\lambda_3^2 - 1) \sum_{i=1}^{\nu} z_o^2 \right\} \quad (2.21)$$

Since the directions of the chain vectors r_o in the unstrained state are entirely random, there will be no preference for the x, y, z directions. Thus, since:

$$\sum_{i=1}^{\nu} x_o^2 + \sum_{i=1}^{\nu} y_o^2 + \sum_{i=1}^{\nu} z_o^2 = \sum_{i=1}^{\nu} r_o^2 \quad (2.22)$$

it may be written as:

$$\sum_{i=1}^{\nu} x_o^2 = \sum_{i=1}^{\nu} y_o^2 = \sum_{i=1}^{\nu} z_o^2 = \frac{1}{3} \sum_{i=1}^{\nu} r_o^2 \quad (2.23)$$

Furthermore, since the mean-square end-to-end distance of the chains $\overline{r_o^2}$ is defined as:

$$\overline{r_o^2} = \sum_{i=1}^N r_o^2 / \nu \quad (2.24)$$

Equation (2.21) can then be written :

$$\Delta S_{el} = -\frac{1}{3} \nu kb^2 \overline{r_o^2} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2.25)$$

The assumption that the mean-square chain vector length in the unstrained state, $\overline{r_o^2}$ is the same as for a corresponding set of free chains, $\overline{r_o^2} = \frac{3}{2b^2}$ leads to the following equation:

$$\Delta S_{el} = -\frac{I}{2} \nu k (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2.26)$$

Assuming that there is no change of volume on deformation, the Helmholtz and Gibbs free energies of elastic deformation can be written using Equation (2.26) as:

$$\Delta A_{el} = -T \Delta S_{el} = \frac{1}{2} \nu k T (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2.27)$$

$$\Delta G_{el} = \Delta A_{el} \quad (2.28)$$

2.4 Flory-Rehner Theory of Gel Swelling

According to the Flory-Rehner theory of swelling, the free energy change during swelling is equal to the sum of the free energy changes of mixing (ΔG_m) and elastic deformation (ΔG_{el}):

$$\Delta G = \Delta G_m + \Delta G_{el} \quad (2.29)$$

Substitutions of Equations (2.10) and (2.28) into Equation (2.29) leads to:

$$\Delta G = kT \left[n_1 \ln v_1 + n_2 \ln v_2 + n_1 \chi_1 v_2 + \frac{1}{2} \nu (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \right] \quad (2.30)$$

Note that the deformation ratios λ_1 , λ_2 , and λ_3 are macroscopic deformation ratios of the network chains and they are equal to the macroscopic deformation ratios of the gel sample. For isotropic swelling,

$$\lambda_1^2 = \lambda_2^2 = \lambda_3^2 = \left(\frac{V}{V_o} \right)^{2/3} = \left(\frac{v_2^o}{v_2} \right)^{2/3} \quad (2.31)$$

where V and V_o are the gel volumes after the gel preparation and after swelling, respectively, and v_2^0 and v_2 are the corresponding volume fractions of crosslinked polymer in the gel. As the gel swells in a solvent, that is as the solvent molecules represented with n_1 penetrate into the gel network, ΔG will decrease. At the swelling equilibrium, ΔG will not change with n_1 . To describe swelling equilibrium, the excess chemical potential $\Delta\mu_1$ is used which can be obtained by differentiations of ΔG with respect to n_1 at constant temperature, pressure, and n_2 :

$$\Delta\mu_1 = \mu_1 - \mu_1^o = \left(\frac{\partial \Delta G}{\partial n_1} \right)_{T,P,n_2} = kT \left[\ln(1-v_2) + v_2(1-1/x) + \chi_1 v_2^2 + v_e V_1 v_2^{1/3} v_2^{o2/3} \right] \quad (2.32)$$

where μ_1 and μ_1^o are the chemical potentials of solvents inside and outside the gel, respectively, ν is the number of chains per unit volume of the network and V_1 is the molar volume of a segment. Since $x \gg 1$ and,

$$v_e = \frac{\rho}{M_c} \quad (2.33)$$

where ρ is the polymer density and $\overline{M_c}$ is the molecular weight of the network chains, equation (2.32) at swelling equilibrium can be written as:

$$\ln(1-v_2) + v_2 + \chi_1 v_2^2 + \frac{\rho}{M_c} V_1 (v_2^{1/3} v_2^{o2/3} - v_2 / 2) = 0 \quad (2.34)$$

Note that the last term $v_2 / 2$ in Equation (2.34) which is negligible at high swelling ratios, is included according to a more rigorous treatment of elastic deformation. Equation (2.34) is known as the Flory-Rehner Equation and widely used in predicting the swelling behavior of uncharged gels in solvents.

2.5 Swelling of Ionic Gels

If the network chains of a gel carry charged units, the gel swells much more than the corresponding uncharged gels. The reason of this excess swelling is the existence of mobile counterions in charged gels. For example, in Figure 2.6, a swollen ionic gel in which the fixed ion is taken to be a cation is schematically represented together with a non-ionic gel of the same crosslink density.

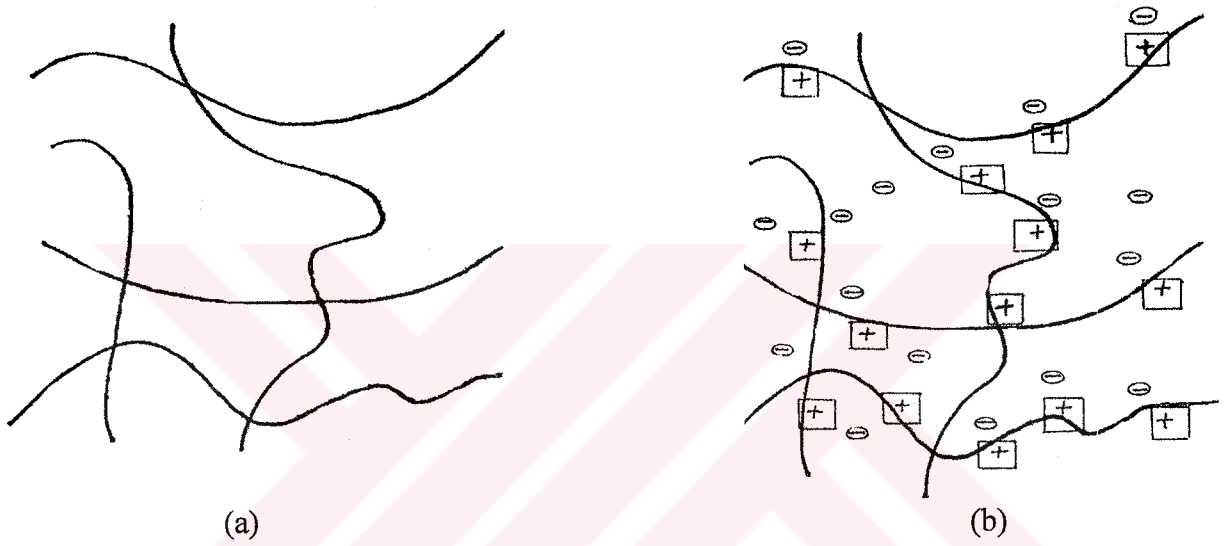


Figure 2.6 Schematic representation of (a) a non-ionic gel, (b) anionic gel with mobile anions inside [24].

Due to the condition of electroneutrality, there are mobile anions inside the gel, whose number is equal to the number of fixed cations. If immersed in water, the ionic gel will swell much more than the uncharged gel due to the concentration difference of charges between the inside and outside of the gel phase. The osmotic pressure (π_i) due to this concentration difference is simply equals to:

$$\pi_i = c_i kT \quad (2.35)$$

where c_i is the number of mobile counterions per gel volume and is equals to:

$$c_i = \frac{f}{V_1} v_2 \quad (2.36)$$

where f is the mole fraction of ionic segments in the network chains. Since the osmotic pressure relates to the excess chemical potential by the equation:

$$\pi = -\frac{\Delta\mu}{V_1} \quad (2.37)$$

the excess chemical potential due to the ionic contribution ($\Delta\mu_i$) can be calculated from Equations (2.35), (2.36), (2.37) as:

$$\Delta\mu_i = -kTfv_2 \quad (2.38)$$

In case of ionic gels, Equation (2.38) must be added to Equation (2.30) to predict the swelling equilibrium. Thus, swelling of ionic gels is described by the following equation:

$$\ln(1-v_2) + v_2 + \chi_1 v_2^2 + \frac{\rho}{M_c} V_1 (v_2^{1/3} v_2^{0.2/3} - V_2/2) - fv_2 = 0 \quad (2.39)$$

According to Equation (2.39), the higher the ionic group contents of the hydrogels, i.e., the higher f , the lower the polymer volume fraction v_2 . Thus, highly swollen hydrogels ($v_2 \ll 1$) can be obtained if a large fraction of an ionic comonomer is used in the gel preparation.

2.6 Elastic Modulus of Swollen Gels

In the previous section, equations describing the changes in the entropy Δs_{el} and Helmholtz free energy ΔA_{el} during the deformation of a gel sample were presented. Since work of deformation W equals to ΔA_{el} , by using Equation (2.27), the following equation for W can be written :

$$W = \frac{1}{2} \gamma kT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2.40)$$

For uniaxial deformation, since $\lambda_2^2 = \lambda_3^2 = \frac{1}{\lambda_1}$ and $\lambda_1 = \lambda$, Equation (2.40) reduces to:

$$W = \frac{l}{2} \nu kT \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \quad (2.41)$$

where λ is the linear deformation ratio (deformed length/initial length) due to the applied force F on the gel sample. By using Equation (2.41), the force of F acting on the gel sample can be calculated :

$$F = \left(\frac{\partial W}{\partial \lambda} \right)_{T, \nu} = \nu kT \left(\lambda - \frac{l}{\lambda^2} \right) \quad (2.42)$$

Equation (2.42) involves a single physical parameter νkT which is only dependent on the crosslink density of the material. This is called the elastic modulus of G of the gel in dried state:

$$G = \nu kT = \frac{\rho}{M_c} RT \quad (2.43)$$

As the gel swells, the elastic modulus decreases due to the decrease in the concentration of the network chains ν . The elastic modulus of swollen gels is given by the following equation:

$$G = \frac{\rho}{M_c} RT \nu_2^{1/3} \nu_2^{2/3} \quad (2.44)$$

3. VOLUME PHASE TRANSITION OF GELS

Using the Flory-Rehner equation derived in the previous section (Equation 2.39) Dusek and Patterson first predicted the possibility of a discontinuous volume phase transition in gels [8]. These authors showed that, under certain conditions, Equation (2.39) yields a three phase equilibrium, i.e., one swollen phase, the other collapsed phase, in coexistence with pure solvent (Figure 2.7). This means that the gel must undergoes an abrupt volume change if one of the external parameters is varied slightly as shown in Figure 2.8. A similar phenomenon in a single polymer chain, known as the coil-globule transition, has been theoretically studied by Ptitsen and Eizner [29]. In a sense, a gel phase transition is macroscopic manifestation of a coil-globule transition.

The theoretically predicted phase transitions have been proved experimentally 10 years later on hydrolyzed acrylamide (PAAm) gels swollen in acetone water mixtures [9]. In these experiments, the gels were placed in acetone-water mixtures of different concentrations to find a proper solvent in which the opification of the gel occurred at room temperature. The next day, half of the gels were swollen, and the remaining gels were collapsed, meaning the gel volume changed discontinuously as a function of acetone concentration. In the following years, a large number of studies have been reported on volume phase transition in gels immersed in solvent s and solvents mixtures. Recently, Kayaman, Okay, and Baysal reported the first observation of a discontinuous volume phase transition in ionic PAAm gels swollen in aqueous solutions of poly(ethylene glycol) (PEG) [4].

The universality of the gel phase transition was confirmed by the observation of phase transition in gels of various polymers. Most of the polymers in which the transition was found had the vinyl chain backbone. As is known three types of polymers exist in nature: polypeptides, polysaccharides, and polynucleotides. These polymers have a backbone structure totally different from each other, and from vinyl polymers.

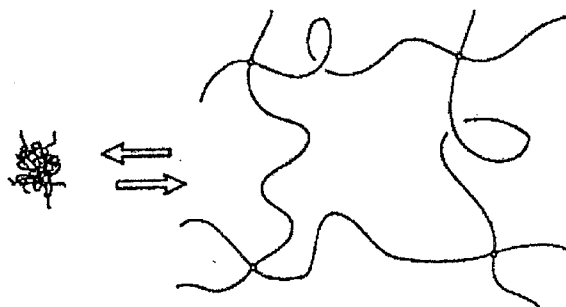


Figure 2.7 Swollen and collapsed phase of a gel [31].

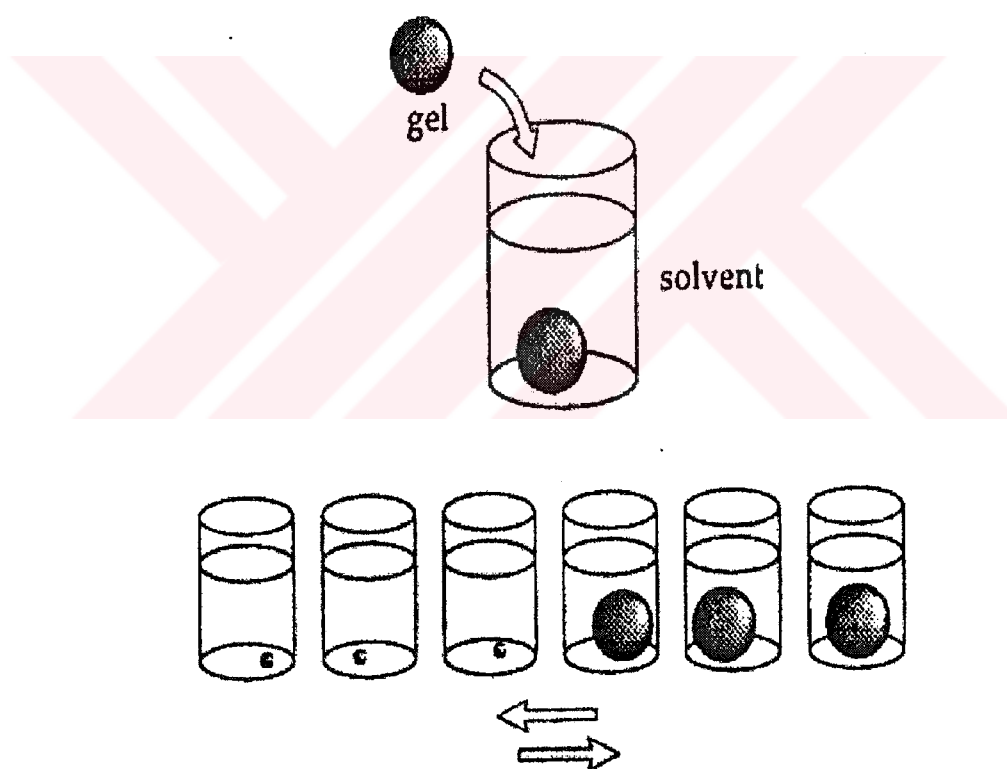


Figure 2.8 Phase transition of gel response to temperature, solvent composition etc [31].

Amiya choose a representative from each one of these polymer groups and crosslinked them by covalent bonds. Gels made of gelatine, agarose and DNA exhibited a phase transition [30].

Many synthetic gels have also been studied and the universality of the phase transition in gels seems to have been well established [32, 33]. It may be concluded that the polymer gels with and without charge can undergo a first order phase transition and, this is an evidence for the universality of the phase transition of polymer gels.

3.1 Molecular Interactions Responsible for the Phase Transition in Gels

Four major molecular interactions play an essential role in the volume phase transition of the gels. These are van der Waals, hydrophobic, hydrogen bonding, and electrostatic interactions (Figure 2.9). The size of a gel sample is very sensitive to the relative magnitude of these interactions. Therefore, by measuring the size of a gel as a function of external variables such as the temperature, pH, solvent composition, one can investigate the local environment of polymer chains. Thus, a gel is a good system for studying molecular interactions.

3.1.1 Van der Waals interactions

A partially hydrolyzed polyacrylamide gel undergoes a phase transition in acetone/water mixtures [9]. The main polymer-polymer affinity responsible for the phase transition is due to the van der Waals interactions. Acetone, a nonpolar solvent had to be added to water in order to increase the attractive interaction between polymers in the network to induce the transition. The transition is also observed when the temperature was varied while the solvent composition fixed near the transition threshold.

3.1.2 Hydrophobic interactions

Water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded and form ordered structures, called ice-bergs, which are similar to the structure of water molecules in ice [34]. Since the formation of ice-bergs lowers both enthalpy and entropy of mixing, this formation is an exothermic process. This is called hydrophobic interaction.

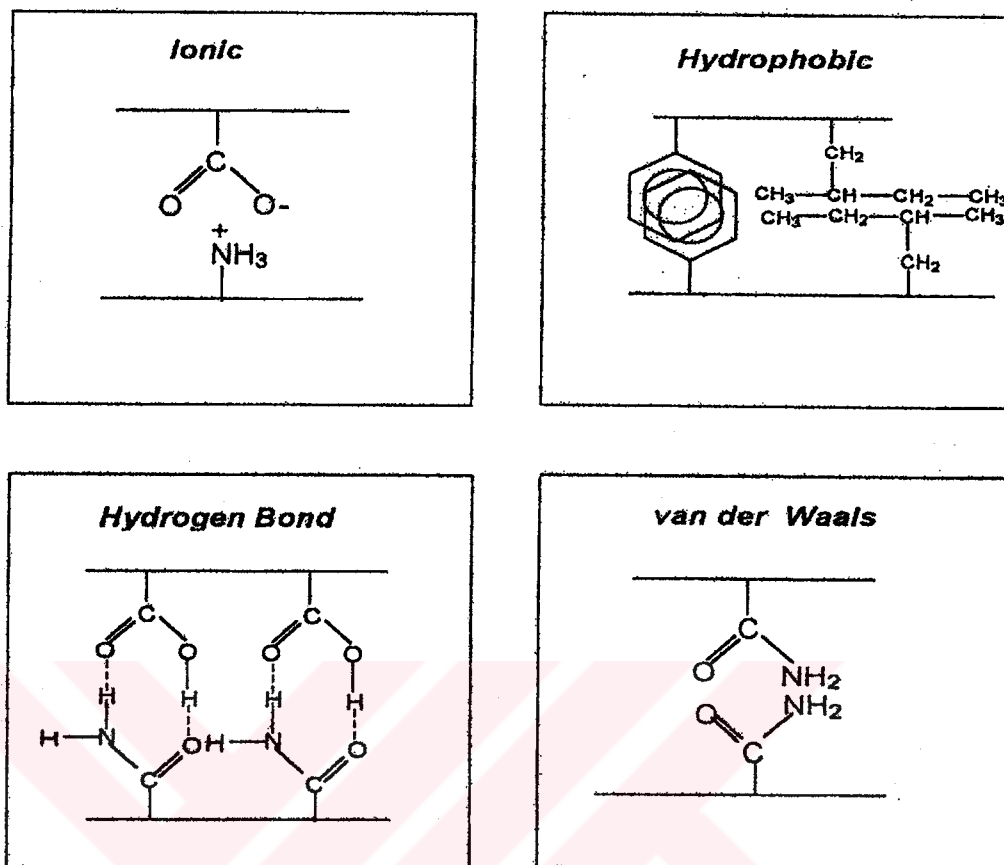


Figure 2.9 Four fundamental interactions for phase transition of a gel [31].

Although the energy of the hydrophobic interaction is on the order of a few kcal/mol, which is on the same order or even smaller than that of hydrogen bonding, hydrophobic interaction plays a very important role in the stabilization of the configuration of hydrogels.

In the case of synthetic polymers, hydrophobic interaction can be controlled by substituting the side group of the polymer chains, which constitute the network. In attempt to find a gel that undergoes a volume phase transition in pure water, Hirokawa and Tanaka studied swelling behavior of PNIPA gels, with side groups more hydrophobic than that of the acrylamide [5]. They observed the collapsing transition at approximately 33.2 °C by increasing the temperature. This temperature dependence, which is opposite to the transition induced by Van der Waals interaction, is due to the hydrophobic interaction of the polymer and water. At higher temperatures the polymer network shrinks and becomes more ordered, but the water

molecules excluded from the polymer network becomes less ordered. As a whole, the gel collapses due to the increase of the entropy of the universe.

3.1.3 Hydrogen bonding interactions

When a hydrogen atom is located between two closely separated atoms having high electronegativity, such as O and N, a hydrogen bond can be formed [35]. Although the bond energy is not very large, (3-9 kcal/mole) it plays an important role in the physical and chemical properties of hydrogels. 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 [36]. For example, one network is poly(acrylic acid) and the other poly(acrylamide). The gel was originally designed and developed by Okano and his colleagues [37]. They 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 describes the cooperative nature of the interaction between two polymers [38]. By slightly ionizing the gel, Ilmain, Tanaka, and Kokufata succeeded in inducing the discontinuous volume transition of the IPN in pure water [36].

3.1.4 Electrostatic interactions

The electrostatic (Coulombic) interaction is a long-range order interaction and inversely proportional to the dielectric constant of the medium. In synthetic polymers, either positive or negative charges are 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 of 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 [39]. Another aspect of the electrostatic interaction can be found in a polyampholyte gel which has both cationic and anionic groups. These polymers can be either positively or negatively charged, and repel each other over short ranges, but attract over long ranges [40]. At neutral pH, such a gel, is shrunken and, at both higher and lower pH is swollen [41]. In the neutral pH both cations and anions are

ionized, and they attract each other, thus the gel shrinks. Otherwise the one of the ionizable groups is neutralized, while the other remains ionized, and the gel swells. The volume change is gradual and continuous.

The observations of phase transitions driven mainly by each of the fundamental interaction as shown in Figure 2.10, allow drawing a general picture of how polymers interact with each other through these interactions.

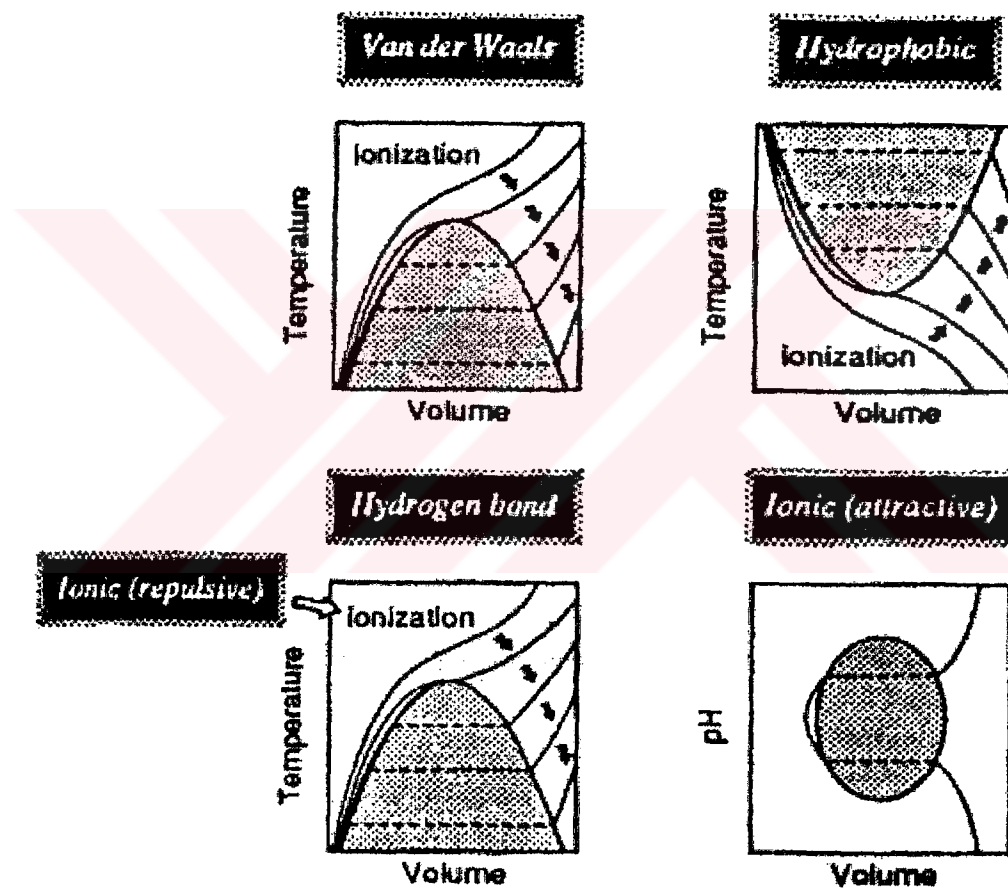


Figure 2.10 The phase transitions of gels induced by one of the fundamental interactions[31].

3.2 Various Stimuli Induced Phase Transitions

As discussed in the previous section, the molecular interactions determine the macroscopic size and the shape of gels. Since these interactions are functions of temperature, polymer concentration, solvent composition, pH, and salt concentration, the volume phase transitions can be induced by controlling one or more of these parameters. Some of the stimuli induced phase transitions are given below:

1. The combination of a temperature sensitive gel and light absorbable molecules makes it possible to induce phase transition of gels by visible light [42]. When the gel absorbs light energy, the temperature of the gel will be partially raised by local heating and equilibrium state will be determined by the competition with thermal diffusion. If the temperature of the gel is higher than the transition temperature, the gel will exhibit phase transition and shrink. If the light intensity is decreased, the gel will swell again. The phase behavior, transmittance, and kinetic properties of such gels have been investigated. PNIPA and chlorophyllin, a combination of a temperature sensitive gel and a chromophore can be given. In the absence of light, the gel volume changes sharply but continuously as the temperature is varied. However, beyond a certain irradiation threshold, the volume change becomes discontinuous. The phase transition is presumably induced by local heating of polymer chains due to the absorption and subsequent thermal dissipation of light energy by the chromophore.
2. If a gel contains ionizable groups, it becomes a pH sensitive gel since the ionization is determined in terms of ionization equilibrium. Extensive studies have been done to develop gels that respond to pH changes [43,44].
3. Some gels have been synthesized that undergo phase transition under an electric field [45]. The most important effect on such phase transition seems to be the migration and redistribution of counter and added ions within the gel.
4. Phase transition in gels can occur in response to biochemical reactions [45]. Polymer gels were synthesized in which a biologically active protein (lectin) was immobilized. The volume phase transitions were observed in such gels when biochemical reactions take place. Such mechano-biochemical gels will be used in devices such as sensors, selective absorbers and biochemically controlled drug release. Recently, various schemes have been developed where a gel can undergo

phase transition when a particular kind of molecule is present. This transition is achieved by embedding biochemically active elements such as enzymes or receptors within the gel that is placed near the transition threshold. When target molecules enter the gel, the active element converts them into other molecules or forms a complex, which disturbs the equilibrium of the gel by inducing the swelling or collapsing phase transition [46].

5. Gels can undergo a phase transition induced by stress [35]. The changes in the diameter and length of cylindrical PNIPA gels were measured under uniaxial stress. The transition temperature and the discontinuity were increased with increasing stress, which indicates the possibility of the uniaxial phase transition of gels. With increasing stress, mechanical work at the phase transition increased and hereafter decreased under large stress. The peak of the mechanical work at the transition point as a function of stress depends on the degree of swelling.

3.3 Phase Transition of Gels in Polymer Solutions

Recently, theoretical calculations using the Flory-Huggins theory predicted the possibility of a discontinuous phase transition in gels immersed in polymer solutions. [47]. This prediction was proved with ionic polyacrylamide P(AAm) or PNIPA gels swollen in aqueous poly (ethylene glycol) (PEG) solutions [4, 23]. It was shown that the volume change of gel 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 linear polymer (PEG) required for a discontinuous volume collapse rises. Melekaslan and Okay showed that the variation of the effective charge density of the gel depending on the medium polarity is responsible for the volume transition of gels in polymer solutions. They pointed out that the charge density of gels represented by the symbol f in Equation (2.39) is not a constant but it decreases as the linear polymer concentration in the solution increases, i.e., as the dielectric constant of the medium decreases [48]. As a result, ionic gels can undergo collapse transition if the value f crosses a critical value.

3.4 Reentrant Phase Transition of Gels

Recently a phenomenon called reentrant phase transition was observed in gels immersed in solvent mixtures or in polymer solutions. In such a transition, the gel first collapses, then reswells, if a particular external parameter such as the solvent composition is continuously varied. Reentrant transitions were observed in PNIPA gels immersed in solvent mixtures such as water-dimethylsulfoxide, water-methanol, water-ethanol mixtures. More recently, Melekaslan and Okay observed reentrant transition in PNIPA gels immersed in aqueous solutions of PEG's of molecular weight 200-400 g/mole [23]. They showed that the collapse of the gel is jumpwise first-order phase transition while their reswelling occurs smoothly at higher PEG concentrations. Calculations using the Flory-Huggins theory indicated attractive interactions between PEG and PNIPA segments, which are responsible for the reentrant transition behavior. Gundogan and Okay predicted theoretically the necessary conditions for the reentrant behavior of gels in terms of the interaction parameters of the components of the system [49].

4. TEMPERATURE SENSITIVE HYDROGELS

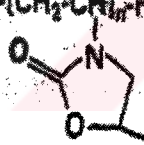
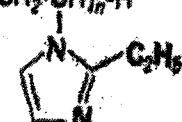
Certain polymers are soluble in water at low temperatures but become insoluble as the temperature rises above the lower critical solution temperature (LCST). Such polymers are called temperature sensitive polymers. The crosslinked derivatives of these polymers swollen in water, known as temperature sensitive hydrogels, are subject of both fundamental and technological interests. The temperature sensitive polymers are especially attractive for various biomedical and pharmaceutical applications. In particular, the temperature sensitive hydrogels based on PNIPA were intensively studied. Since the publication of the first patent on the preparation of PNIPA gel by Sprech in 1956, it becomes the most popular member of the temperature sensitive polymers [50]. A large number of studies have been reported on PNIPA gels from different aspects, such as thermal properties, effects of various additives, comonomers on their swelling behavior. Fast responsive PNIPA gels with a macroporous structure were prepared recently [51]. There has been a steady increase in the number of publications describing preparation, characterization, and applications of temperature sensitive hydrogels. Most of the temperature sensitive polymers belong to three types, as shown in Table 4.1 namely poly(N-substituted(methyl)acrylamides), poly(N-vinyl-N,N-disubstituted amides), particularly poly(N-vinyl caprolactam), and ethylene oxide –containing polymers [52].

Most of the temperature sensitive hydrogels are the derivatives of polyacrylamides (PAAm). The ratio of the hydrophobic to hydrophilic units within the side chains of PAAm is a decisive factor in determining whether the gel will exhibit thermoswelling or thermoshrinking behavior. The sensitivity of the swelling behavior to the chemical structure of the pendant groups was recently demonstrated by Seker and Ellis [53]. In general, lengthening the side chain affects strongly the LCST of the gel. However, even simple isomeric rearrangements within the side group leads to a surprisingly large change in LCST relative to the other derivatives.

Table 4.1 Examples for temperature sensitive polymers and their LCST [52].

Polymer	LCST
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \\ \\ \text{CO}-\text{NR}_1\text{R}_2 \end{array}$	
$\begin{array}{c} \text{R}_1 \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \quad \begin{array}{c} \text{R}_2 \\ -\text{CH}_2\text{CH}_3 \\ -\text{CH}_2\text{CH}_2\text{CH}_3 \\ -\text{CH}(\text{CH}_3)_2 \end{array}$	74 22 32.2-34.3 ^a
$\begin{array}{c} \text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \text{Cyclopropyl} \\ \\ \text{Cyclohexyl} \end{array}$	67 27
$\begin{array}{c} \text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} -(\text{CH}_2)_3-\text{OCH}_3 \\ \\ -(\text{CH}_2)_3-\text{OC}_2\text{H}_5 \\ -(\text{CH}_2)_3-\text{OCH}(\text{CH}_3)_2 \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -\text{CH}(\text{CH}_3)_2 \\ -\text{CH}_2\text{CH}_3 \\ -\text{CH}(\text{CH}_3)_2 \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -(\text{CH}_2)_3-\text{O}-\text{CH}_3 \\ -(\text{CH}_2)_3-\text{O}-\text{CH}_3 \\ -\text{C}(\text{CH}_3)_2-\text{CO}-\text{NH}-\text{R}_1 \end{array}$	47 10 25.3 5.2 20.6 22.7 26 13.8 12.4 40.6 41.6
$\begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \\ -\text{CH}_3 \\ -\text{CH}_3 \\ -\text{CH}_2\text{CH}_3 \\ -\text{CH}(\text{CH}_3)_2 \\ -\text{CH}_2\text{CH}_2\text{CH}_3 \\ -\text{CH}_2\text{CH}_3 \\ -(\text{CH}_2)_2-\text{O}-\text{CH}_3 \end{array}$	35 20 3 65 38 65 18
$\begin{array}{c} \text{R}_1 = \\ -\text{CH}_3 \\ -\text{CH}_2\text{CH}_3 \\ -\text{CH}(\text{CH}_3)_2 \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3 \\ -\text{CH}_2\text{CH}(\text{OCH}_3)_2 \\ -\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_3)_2 \end{array}$	55
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \\ \\ \text{CO}-\text{N} \end{array}$	5
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \\ \\ \text{CO}-\text{N} \end{array}$	16
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \\ \\ \text{COO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \\ \text{H}-(\text{CH}_2-\text{C}(\text{CH}_3)_2)_m-\text{H} \\ \\ \text{COOH} \end{array}$	43 ^b , 53-56 ^b

(Table 4.1 continues)

$\begin{array}{c} \text{H}-(\text{CH}_2-\text{C}(\text{CH}_3))_n-\text{H} \\ \\ \text{CO}-\text{NR}_1\text{R}_2 \\ \begin{array}{cc} \text{R}_1 & \text{R}_2 \\ \text{H} & -\text{CH}(\text{CH}_3)_2 \\ \text{H} & -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3 \\ \text{H} & -(\text{CH}_2)_3-\text{OCH}_3 \\ \text{H} & -(\text{CH}_2)_3-\text{OC}_2\text{H}_5 \\ \text{H} & -(\text{CH}_2)_3-\text{OCH}(\text{CH}_3)_2 \end{array} \\ \text{H}-(\text{CH}_2-\text{C}(\text{CH}_3))_n-\text{H} \end{array}$	
$\begin{array}{c} \text{COO}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3 \\ m = 4 \\ m = 8 \\ m = 22 \end{array}$	43 35 58 34.3 11.1
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \\ \\ \text{NR}_1-\text{COR}_2 \\ \begin{array}{cc} \text{R}_1 & \text{R}_2 \\ -\text{CH}_3 & -\text{CH}_2\text{CH}_2\text{CH}_3 \\ -\text{C}_2\text{H}_5 & -\text{C}_2\text{H}_5 \\ -\text{CH}_2\text{CH}_2\text{CH}_3 & -\text{CH}_3 \end{array} \\ \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \end{array}$	56.2 85.2 103.5
	40-45° 40-45° 40-45° 32-40°
	40
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH}(\text{OCH}_3))_n-\text{H} \\ \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} \end{array}$	34 38
	
$\begin{array}{l} \text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H} \quad \text{MW } 4 \cdot 10^6 \\ \text{HO}-(\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O})_n-\text{H} \quad \text{MW } 58,000 \\ \text{MW } 1,000 \end{array}$	96 20
Methylcellulose	39
Hydroxypropylcellulose	49
Methyl(hydroxypropyl)cellulose MW 174,000	42-46°
Methyl(hydroxyethyl)cellulose MW 165,000	59
Ethyl(hydroxyethyl)cellulose	60
	55-70°

The swelling curves of a series of alkyl derivatives of PAAm's are shown in Figure 4.1 as a function of temperature. It is seen that both the degree of swelling and the LCST are strongly dependent on the nature of the side group. As the number of methylene groups on the side chain increases, LCST shifts to lower temperatures. The surface area of the side group is responsible for the observed transition temperature. An additional structural parameter that affects the thermosensitivity properties of the gels is the rigidity of the substituent.

The LCST of mono- and di-N-substituted acrylamide polymers can be modified easily by copolymerization with other monomers. For example, water soluble hydrophobic polymers can be made temperature sensitive with a LCST, if a hydrophilic comonomer is also added into the monomer mixture.

Similarly, water-soluble polymers can be made to possess an LCST by copolymerization with a hydrophobic monomer. An increase in the overall hydrophobicity of the copolymer lowers the LCST, leading in some cases to a polymer insoluble in water. Likewise, a decrease in the hydrophobicity of the copolymers can raise the LCST and may result in a hydrophilic polymer freely soluble at all temperatures. In an effort to demonstrate how the LCST of the polymers can be varied by adjusting the comonomer composition, Liu and Zhu have prepared several series of copolymers from N-substituted acrylamides with varying degree of hydrophobicity. including N-ethylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, and N-t-butylacrylamide [54]. A decrease in the LCST can be achieved by increasing the hydrophobicity of the network chains. Larger alkyl chains produced dramatic decrease in the gel transition temperature.

The structure of the polymers, particularly that of the alkyl group of acrylamide is important to determine temperature sensitivity and solution behavior of polymers. A better understanding of the properties of N-substituted polyacrylamides should help in development of new temperature sensitive hydrogels and to improve the temperature sensitivity of the gels.

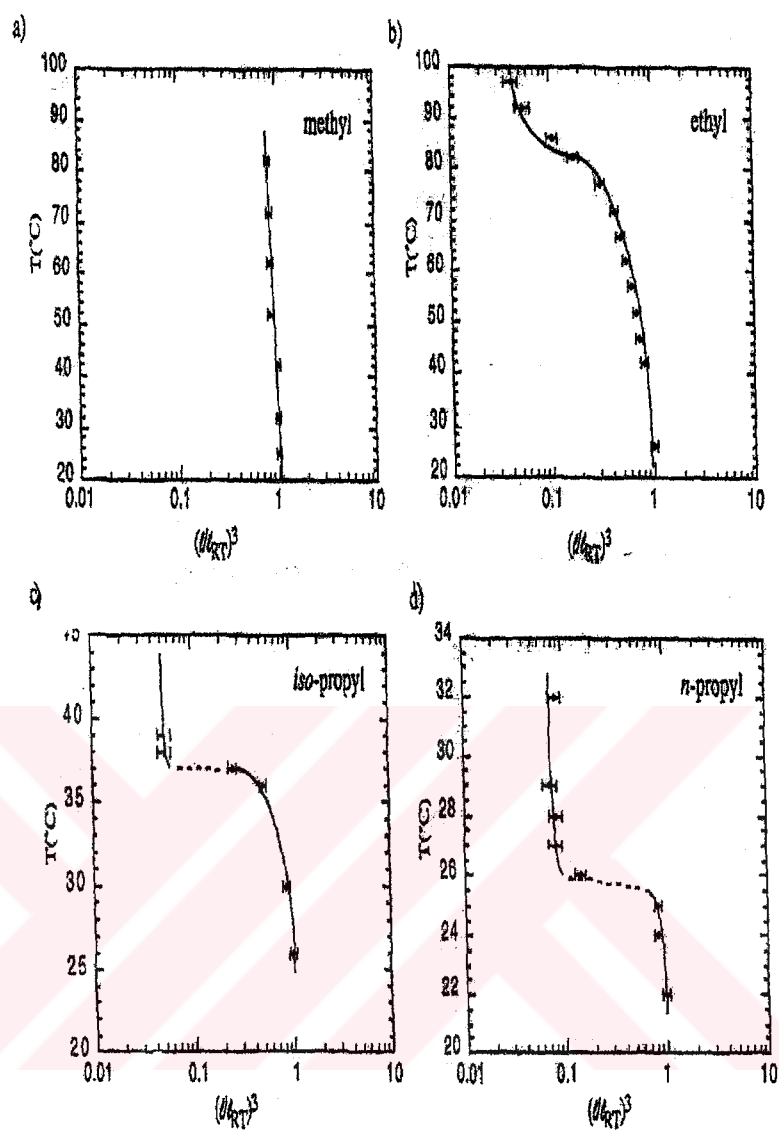


Figure 4.1 Swelling behavior of the n-alkylacrylamides with increasing temperature as a function of amide alkyl substituent: (a) methyl; (b) ethyl; (c) isopropyl; (d) n-propyl. The swelling is characterized by volume [53].

5. EXPERIMENTAL

5.1 Materials

N-butylacrylamide (TBA, Fluka), N,N'-methylenebis (acrylamide), (BAAm, Merck), potassium persulfate (KPS) and 2,2'-azobisisobutyronitrile (AIBN, Merck) were used as received. Acrylamide (AAm, Merck) was crystallized from acetone/ethanol mixture (70/30 by volume) below 30°C. 2-acrylamido-2-methylpropane sulfonic acid (AMPS - H⁺, Merck) was crystallized from boiling methanol. 2 acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) stock solution was prepared by dissolving 20 g of AMPS-H⁺ in about 40 ml of distilled water and adding to this solution 10 ml of a 30% NaOH solution under cooling. Then, the solution was titrated with 1 M NaOH to pH=7.00 and finally, the volume of the solution was completed to 100 ml with distilled water. 1 ml of AMPS stock solution thus prepared contained 0.966 mmol AMPS. Distilled and deionized water was used for the experiments. Reagent-grade solvents tetrahydrofuran (THF), 2-propanol, t-butanol, methanol, ethanol, acetone, dimethylsulfoxide (DMSO), were used without further purification.

5.2 Synthesis of the Hydrogels

TBA gels were prepared by free-radical crosslinking copolymerization of TBA and AAm in the presence of BAAm as the crosslinker in t-butanol-water mixture (1:1) by volume. TBA mole fraction in the monomer mixture was fixed at 0.60 throughout the study. AMPS was used as the ionazable comonomer. The total monomer concentration was fixed to 5 %. A series of preliminary experiments were carried out to find the optimum condition for the gel formation. For this purpose, the types of the solvent and the initiator as well as the polymerization temperature were taken as the independent parameters.

The insolubility of TBA in water led to testing of solvents such as methanol, t-butanol, 2-propanol, tetrahydrofuran for the polymerization. Because of the widely

differing solubility characteristics of TBA and AAm monomers, mixtures of these solvents with water were used to obtain effective copolymerization. Methanol and t-butanol were especially selected because of their low chain transfer constants for the polymerization of AAm [55], their miscibility with water [56], and their good solvency for TBA and AAm [57].

AIBN and KPS were used as initiators in the system appropriate to their solubility at the beginning of the experiments. AIBN at various initiator-to-monomer mole ratios did not initiate the TBA/AAm copolymerizations in any solvent or solvent-water mixtures. KPS was used at three different initiator-to-monomer mole ratios, namely at 1/250, 1/500, and 1/1000. The initiation was succeeded for the three cases but the ratio 1/500 was the optimum from the point of view of polymerization kinetics and of the post treatment process of the gels formed.

After testing variety of different solvents, initiators and synthesis temperatures, it was found that TBA/AAm based hydrogels at 5% monomer concentration can be best prepared in 1/1 t-butanol/water by volume, as the polymerization solvent, at 50 °C in the presence of KPS as the initiator. In the experiments, the mole fraction of the ionic comonomer AMPS in the monomer mixture x_i , was varied between 0 and 0.03, while the crosslinker ratio X (the mole ratio of the crosslinker BAAM to the monomers TBA, AAm and AMPS) and initiator ratio (the mole ratio of the initiator KPS to the monomers TBA, AAm and AMPS) were fixed at 1/80 and 1/500, respectively. Details for the preparation of the hydrogels with 60 mol % TBA and 1 mole % AMPS ($x_i=0.010$) in the comonomer feed composition are given in the following scheme:

TBA (0.359 g), AAm (0.130 g), BAAM (0.0091 g), and KPS (0.0025 g) were dissolved in 1/1 t-butanol-water mixture, and AMPS stock solution (0.049 ml) was added to give a total volume of 10 ml. To eliminate oxygen from the polymerization system nitrogen was bubbled through the solution for 15 min. Then the solution was transferred to glass tubes of 5 mm internal diameters and 150 mm long. The glass tubes were then sealed, immersed in a thermostated bath at 50 ± 0.4 °C and the polymerization was conducted for 24 h. After polymerization, the reaction was quenched by cooling the reaction mixture in an ice-water bath. Then the hydrogels, 5 mm in diameter, were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water for one day to wash out any soluble

polymers, unreacted monomers and initiator. The water was replaced for several times.

For comparison, hydrogels based on AAm and AMPS were also prepared at the same crosslinker ratio (1/80), temperature (50 °C) and monomer concentration (5%). In this experiment, only water instead of t-butanol-water mixture was used as the polymerization solvent.

5.3 Polymer Network Concentration at the State of the Gel Preparation

The presence of a solvent during the gel formation process is known to produce supercoiled polymer chains in the dry state so that the increase of their dimensions during swelling does not require much loss of their conformational entropy. As a result, the mechanical properties and the swelling behavior of gels sensitively depend on the degree of dilution at which they are formed.

The degree of dilution of poly(TBA-co-AAm) networks after their preparation represented by v_2^o , the volume fraction of crosslinked polymer after the gel preparation. In order to determine the v_2^o values, the hydrogels after the extraction were carefully deswollen in a series of water acetone mixtures with increasing acetone contents. This solvent exchange process facilitated final drying of the hydrogels samples. The collapsed samples after the treatment with acetone as a final solvent were dried in under vacuum to constant weight v_2^o was calculated as:

$$v_2^o = \left[1 + \frac{(q_F - 1)\rho}{d_1} \right]^{-1} \quad (5.1)$$

where q_F is the mass swelling ratio after the gel preparation (mass of gel after preparation /mass of dry gel), ρ and d_1 are the densities of crosslinked polymer and the t-butanol-water mixture respectively. [It is assumed that $d_1 = (d_{\text{butanol}} + d_{\text{water}})/2 = (0.78 + 1)/2 = 0.89$ g/ml and $\rho = 1.35$ g/mL]. Determination of the q_F values of the hydrogels prepared without using the ionic comonomer AMPS was not possible due to the difficulty in taking the gel samples out of the reaction tubes. These non-ionic TBA/AAm based hydrogels were very soft and sticky so that a few drops of methanol have to be added on the gel samples to separate them from

the glass surface. As a result, mass of the gel after its preparation could not be determined and, qF and v_2^o as well.

5.4 Swelling Measurements

Swelling measurements, were carried out at various temperatures between 3 °C and 75°C. Various solvents such as water, methanol, ethanol, DMSO, as well as their mixtures with water of various compositions were used in the swelling experiments.

After the hydrogels were freed from the glass tubes, they were cut into samples of about 1 cm in length. Then, each sample was placed in vials with an excess of solvent or solvent mixture at a given temperature. The volume of the solvent mixture in the vial was much larger than the gel volume so that the composition of the solvent mixture was practically unchanged. In order to reach the equilibrium of swelling, the hydrogels were immersed in solvents and solvent mixtures for at least one week during which the solvent or the solvent mixture was replaced for several times. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel.

The equilibrium volume swelling ratio of the hydrogels V/V_o (volume of equilibrium swollen gel/ volume of the gel just after preparation) was calculated as:

$$\frac{V}{V_o} = \left(\frac{D}{D_o} \right)^3 \quad (5.2)$$

where D and D_o are the diameters of the hydrogels after equilibrium swelling and after preparation, respectively. To eliminate the error coming from the evaporation of the polymerization solvent t-butanol, the internal diameter of the glass tubes (5 ± 0.3 mm) was taken as the initial diameter of the gel samples throughout the study. The volume swelling ratio q_v was calculated :

$$q_v = \frac{V/V_o}{v_2^o} \quad (5.3)$$

Each swelling ratio reported in this study is at least an average of four separate measurements; standard deviations of the measured swelling ratios were less than 10 % of the mean value.

To obtain hydrogels at various degree of swelling, equilibrium swollen gels were placed in sealed 50 ml vials at room temperature to evaporate a desired amount of water . This procedure ensured uniformity of the network concentration throughout the gel sample. After a given evaporation time (a few minutes up to a few days), the diameters of partially swollen gels were measured from which their swelling ratios were calculated by use of Equation (5.2).

5.5 Mechanical Measurements

The mechanical measurements were conducted in a thermostated room of 23 ± 0.5 °C. Uniaxial compression measurements were performed on hydrogels at different degree of swelling and after their preparation. The key parts of the apparatus used for measuring stress-strain data on the hydrogels are shown in Figure 5.1.

Briefly, cylindrical gel sample after preparation of 5 mm in diameter and 13 mm in length was placed on a digital balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The force acting on the gel was calculated from the reading of the balance m :

$$F = mg \quad (5.4)$$

where g is the gravitational acceleration, (9.803 m/s^2). The resulting deformation $\Delta l = l_o - l$, where l_o and l are the initial undeformed and deformed lengths, respectively, was measured using digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm . The force and the resulting deformation were recorded after 15 s of relaxation. The measurements were conducted up to about 20% compression. The sample weight loss during the measurements due to water evaporation was found to be negligible. The deformation ratio λ (deformed length/initial length) was calculated as:

$$\lambda = 1 - \frac{\Delta l}{l_o} \quad (5.5)$$

The corresponding stress f was calculated as:

$$f = F / A \quad (5.6)$$

where A , is the cross-sectional area of the specimen, i.e.,

$$A = \pi \left(\frac{D_o}{2} \right)^2 \quad (5.7)$$

As pointed out in the theoretical section, for uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form :

$$f = G(\lambda - \lambda^{-2}) \quad (5.8)$$

where G is the elastic modulus of the gel sample.



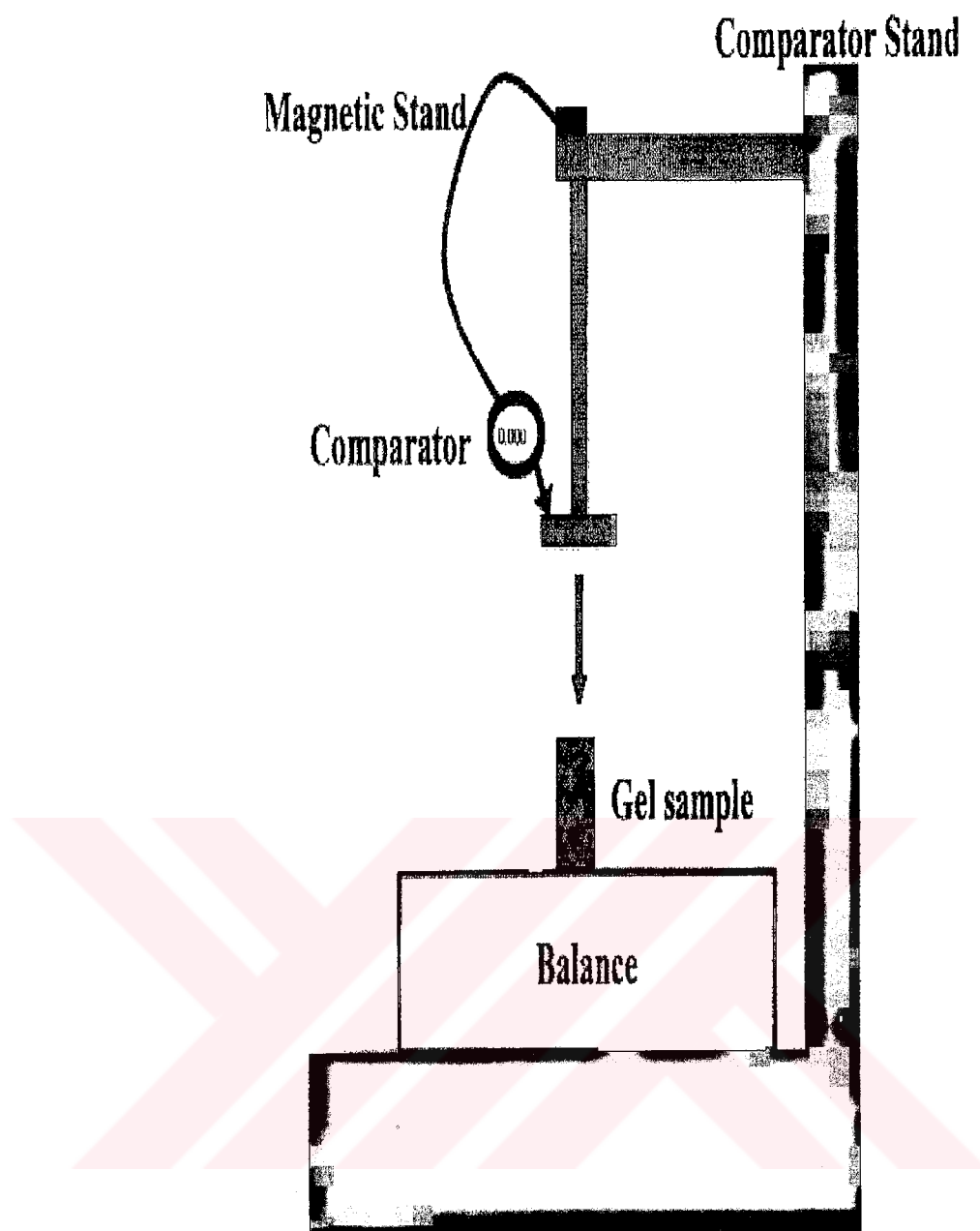


Figure 5.1 Uniaxial compression apparatus for measuring stress-strain data [51].

6. RESULTS AND DISCUSSION

A series of poly (TBA-co-AAm) hydrogels were prepared at a fixed crosslinker ratio (1/80) and monomer concentration (5wt %) but at various charge densities, i.e., at various AMPS contents. The TBA mole fraction in the comonomer mixture was fixed at 0.60 throughout this study. A set of preliminary experiments were carried out to find the optimum reaction conditions of the crosslinking TBA-AAm copolymerization. Due to the different solubility characteristics of the monomers TBA, AAm, and of the crosslinker BAAM, the crosslinking copolymerizations were difficult to achieve. TBA monomer is soluble in organic solvents such as methanol, ethanol, THF, or t-butanol but insoluble in water. In contrast, both AAm and BAAM are soluble in water but insoluble in organic solvents. Several solvents including methanol, ethanol, t-butanol, 2-propanol, as well as their mixtures with water were tested in the copolymerization experiments. No gel formation was observed if the crosslinking copolymerization is conducted in methanol or methanol-water mixtures. Also, other solvents and solvent mixtures were unsuccessful except t-butanol or t-butanol/water mixtures. A minimum of 50 v/v % t-butanol in water was required to obtain gels at 5% initial monomer concentration. All the hydrogels reported here were then prepared in 1/1 t-butanol-water mixtures. Moreover, compared to the AIBN initiator, KPS was found to be successful to initiate and to complete the reactions. Complete monomer conversions and reproducible results were obtained at a reaction temperature of 50 °C for the ionic gels, and 60 °C for the non-ionic gel. It was also observed that the comonomer feed compositions containing AMPS as the ionic comonomer led to the formation of transparent gels, whereas white or opaque gels were obtained in the absence of AMPS. This indicates that a micro phase separation occurs during the formation of non-ionic gels in t-butanol-water. Furthermore, hydrogels prepared in the presence of more than 3% AMPS were too weak to withstand the swelling and mechanical measurements. Therefore, the ionic group (AMPS) content of poly(TBA-co-AAm) hydrogels was only varied between 0 and 3 mole %. All the hydrogels samples after

preparation were subjected to gravimetric tests to determine the monomer conversions and the gel fractions. Swelling and elasticity measurements were also conducted on the hydrogels samples.

6.1 Monomer Conversions and Gel Fractions

The characteristics of poly(TBA-co-AAm) hydrogels are compiled in Table 6.1. In column 1, the AMPS contents of the hydrogels are given in terms of the mole fractions x_i . In the second column of the Table 6.1 the weight swelling ratios of the hydrogels after their preparation qF (mass of gel after preparation /mass of dry gel) are collected. qF decreases slightly with increasing AMPS content of the hydrogels from 12.7 to 9.6. It must be noted that the qF value of the non-ionic gels ($x_i=0$) cannot be determined because of their stickiness and softness. From the qF values, the volume fraction of the crosslinked polymer after the gel preparation v_2^o was calculated using Equation (5.1). The v_2^o values of the hydrogels are also shown in column 3 of the table. Assuming that the monomer conversions and the gel fractions are complete after the crosslinking TBA-AAm copolymerization, one may theoretically calculate the v_2^o value of the hydrogels using the equation:

$$v_2^o = \frac{c}{100\rho} \quad (6.1)$$

where c is the initial monomer concentration. Since $c=5$ wt % and $\rho=1.35$ g/ml, the theoretical value of v_2^o calculated as 0.04. It is seen that the experimental v_2^o values listed in Table 6.1 are larger than the theoretical one. This would indicate a monomer conversion higher than 100%, or, the presence of residual water in the dried gel samples. Indeed, in case of PAAm or PNIPA gels, trapped or bounded water was observed in gel samples, even after several months of drying in vacuum [51]. From the v_2^o values it may be concluded that the monomer conversions and the gel fractions were complete after the free-radical crosslinking copolymerization of TBA and AAm.

Table 6.1 The characteristic data of (TBA-co-AAm) based hydrogels. x_i = mole fraction of AMPS in the comonomer mixture, qF = weight swelling ratio of the hydrogels after their preparation, v_2^0 = volume fraction of crosslinked polymer after the gel preparation, V/V_0 = normalized equilibrium volume swelling ratio (volume of swollen gel/volume of gel after preparation), q_v = equilibrium volume swelling ratio (volume of swollen gel/volume of dry gel), G_0 = elastic moduli of the hydrogels after their preparation.

x_i	qF	v_2^0	V/V_0	q_v	G_0 / Pa
0.000	-	-	0.30	-	-
0.005	12.7	0.053	2.49	47	347
0.010	12.0	0.057	10.00	175	382
0.015	11.1	0.061	21.00	344	403
0.020	9.6	0.071	36.40	512	447

6.2 Equilibrium Swelling Degrees of the Hydrogels in Water at Room Temperature

The equilibrium swelling degrees of the hydrogels V/V_o (volume of the equilibrium swollen gel/ volume of gel after preparation) were first measured at room temperature (23 ± 0.5 °C) in water. From the V/V_o values, the equilibrium volume swelling ratios q_v (volume of the equilibrium swollen gel/volume of dry gel) were calculated using equation (5.3). The results are also collected in Table 6.1. In Figure 6.1, both V/V_o and q_v values of the hydrogels are plotted as a function of the AMPS mole fraction x_i of the hydrogels. It is seen that the swelling ratio increases with increasing AMPS content of the hydrogels. This is a consequence of the osmotic pressure exerted by the counterions of AMPS units in the network chains. According to Equation (2.35), this osmotic pressure increases as the concentration of the counterions (Na^+) increases. Another point shown in Table 6.1 and Figure 6.1 is that the non-ionic gel ($x_i=0$) exhibits a very low volume swelling ratio ($q_v = 0.60$), i.e., it is in the collapsed state in water at room temperature (23 °C). This indicates that the LCST of poly(TBA-co-AAm) gel is below 23 °C. Moreover, q_v increases with x_i first slightly up to $x_i=0.01$ but then rapidly as x_i is further increased. Hydrogels with $x_i \geq 0.03$ were too weak to withstand the swelling measurements. These samples broken down into small gel particles during the swelling process.

6.3 Comparison of the Swelling Degrees of the Poly(TBA-co-AAm) Hydrogels with Those of PNIPA and PAAm Hydrogels

In Figure 6.2, the equilibrium swelling ratios of poly(TBA-co-AAm) hydrogels are compared with those of PNIPA and PAAm hydrogels. The swelling data of NIPA and PAAm gels were taken from the literature [23, 48]. Since the TBA monomer is much more hydrophobic than both NIPA and AAm monomers, one may expect that the poly(TBA-co-AAm) gels swell in water much less than the PNIPA and AAm gels. However, Figure 6.2 shows an opposite behavior. The swelling ratios of the present hydrogels increases with x_i rapidly and V/V_o becomes 36.4 at $x_i=0.02$. In case of PNIPA or PAAm gels, the increase of V/V_o with x_i is less dramatic; about 40 to 60 %

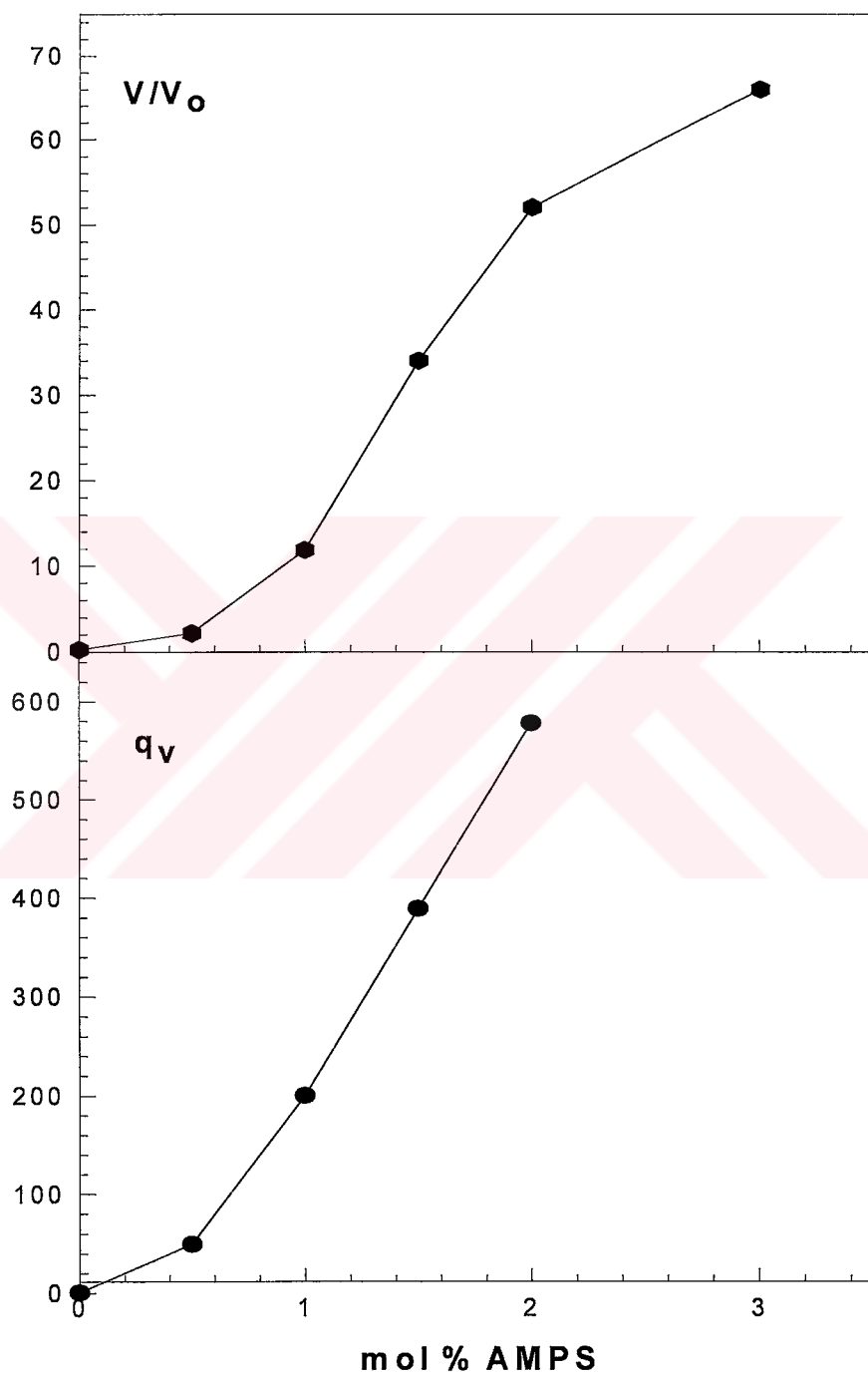


Figure 6.1 Dependences of the volume swelling ratios V/V_0 and q_v on the mol % AMPS of poly(TBA-co-AAm) hydrogels. Temperature = 23 ± 0.5 C°

AMPS ($x_i=0.4-0.6$) are needed to obtain the same swelling ratio as the poly(TBA-co-AAm) hydrogels. This unexpected behavior can be explained with a decrease in the crosslinking efficiency of BAAm in TBA/AAm copolymerization.

Due to the different solubility characteristics of TBA and AAm monomers as well as due to the necessity of use of an organic solvent in the crosslinking process, a part of the crosslinker BAAm is expected to be consumed by the side reactions or remain unreacted in reaction solution.. As a result, the gels formed exhibit high swelling ratios.

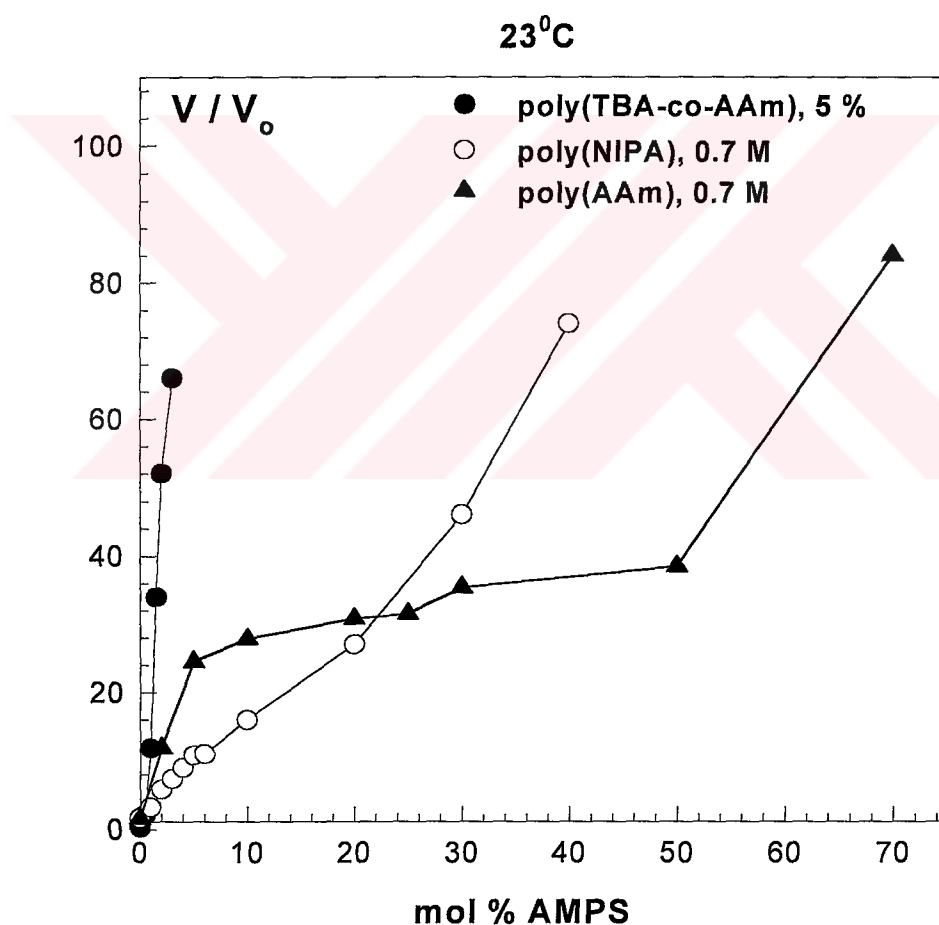


Figure 6.2 Comparison of the swelling ratios V/V_o of three types of hydrogels in water at 23 °C. Experimental data for PNIPA and PAAm were taken from ref. [23,48].

6.4 Crosslink Densities of the Hydrogels

Uniaxial compression measurements were performed on hydrogels after their preparation and at various degree of swelling. The stress f acting on the gel sample and the resulting strain α were measured up to about 20 % compression in order to remain in the Gaussian regime. In Figure 6.3, the stress-strain data of the hydrogels just after their preparation are correlated according to Equation (5.8). From the slopes of these dependencies, the elastic moduli G_o of gels after preparation were calculated. These data are collected in column 6 of Table 6.1.

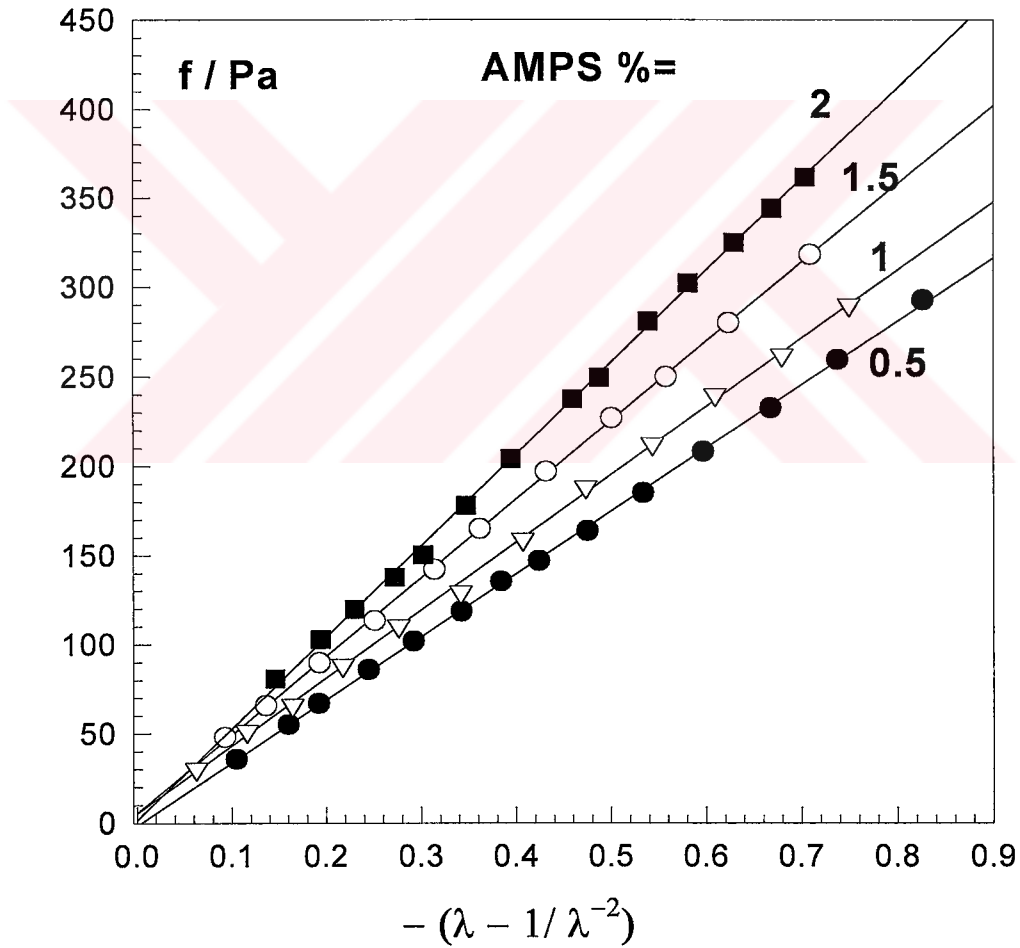


Figure 6.3 Stress-strain data of the hydrogels correlated according to Equation (5.8).

The AMPS contents of the hydrogels are indicated in the figure.

It is seen that G_o values are in the range of 300-400 Pa, much lower than the corresponding PNIPA [51] and PAAm [58] hydrogels. Furthermore, G_o increases further as the AMPS content of the hydrogels increases. This is also illustrated in Figure 6.4, showing the variation of G_o with the AMPS mole fraction x_i . Figure 6.4 also shows that G_o versus x_i dependence is linear. By linear regression, the modulus G_o of the non-ionic gel was calculated as 314 Pa. As explained in the theoretical section, the elastic modulus G of gels depends both on their crosslink densities and their swelling ratios. Since $v_2 = v_2^o$ for gels after preparation, equation (2.44) reduces to the following equation for the elastic modulus G_o after the gel preparation:

$$G_o = \frac{\rho}{M_c} RTv_2^o \quad (6.2)$$

Using the experimental G_o and v_2^o values of the hydrogels together with Equation(6.2) the crosslink densities of the hydrogels in terms of $\overline{M_c}$, the molecular weight of the chains was calculated. For these calculations, the following constants were used: $\rho=1350 \text{ kg/m}^3$, $R=8.314 \text{ J/mole-K}$ and $T=296 \text{ K}$. The calculated values of $\overline{M_c}$ are shown in Figure 6.5 plotted as a function of the mole fraction of AMPS in the network chains x_i . Interestingly, addition of the ionic comonomer AMPS in the comonomer mixture decreases the molecular weight of the network chains M_c , i.e., increases the crosslink density of the hydrogels. This indicates that the crosslinking efficiency of BAAM increases in the presence of the ionic comonomer AMPS. The reason of this increase is presently unclear.

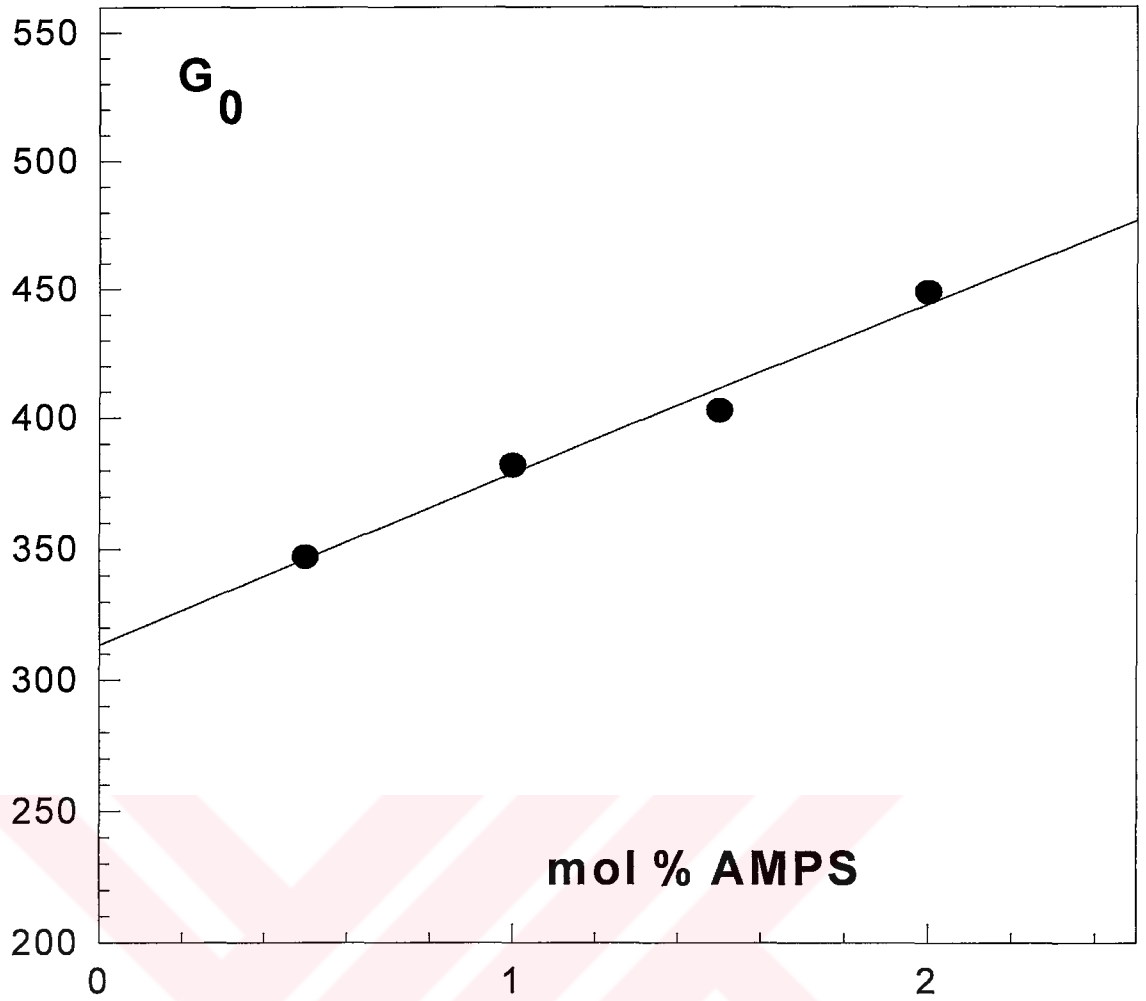


Figure 6.4 Variation of the elastic modulus of hydrogels after preparation G_0 with the mol % of AMPS in the network chains. The line shown is the linear regression line to the data points from which G_0 of the non-ionic gels was calculated.

If one assumes that all the crosslinker (BAAm) molecules form effective crosslinks in the final hydrogels, the chemical value of $M_c(M_{c,chem})$ can be calculated by the following equation:

$$M_{c,chem} = \frac{M_r}{2X} \quad (6.3)$$

where X is the crosslinker ratio (moles of BAAm/moles of monomers) and M_r is the molecular weight of polymer repeated units. Using the molecular weight of the TBA and AAm monomers (127 and 71 g/mol, respectively), M_r was calculated as 104.6 g/mol. The experimentally fixed value of $X=1/80$ together with equation (6.3) thus

yields $M_{c,chem}=4184$ g/mol. Comparison of the experimentally determined M_c values (in the order of 10^5 g/mol) with $M_{c,chem} (\cong 10^3)$ indicates that a very large fraction of the crosslinker BAAM is indeed wasted by the side reactions, such as cyclization and multiple crosslinking reactions.

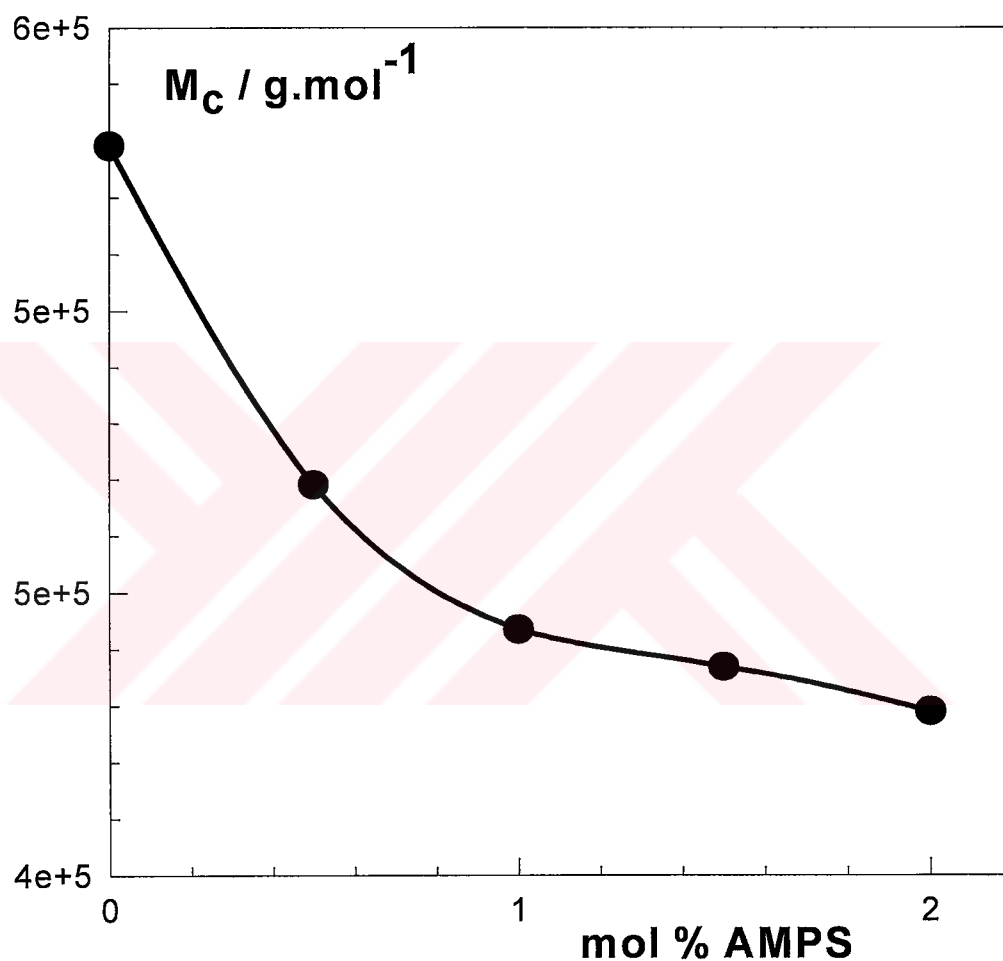


Figure 6.5 Variation of the molecular weight of the network chains M_c with the mol % of AMPS of the network chains.

6.5 Elastic Behavior of the Hydrogels

The elastic moduli G of the hydrogels were also measured at various swelling degrees as well as at equilibrium swelling. The results are collected in Figure 6.6, showing the variation of the modulus G with the swelling ratios V/V_0 of gels. Experimental data points were obtained using hydrogels of various AMPS contents, as indicated in the Figure 6.6.

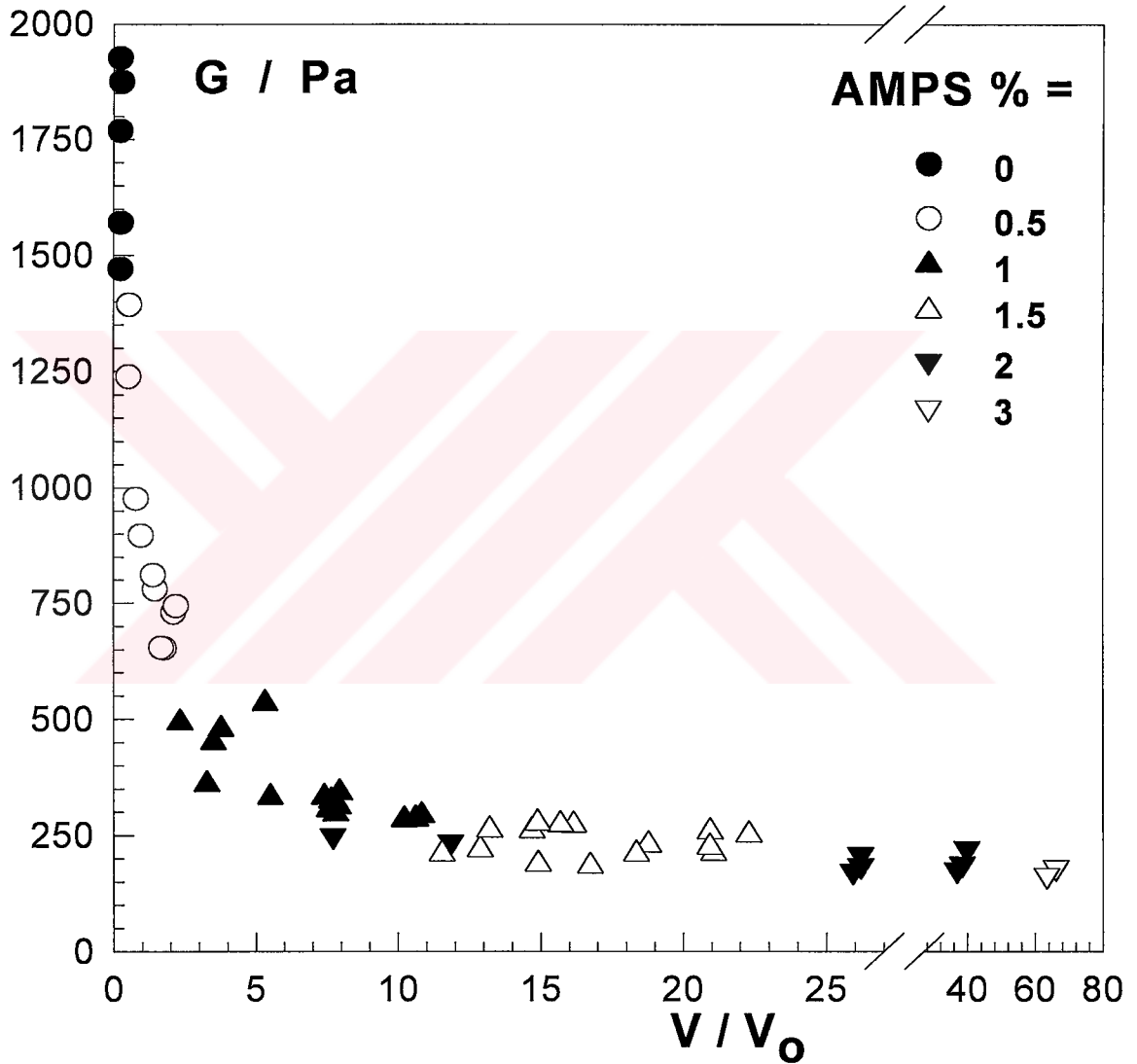


Figure 6.6 Variation of the elastic moduli of the hydrogels with their swelling ratios V/V_0 . The AMPS content of the hydrogels are indicated in the figure.

It is seen that the moduli G of the hydrogels are about 250 Pa at high swelling ratios. In the range of V/V_o below 5, the modulus rapidly increases as the swelling ratio (i.e., the gel volume) decreases. This increase in the modulus is a result of increasing concentration of the network chains in the hydrogels. Dividing equation (2.44) to equation (6.2), one may obtain the ratio of the modulus at a given degree of swelling to that at the preparation condition (G/G_o):

$$G/G_o = (V/V_o)^{-1/3} \quad (6.4)$$

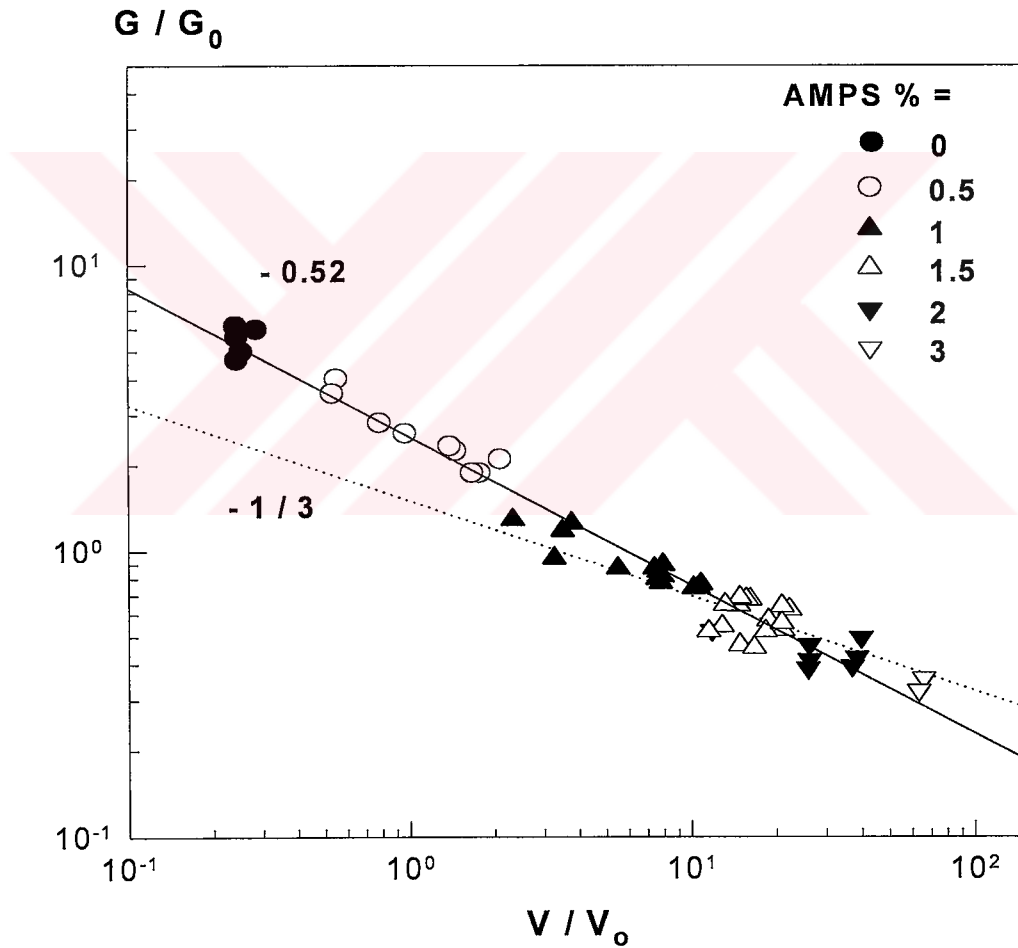
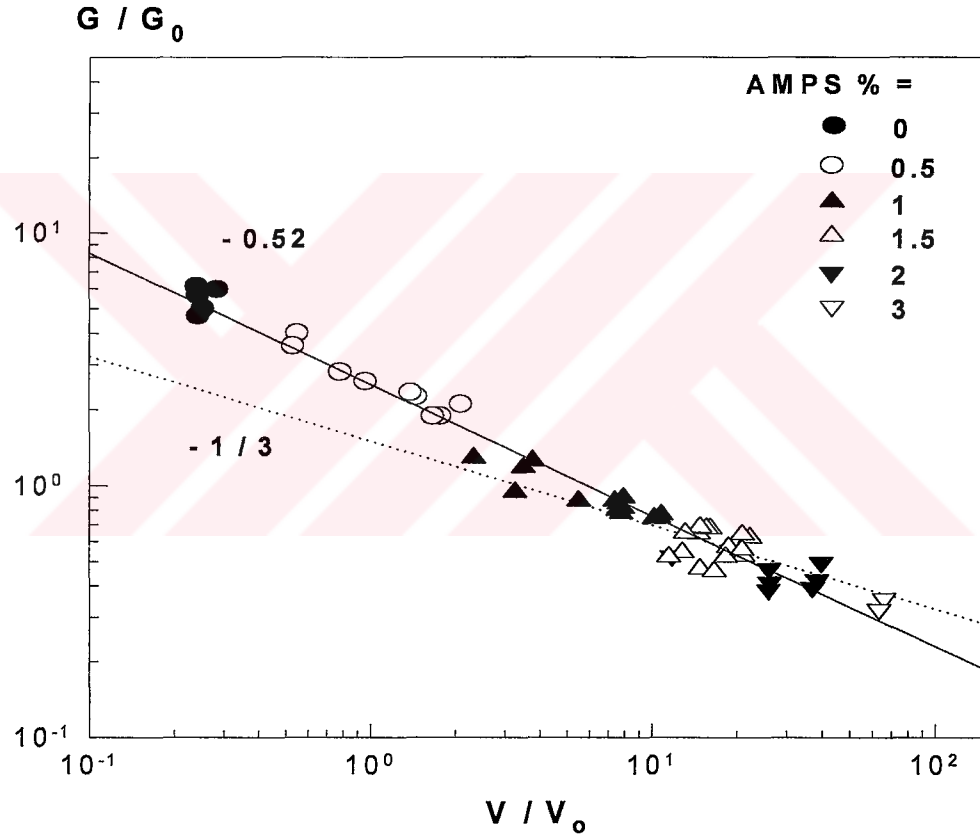


Figure 6.7 Variation of the reduced modulus G/G_o with the volume swelling ratio V/V_o of the hydrogels. AMPS content of the hydrogels are indicated in the figure.

It is seen that the moduli G of the hydrogels are about 250 Pa at high swelling ratios. In the range of V/V_0 below 5, the modulus rapidly increases as the swelling ratio (i.e., the gel volume) decreases. This increase in the modulus is a result of increasing concentration of the network chains in the hydrogels. Dividing equation (2.44) to equation (6.2), one may obtain the ratio of the modulus at a given degree of swelling to that at the preparation condition (G/G_0):

$$G/G_0 = (V/V_0)^{-1/3} \quad (6.4)$$



It is seen that, assuming that the network chains behave Gaussian, this ratio (called the reduced modulus) does not depend on the crosslink density and only depends on the swelling ratio V/V_0 . Furthermore, a double logarithmic G/G_0 versus V/V_0 plot should give a scaling exponent of $-1/3$. The data points shown in Figure 6.6 are given in Figure 6.7 in the form of the double logarithmic G/G_0 - V/V_0 plot. The dotted line in the Figure illustrates the theoretical slope of $-1/3$, as predicted for the Gaussian chains. The solid line is best fit to all data points, which gives a scaling

parameter of $-0.52 \cong -1/2$. The discrepancy between the theory and experiment may be due to the experimental error and/or due to the non-Gaussian behavior of the poly(TBA-co-AAm) network chains.

6.6 Swelling Behavior of the Hydrogels in Solvent Mixtures

Poly(TBA-co-AAm) hydrogels were subjected to swelling measurements in the following solvent mixtures: DMSO-water, ethanol-water, and methanol-water. The swelling measurements were carried out at two different temperatures, namely at room temperature (23 ± 0.5 °C) and at 3 ± 0.3 °C (the temperature inside the refrigerator). The composition of the solvent mixtures was varied between 0 and 100 %. In all of these solvent mixtures, it was observed that the hydrogels exhibit reentrant conformational transitions, i.e., the hydrogels first deswell but then reswell as the solvent composition is continuously varied. For example, in Figure 6.8, the swelling behavior of the hydrogels with 1 % AMPS ($x_i=0.01$) immersed in DMSO/water mixtures is illustrated. Here, the swelling ratio V/V_o is plotted as a function of the DMSO volume fraction of the solvent mixture. For comparison, the swelling behavior of PAAm hydrogels is also shown in Figure 6.8. It is seen that the PAAm gel slightly deswells as the DMSO content of the solvent mixture increases. In contrast, poly(TBA-co-AAm) hydrogel is swollen below 32 % DMSO. If the DMSO content is further increased, the gel undergoes a first-order volume phase transition from the swollen to collapsed state and remains in the collapsed state up to about 70 % DMSO. If the DMSO content of the solvent mixture is further increased, the gel swells again rapidly and, remains in the swollen state up to 100 % DMSO. In the following paragraphs, this interesting feature of the poly(TBA-co-AAm) hydrogels in three different solvent mixtures will be shown.

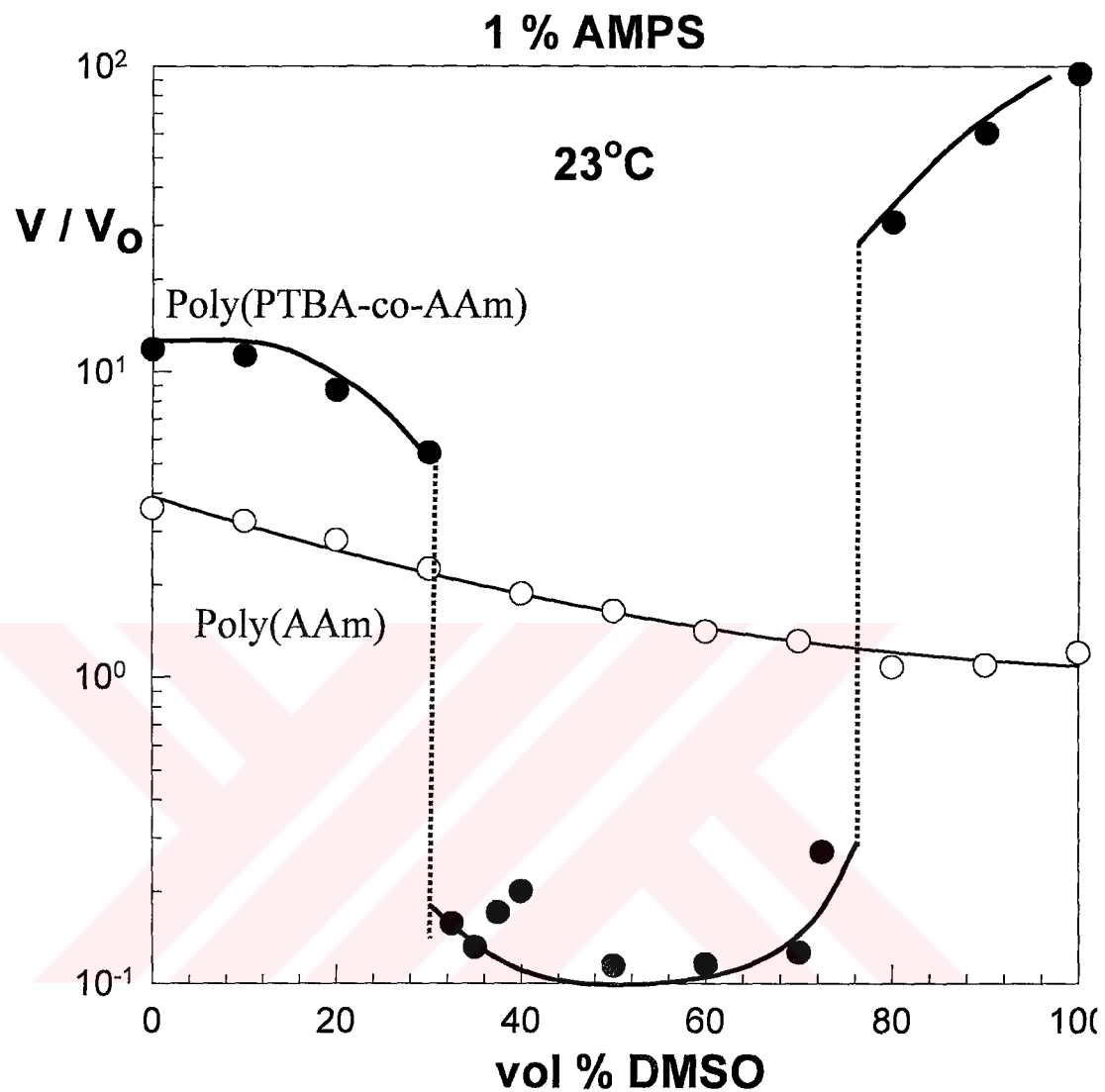


Figure 6.8 Swelling ratio V/V_0 of the hydrogels plotted as a function of the volume fraction of DMSO in DMSO/water mixtures. (•) =poly(TBA-co-AAm) hydrogel, (o)=PAAm hydrogels. The dotted lines represent the phase transition regions. Both hydrogels contain ionic comonomer AMPS at 1 mol%.

6.6.1 DMSO/water mixtures

In Figure 6.9, the variations of the degree of swelling V/V_0 of both non-ionic and ionic poly(TBA-co-AAM) hydrogels are shown as a function of the DMSO content of DMSO/water mixtures. The solid curves only show the trend of data. The dotted lines illustrate the phase transition regions. The collapsed region is illustrated by the shaded area. The swelling measurements were carried out at 3 °C and 23 °C in Figures 6.9A and 6.9B, respectively. It is seen that at 3 °C (Figure 6.9A) the gels are swollen both in water and DMSO separately. Decreasing the swelling temperature from 23 to 3 °C increases the extent of reentrant transition behavior of gels. Addition of DMSO to water or, water to DMSO results in the deswelling of the gels. Moreover, increasing the ionic group content of the hydrogels also increases their swelling ratios in water or in DMSO. Within a certain range of DMSO content, the gels are in collapsed state in DMSO/water mixtures. Figure 6.9A also shows that the range of DMSO content in which the gels are collapsed becomes shorter as the ionic group content of the hydrogels increases. Similar types of swelling and deswelling transitions were also observed at 23 °C, as seen in Figure 6.9B. Only difference observed was in the swelling behavior of the non-ionic gel. This gel is collapsed in water and remains in the collapsed state up to about 80 % DMSO. As the DMSO content is further increased, the non-ionic gels undergo a continuous swelling transition.

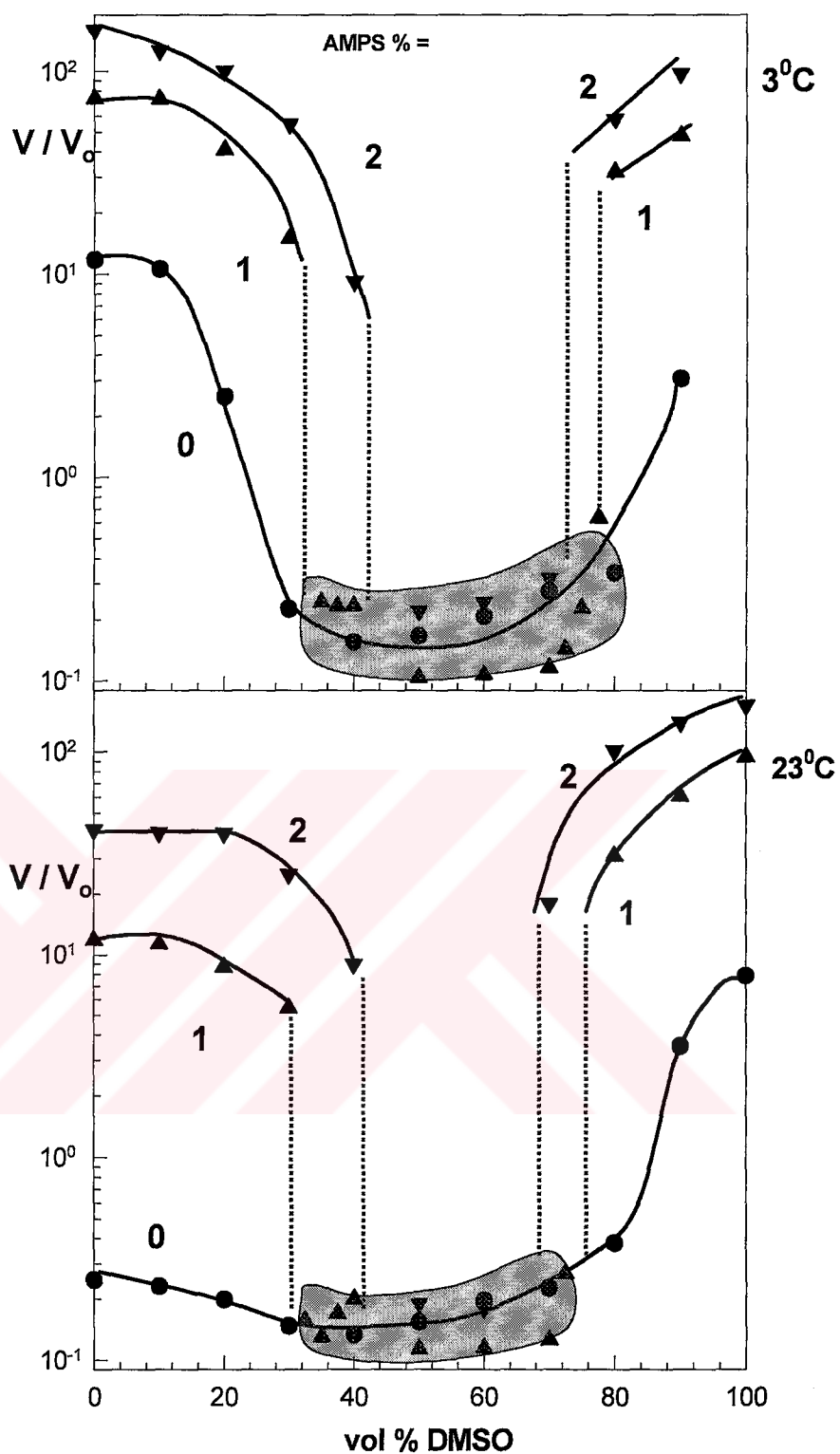


Figure 6.9 Variation of the swollen degree V/V_0 of the hydrogels with the DMSO content of DMSO/water mixtures. Ionic group (AMPS) contents of the hydrogels are indicated in the Figure. Temperature = 3°C (A) and 23°C (B)

6.6.2. Ethanol/water mixtures

The dependence of the degree of swelling V/V_0 of the hydrogels on the content of ethanol/water mixture is illustrated in Figure 6.10. Here, again, the swelling temperatures were 3 °C and 23 °C in Figures 6.10A and 6.10B respectively. The results show that the swelling behavior of the hydrogels in ethanol/water mixtures is similar to that in DMSO/water mixtures.

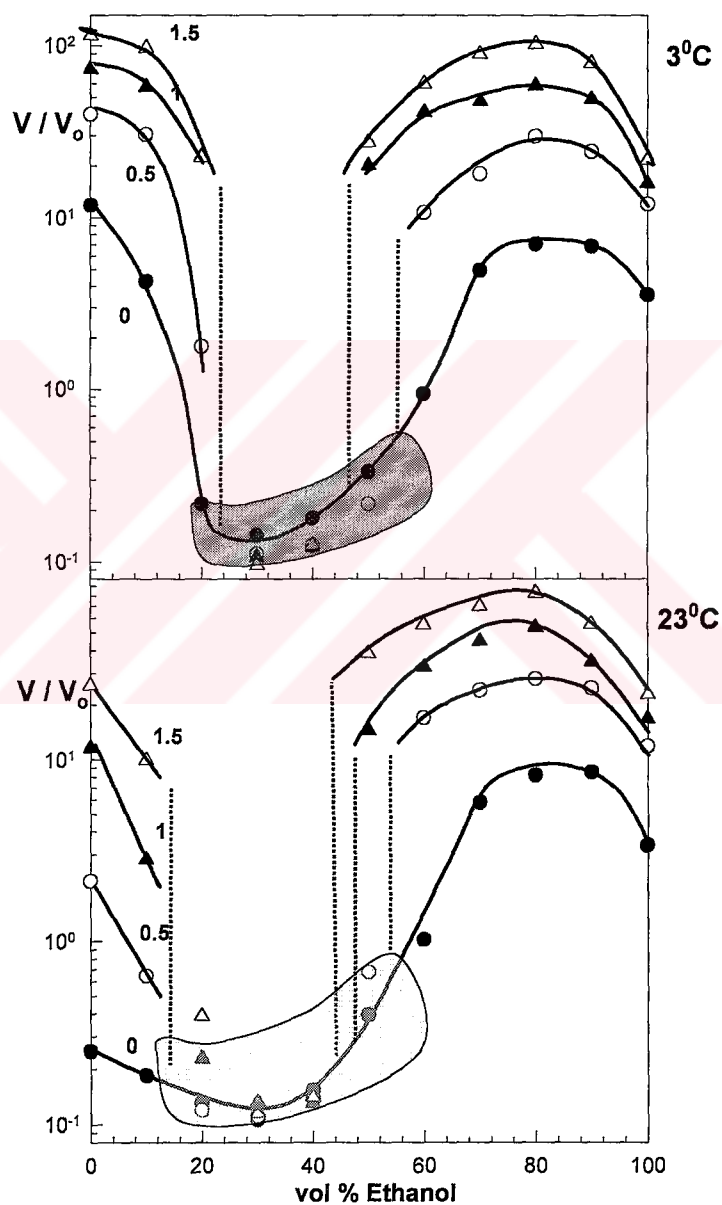


Figure 6.10 Variation of the swelling degree V/V_0 of the hydrogels with the ethanol content of the mixtures at 3 °C and 23 °C.

The gels are in collapsed state within a certain range of ethanol contents, outside of which they remain in the swollen state. In Figures 6.11 and 6.12, the swelling ratios of the hydrogels in DMSO/water mixtures are compared with those in ethanol/water mixtures. The AMPS contents of the hydrogels are 0 and 0.5 % in Figures 6.11 and 6.12 respectively. It is seen that if ethanol is replaced with DMSO, the deswelling and the reswelling of the hydrogels start later, i.e., at higher DMSO contents. Thus compared to ethanol a larger amount of DMSO is required in order to bring the hydrogels in the collapsed state in the solvent mixture. In other words, the reentrant phase transition is shifted to lower water contents if ethanol is replaced with DMSO as the cosolvent of water.

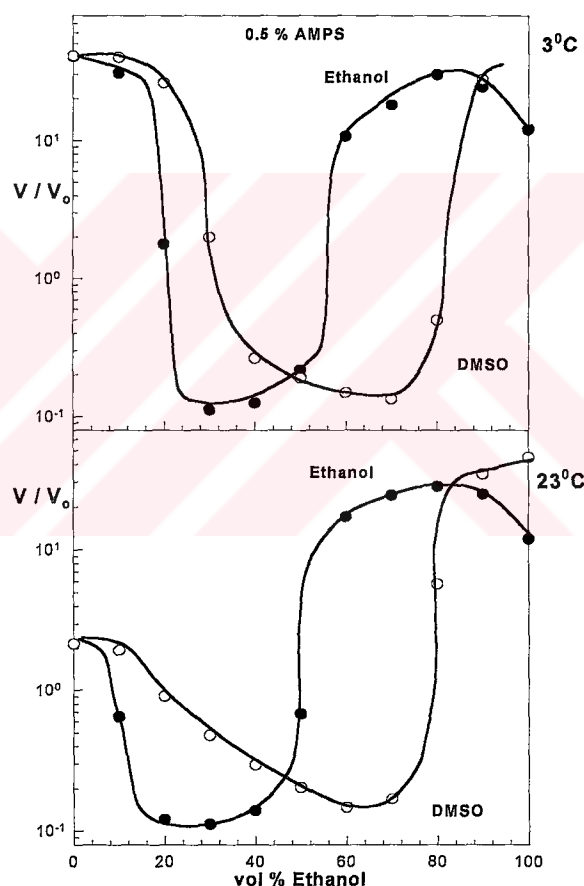


Figure 6.11 Swelling ratio of the hydrogels V/V_0 in solvent mixtures (●) =in ethanol/water, (○) =in DMSO/water, mol % AMPS =0.5

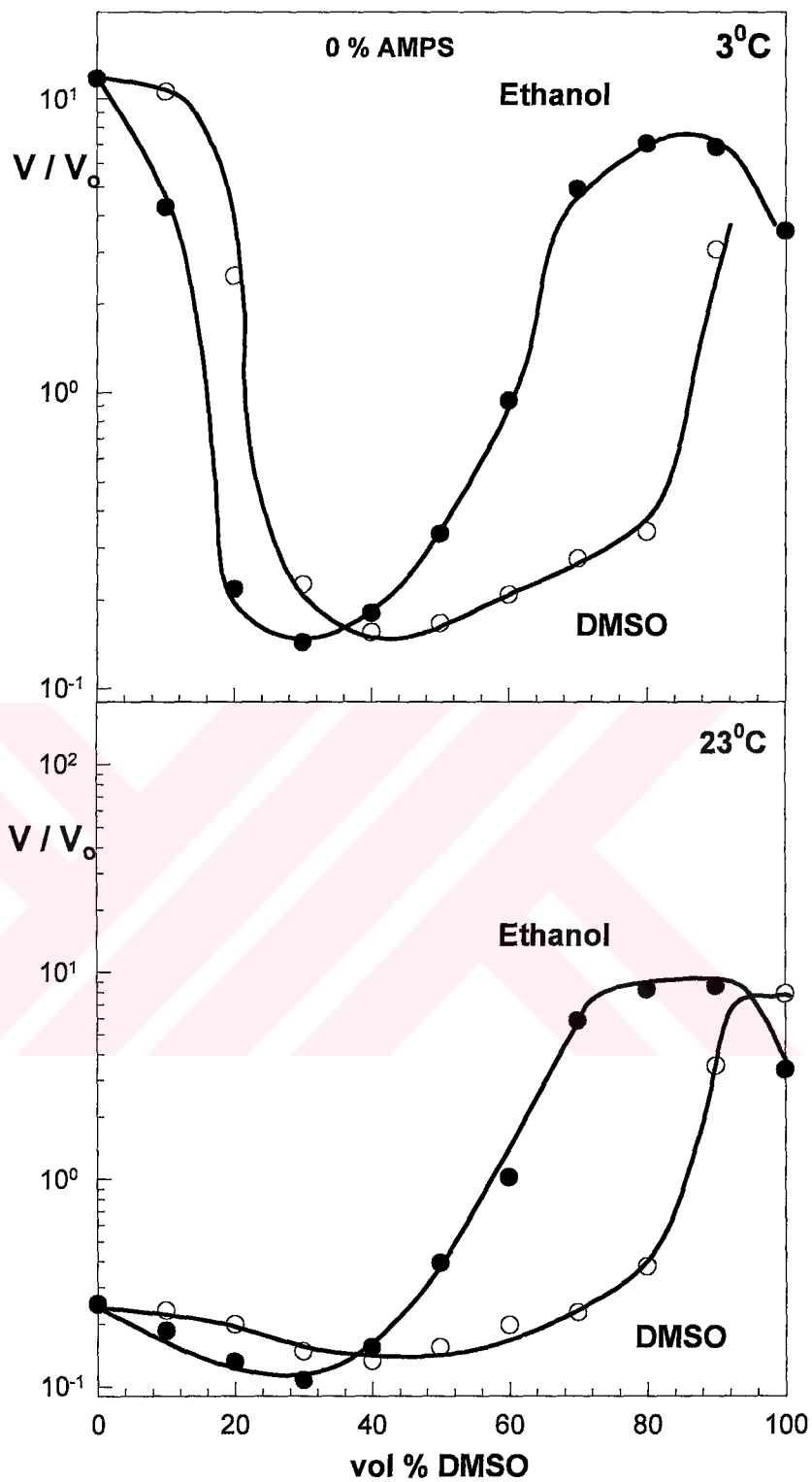


Figure 6.12 Swelling ratio of the hydrogels V/V_0 in solvent mixtures. (●) = in ethanol/water, (○) = in DMSO/water, mol % AMPS = 0, Temperature = 3 °C and 23 °C.

6.6.3 Methanol/water mixtures

The swelling behavior of the hydrogels in methanol/water mixtures is illustrated in Figure 6.13. Compared to the previous results observed in DMSO/water or ethanol/water mixtures, the hydrogels exhibit continuous deswelling and swelling transitions in methanol/water mixtures. Also, the range of methanol content in which the gels are collapsed is relatively short.

6.6.4 Intermolecular interactions

In section 6.6, it was shown that the PAAm gel deswells slightly as the DMSO content in the DMSO/water mixture increases, while the present poly(TBA-co-AAm) hydrogels exhibit reentrant conformational transitions in the same solvent mixture. Since the only difference between these two hydrogels is the existence of t-butyl groups in poly(TBA-co-AAm) networks, the results reveal that the t-butyl groups are responsible for the reentrant transition behavior of poly(TBA-co-AAm) hydrogels. As can be seen from Figure 6.8, the volume of the poly(TBA-co-AAm) hydrogel is about hundred fold larger than that of PAAm gel of the same ionic group content. This means that the incorporation of t-butyl groups on the network chains creates attractive interactions between the network and DMSO segments so that DMSO becomes a good solvent for the poly(TBA-co-AAm) network. Thus, water and DMSO molecules taken separately are good solvents for the present networks. However, in mixtures, since water molecules are hydrogen bonded with DMSO, the attractive water-DMSO interactions dominate over the water-poly(TBA-co-AAm) or DMSO-poly(TBA-co-AAm) interactions. As a result, addition of DMSO to water or water to DMSO decreases the water content of the gel phase so that the gel contracts and attains a minimum volume at 32-70 % DMSO. Thus, the reentrant swelling behavior of the hydrogels in DMSO/water mixtures is due to the competition of two attractive interactions. DMSO is attracted both by water and by the t-butyl groups of the network chains. At low or high DMSO contents, water-polymer or DMSO-polymer attractive interactions dominate over water-DMSO interactions so that the gel is swollen. However, at intermediate DMSO contents, water-DMSO interactions dominate the swelling process and the gel collapses by excluding both the DMSO and water molecules.

If DMSO is replaced with a less polar solvent, such as ethanol, the reentrant phase transition regions shift to higher water contents (Figures 6.11 and 6.12). This is expected to be due to the increasing extent of attractive interactions between the *t*-butyl groups of the network chains and ethanol, which induces a reentrant conformational transition earlier. The results presented in this section thus reveal that the relative magnitude of the interactions among the network, water, and the cosolvent determines the reentrant behavior of the hydrogels.

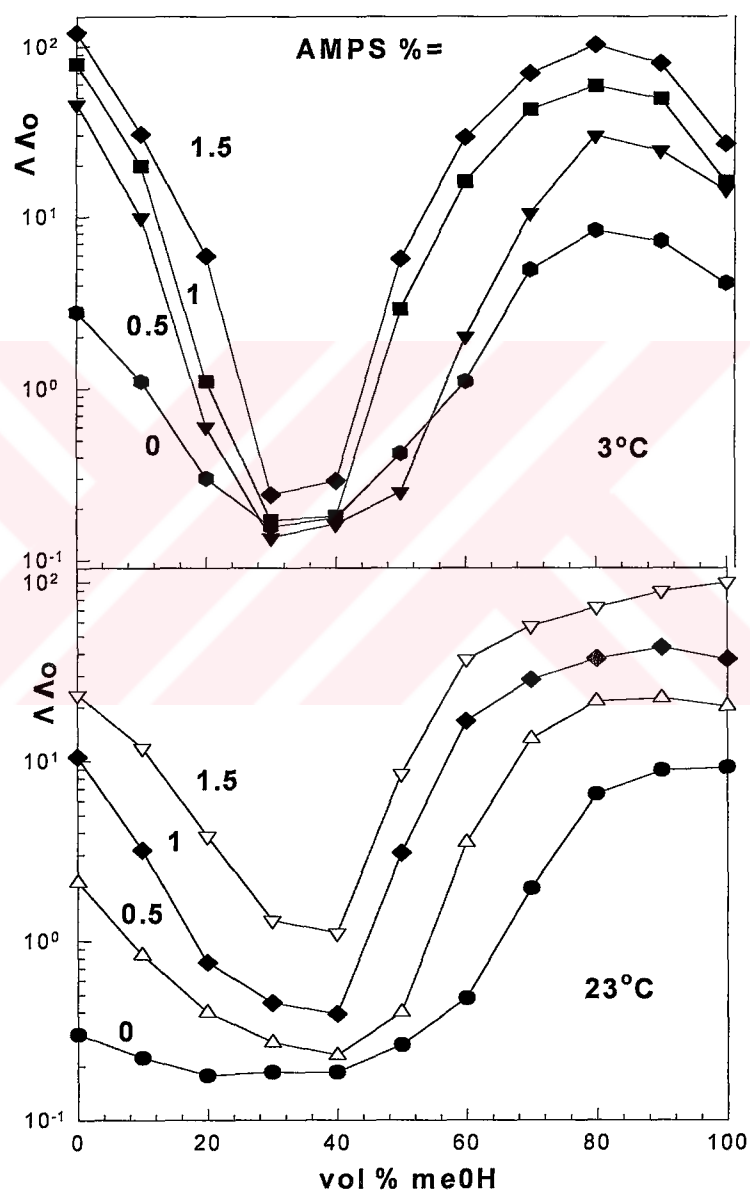


Figure 6.13 Swelling ratio of the hydrogels in methanol-water mixtures at 3°C and 23 °C. Ionic group AMPS contents of the hydrogels are indicated in the figure.

6.7 Temperature Sensitive Swelling Behavior of the Hydrogels in Water

In this section, the swelling degrees of the hydrogels in water were measured at various temperatures between 3.2 and 75 °C. The results are collected in Figure 6.14 as the dependence of the volume swelling ratio V/V_o on the swelling temperature. It is seen that the non-ionic gel is swollen below 8 °C, while it is collapsed above 20 °C. The gel undergoes a swelling-to-deswelling transition between 8 and 20 °C. Figure 6.14 also shows that compared to PNIPA gels, the swelling transition of poly(TBA-co-AAm) gel occurs smoothly probably due to the temperature insensitive AAm segments in the network chains. The LCST of poly(TBA-co-AAm) network chains with 60 % TBA is thus between 8 and 20 °C, which is much lower than the LCST of PNIPA. Moreover, Figure 6.14 also shows that the introduction of ionic groups into the hydrogels significantly influences their temperature sensitive swelling behavior. As the AMPS content of the hydrogels increases, the deswelling transition region shifts to higher temperature and becomes broader.

The results shown in Figure 6.14 can be explained as follows: when the poly(TBA-co-AAm) network is immersed into water, two phenomena are simultaneously observed. One is hydrophobic hydration, in which the water molecules form ordered cagelike structures around the network chains. The other is hydrophobic interaction, or association of hydrophobic t-butyl groups. At low temperatures, the gel is swollen in water because the hydration effect of water molecules dominates over the association forces between the t-butyl groups. However, at high temperatures, water molecules surrounding the network chains start to dissociate so that the hydrophobic interaction dominates over the hydrophobic hydration. As a result, the hydrogel is in collapsed state in water at high temperatures. One may expect that the association forces between the t-butyl groups are much stronger than those between iso-propyl groups. As a result, the poly(TBA-co-AAm) network chains start to collapse earlier, i.e., at lower temperatures than the corresponding PNIPA chains.

If AMPS segments are introduced into the poly(TBA-co-AAm) network chains, they exhibit a higher degree of swelling than the corresponding uncharged network chains. This is due to the osmotic pressure of counterions (Na^+) of AMPS units inside the gel. This osmotic pressure together with the effect of the hydrophobic hydration dominates the swelling process of the network chains so that the temperature required for the deswelling transition shifts to higher values.

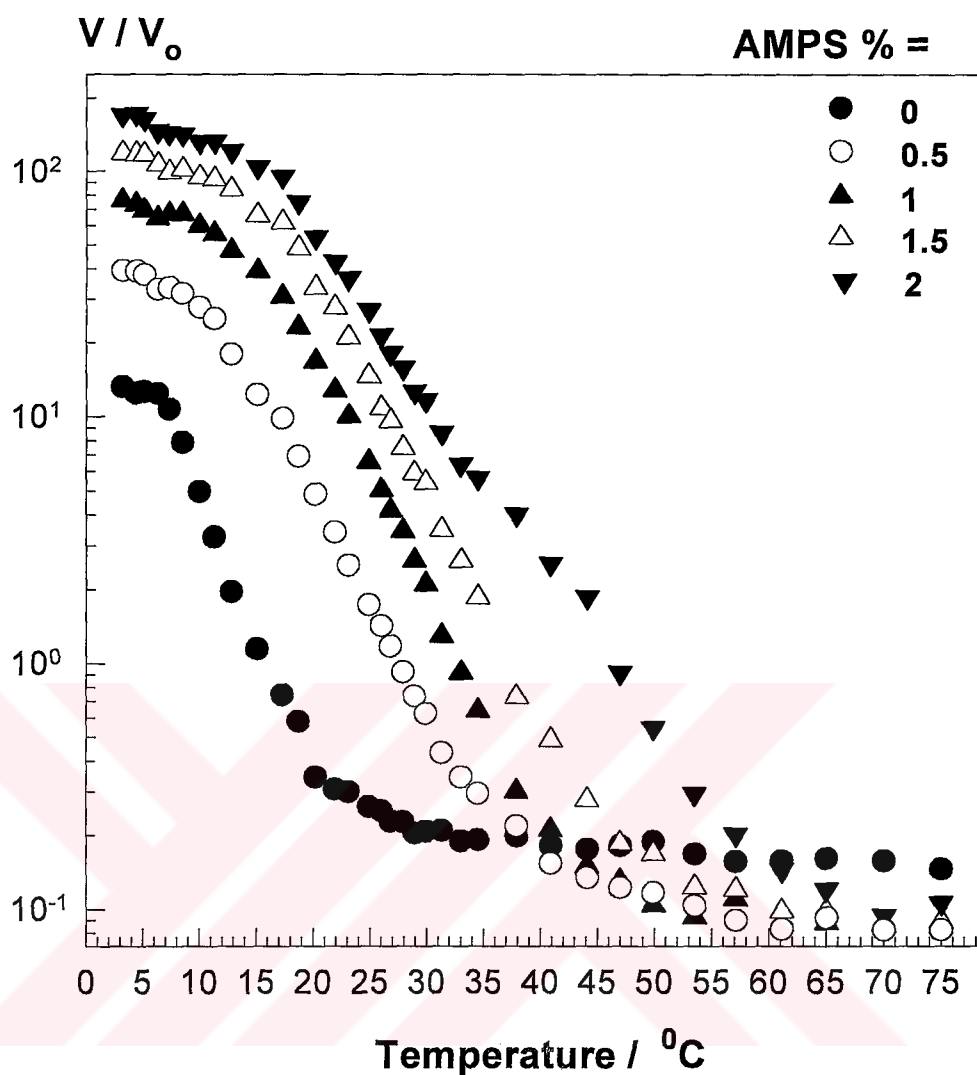


Figure 6.14 Variation of the equilibrium volume swelling ratios of the hydrogels V/V_0 in water with temperature. The AMPS content of the hydrogels are indicated in the Figure.

7. CONCLUSIONS

Poly(TBA-co-AAm) hydrogels of various charge densities were prepared at 5 %, initial monomer concentration in t-butanol-water mixture (1:1) as the polymerization solvent. The mole fraction of TBA in the comonomer mixture was fixed at 0.60 throughout the study. The crosslinker ratio was also fixed at 1/80 while the ionic group (AMPS) contents were varied between 0 and 2 % ($\chi=0.02$). The hydrogels thus prepared were subjected to swelling and mechanical measurements. The conclusions that can be drawn from the experimental results can be summarized as follows:

- 1) The hydrogels swell in water much more than the corresponding PAAm or PNIPA hydrogels. This indicates that a large fraction of the crosslinker BAAm is wasted by the side reactions or remained unreacted in the reaction solution during the free-radical crosslinking copolymerization of TBA and AAm in t-butanol –water.
- 2) The elastic moduli of the hydrogels after preparation were found to be in the range of 300-400 Pa, much lower than the moduli of the corresponding PAAm or PNIPA hydrogels. From these data, the molecular weight of the network chains M_c was calculated to be in the order of 10^5 g/mole.
- 3) The scaling parameter between the reduced modulus G/G_0 and the swelling ratio V/V_0 was calculated as $-0.52 \cong -1/2$, compared to the value of $-1/3$, as predicted for the Gaussian chains.
- 4) The swelling behavior of the hydrogels in DMSO/water, ethanol/water, and methanol/water mixture was investigated in detail. It was found that the hydrogels exhibit reentrant conformational transitions in these solvent mixtures. It was also shown that the t-butyl groups on the network chains are responsible for the reentrant behavior.
- 5) Poly(TBA-co-AAm) network chains with 60 % TBA exhibit a swelling-to-deswelling transition between 8 and 20 °C. The temperature interval in which the deswelling occurs shifts to higher values if ionic groups are introduced on the network chains.

The preparation of fast-responsive poly(TBA-co-AAm) hydrogels would be one of the aims of the future studies. This may be achieved by creating a macroporous structure in the networks. Moreover, replacement of AAm units by the NIPA units is expected to decrease further the transition temperature of the hydrogels.



REFERENCES

- [1] Tanaka, T., 1981, *Sci. Am.*, **244**, 10.
- [2] Funke, W. Okay, O., and Muller, B.J., 1998, *Adv. Polym. Sci.*, **136**, 142
- [3] Yamauchi, A., 1990, *Organic Polymer Gels*, Tokyo.
- [4] Kayaman N., Okay, O. and Baysal B.M., 1997, *Polym. Gels Networks*, **5**, 167.
- [5] Hirokawa, Y. and Tanaka T., 1984, *J. Chem., Phys.*, **81**, 6379.
- [6] Hirotsu, S., Y. Hirokawa and Tanaka, T., 1987, *J. Chem. Phys.*, **87**, 1392.
- [7] Okano, T., 1998, *Biorelated Polymers and Gels*, Academic Press, Boston.
- [8] Dusek, K. and Patterson, D., 1968, *J. Polym. Sci, Part A-2*, **6**, 1209.
- [9] Tanaka, T., *Phys. Rev. Lett.*, 1978, **40**, 820.
- [10] Tanaka, T., Fillmore, D.J., Sun, S-T., Nishio, I., Swislow, G. and Shah A., 1980, *Phys. Rev. Lett.*, **45**, 1636.
- [11] Takoka, T., Berker, N., Du, R., Enoki T., Grosberg, A., Kardar, M., Oya T., Tanaka K., Wang, G., Yu, X., and Tanaka T., 1999, *Phys. Rev. Lett.*, **82**, 4863.
- [12] Kokufuta, E and Nakaizumi, S., *Macromolecules*, 1995, **28**, 1704.
- [13] Irie, M., Misumi, Y. and Tanaka, T., 1993, *Polymer*, **34**, 4531.
- [14] Mamada, A, Tanaka, T., and Irie M., 1990, *Macromolecules*, **23**, 1517.
- [15] Ilavsky, M., 1982, *Macromolecules*, **15**, 782.
- [16] Hirokawa, Y., Tanaka, T. and Katayama, S., 1984, *Microbial Adhesion and Aggregation*, Edited by Marshall, K.C., Springer Verlag, Berlin.
- [17] Tanaka, T., Nishio, I. and Sun, S-T., 1987, *Science*, **218**, 467.
- [18] Ohmine, I. and Tanaka, T., 1982, *J. Chem. Phys.*, **11**, 5725.
- [19] Shenoy, S.L., Painter, P.C. and Coleman, M.M., 1999, *Polymer*, **40**, 4853-4863.
- [20] Katayama, S., Hirokawa, Y. and Tanaka, T., 1984, *Macromolecules*, **17**, 2641.
- [21] Katayama, S. and Ohata, A., 1985, *Macromolecules*, **18**, 2781.
- [22] Amiya, T., Hirokawa, Y., Hirose Y., Li, Y. and Tanaka, T., 1987, *J. Chem. Phys.*, **86**, 2375.
- [23] Melekaslan, D. and Okay, O., 2001, *Macromol. Chem. Phys.*, **202**, 304-312.
- [24] Flory, P.J., 1953, *Principles of Polymer Chemistry*, Cornell University Pres, Ithaca, New York.
- [25] Treloar, L.R.G., 1975, *The Physics of Rubber Elasticity*, 3rd Edition, Clarendon Pres, Oxford.
- [26] Kuhn, W., 1934, *Kolloidschr*, **68**, 2.
- [27] Kuhn, W., 1936, *Kolloidschr*, **76**, 258.
- [28] Guth, E. and Mark, H., 1934, *Monotsch. Chem.*, **64**, 93.
- [29] Ptitsen, O.B., Eizner and E. Yu., 1965, *Biofizika*, **10**, 3.
- [30] Amiya, T. and Tanaka, T., 1987, *Macromolecules*, **20**, 1162
- [31] Harland, R.S. (Editor), Prudhomme, R.K. (Editor), 1992, *Polyelectrolyte Gels, Properties, Preperation, and Applications*, American Chemical Society, Washington.
- [32] Siegel, R.A. and Fiestone, B.A., 1988, *Macromolecules*, **21**, 3254.

- [33] **Ilavsky, M.**, 1978, *Macromolecules*, **59**, 5151.
- [34] **Tanford, C.**, 1980, *The Hydrophobic Effect*, Willey, New York.
- [35] **Gianetti, G., Hirose, Y., Hirokawa, Y. and Tanaka, T.**, 1988, *In Molecular Electronic Devices*, Elsevier Appl. Sci., London.
- [36] **Ilmain, F., Tanaka, T. and Kokufuta, E.**, 1991, *Nature*, **349**, 400.
- [37] **Okano, T., Bae, Y.H., Jacobs, H., and Kim, S.W.**, 1990, *J. Controlled Release*, **11**, 255.
- [38] **Okano, T., Bae, Y.H. and Kim, S.W.**, 1992, *Modulated Control Release System*, CRC Pres, New York.
- [39] **Shibayama, M. and Tanaka, T.**, 1993, *Advances in Polymer Science*, **109**, 1-62.
- [40] **Khoklov, A.R. and Kachatvian, K.A.**, 1982, *Polymer*, **23**, 1742.
- [41] **Myoga, A. and Katayama S**, 1987, *Polym. Prep.*, Japan, **36**, 2852.
- [42] **Suzuki, A., and Tanaka, T.**, 1990, *Nature*, 346:445.
- [43] **Siegel, R.A., Faramalzian, M, Firestone, B.A and Moxley, B.J.**, 1988, *J. Controlled Release*, **8**, 179.
- [44] **Ricaka, J. and Tanaka, T.**, 1984, *Macromolecules*, **17**, 2916.
- [45] **Kokufuta, E. and Tanaka, T.**, 1991, *Nature*, 349:400.
- [46] **Kokufuta, E., Zhang, Y-Q and Tanaka, T.**, 1991, *Nature*, **351**,302.
- [47] **Vasilevskaya, V.V. and Khokhlov A.R.**, 1992, *Macromolecules*, **25**, 384.
- [48] **Melekaslan, D. and Okay, O.**, 2000, *Polymer*, **41**, 5737.
- [49] **Gundogan, N.and Okay, O.**, *J. Appl. Polym. Sci.* (In press)
- [50] **Sprech, E.H., Newman, A. and Nejer, H.T.**, 1956, *US Pat.*, No: 2773063.
- [51] **Sayil, C., Okay, O.**, *Polymer*, 2001, **42**, 7639.
- [52] **Galaev, I.Y. and Mattiasson, B.**, 1993, *Enzyme Microb. Technol.*, 15:354.
- [53] **Seker, F., Ellis, B.**, 1998, *J. Polym. Sci.*, **36**, 2095-2102.
- [54] **Liu, H.Y. and Zhu, X.X.**, 1999, *Polymer*, **40**, 6985-6990.
- [55] **Thomas, W.M. and Wang, D.W.**, Acrylamide Polymers, *In Encylopedidia of Polymer Science and Engineering*, 2nd ed.; **Mark, H.F., Bikales, N.M., Overberger, C.G. and Menges, G.**, 1986, Wiley, **1**, 169-211
- [56] **The Merck Index**, 10th ed.; Windholdz, M., Ed.; Merck:Rahway, N.J., 1983, 1521 and 5816.
- [57] **Hocking , M.B., Klimchuk, K.A. and Lowen, S.**, 2001, *J. of Polym. Sci.: Part A: Polymer Chemistry*, **39**, 1971.
- [58] **Durmaz, S., Okay, O.**, 2002, *Polymer*, **43**, 1217.

BIOGRAPHY

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