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faculty of mathematics and physics

Swelling and Mechanical Behavior of One- and Two-Components Polyelectrolyte Hydrogels

Doctoral thesis

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CONTENTS

List of Used Symbols and Shortenings

T – temperature

T_g – glass transition temperature

M – molecular weight
M_0 – the molar mass of the monomer

M_c – molecular weight between crosslinks

n – number of the statistical segments in the polymer chain

r – the number of equivalent segments of the macromolecule

n_p – the number of polymer chains in the sample

s – the number of monomer units in the statistical segment.

l – length of the statistical segment

p – the density of probability

h – the end-to-end distance in the deformed or reference states

$\sqrt{\overline{h}^2}$ – the root-mean-square length

N_A – Avogadro constant
R – the gas constant
k – Boltzmann constant

κ – the inverse of the Debby radius of the ion atmosphere

S – the entropy of the chain

Λ_x, Λ_y, Λ_z – relative deformational ratios in the direction of the main axes of strain related to the reference network state

λ – the extension ratio related to an isotropic state

L – deformed length of the sample in the swollen isotropic state

L_s – initial length of the sample in the swollen isotropic state

$\left\langle \alpha_s^2 \right\rangle$ – the dilatation factor of chain in the swollen state

$\langle \alpha_0^2 \rangle$ – dilatation factor in the dry isotropic state

v_2 – volume fraction of the polymer in the swollen gel

v_0 – volume fraction of the polymer at network formation

σ – stress

G – equilibrium shear modulus

ν_s – the concentration of polymer chains in the swollen gel

ν_d – the concentration of EANCs (relative to the dry state)

N – the number of segments (monomers) of the chain

χ – Flory-Huggins interaction parameter

n_i – the number of moles of ions of the ith type in the gel

b_0 – the length of the monomer unit

n_j – the number of moles of ions of the j-th type in the gel

μ_1 – the chemical potential of the solvent

μ_2 – chemical potential of the polymer

V – volume

V_1 – the molar volume of the solvent

c_- – concentration of co-ions

f_+ , f_- – activity coefficients of co-ions

D_m – the dielectric constant of the medium

ρ – density of the substance

D – sample diameter

X – the inverse swelling ratio relative to the state of network formation

f_c – functionality of junctions

Z – the degree of polymerization of the chain

α_s – the linear swelling ratio

V_g – gel volume

i – the effective degree of ionization

ϕ – the osmotic coefficient (correction factor for the degree of ionization of fixed charges)

f – force

ΔF – the overall change in free energy during deformation

H – enthalpy

G_1 – the modulus after preparation

P – swelling pressure

T_c – the temperature of the transition from the expanded to the collapsed state

Q – swelling degree relatively to the dry state

Q_w – the swelling degree in water

x_S – molar fraction of ionic comonomer

Δ – extent of the collapse

M_{os}^{app} – osmotic modulus

Eq. – equation

EANC – elastically active network chains

IPAAm – N(isopropylacrylamide)

IPMAm – N(isopropylmethacrylamide)

DEAAm – diethylacrylamide

MNa – sodium methacrylate

Q_S – trimethylammonium chloride

MBAAm – N,N–methylenebisacrylamide

TEMED – N,N,N',N'-tetramethylethylenediamine

AAm – acrylamide

IPN – interpenetrating polymer network

1. Introduction

Polymer chains can be connected in covalent multifunctional junctions and in such a case the chemical polymer network is formed so that whole sample is a "single molecule" (1). When such network is immersed in solvent it swells and we receive a swollen network – a gel. If water is used as a solvent we are speaking about hydrogel. In the case that charges are bound on polymer chains, the polyelectrolyte network is formed. Such charged network exhibits very high swelling degree in water and forms a polyelectrolyte hydrogel (2) (3) (4). Although main constituent of a gel is a solvent, it retains its shape (a feature characteristic of the solid state of matter); when it is deformed its response is that of an elastic body. As degree of swelling is very high polyelectrolyte hydrogels exhibit also some liquid-like properties. In other words, the gel is a form of matter intermediate between a solid and a liquid. Gels are objects, which exhibit an equilibrium modulus after deformation; the modulus is due to the presence of covalent crosslinks in the structure.

Softness, elasticity, and the capacity to store a liquid make gels unique materials. Progress in biology and polymer science is unveiling the usefulness of functions of biological molecules and promises new development in gel technologies. These systems have found a wide range of special applications: as ion-exchange resins and membranes (2) (3), subcutaneously implanted drug-delivery systems (4), as moisture-retaining media for agricultural purposes in arid regions, in skin-moistening creams, and as "super absorbents" in baby napkins. All these factors bring us to realize the importance and need of establishing gel sciences and technologies.

Due to presence of crosslinks, various properties of individual network chains become visible on a macroscopic scale. In addition to the liquid- and solid-like properties, a gel can change its physical properties with a change of external parameters (temperature, pressure...), e.g. gel is able to change drastically its swelling (volume) with temperature. In such case the shape of network chains is changing; in *Fig. 1.1* the two states of gel chains in shrunken (collapsed) and swollen (expanded) states, which correspond to the liquid and the gas states of fluids, respectively, are shown (5). When the change in the volume of a gel with a change of external parameters exhibits a jump-wise character, we are speaking about the first-order phase transition (collapse). The phase transition of gels is one of the most interesting phenomena that allow us to explore the principles underlying the molecular interactions and recognition, which exist in synthetic and biological polymers. The polymer network changes its volume in response to a change in environment: temperature, solvent composition, mechanical strain, electric field and exposure to light, etc. Such gels belong to the group of responsive ("smart") gels (5) (6). The prediction and understanding of the collapse phenomenon on molecular level can open the door to a wide variety of technological applications in chemical, medical, electrical, and many other industrial fields.

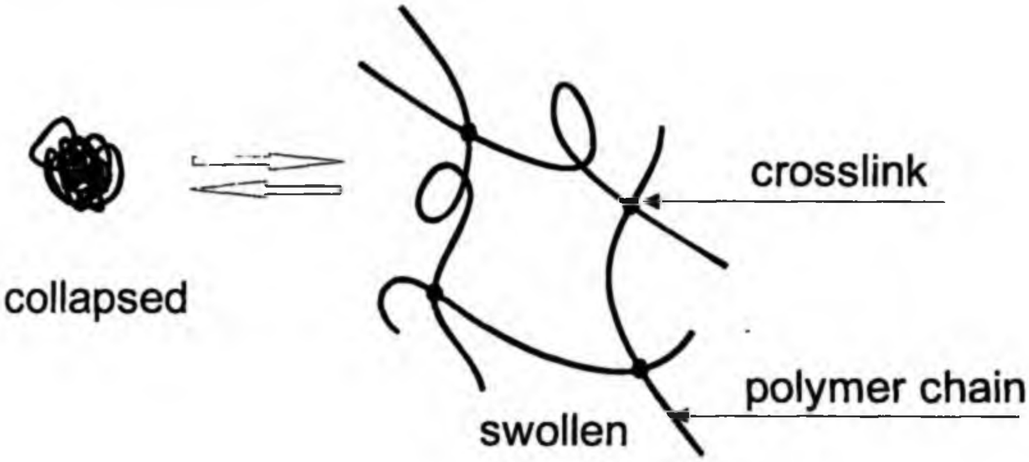

Fig. 1.1 . Schematic representation of gel chains in collapsed and swollen states (taken from (5)*)*

The collapse phenomenon was mostly observed for polyelectrolyte hydrogels. Their characteristic behavior is due to the fact that the network chains contain ionizable groups which are bound to polymer chain. When the gel is submerged in an aqueous solution, water molecules penetrate the gel and cause the dissociation of these groups. The small, mobile counterions are dissolved in the interior solution of the gel, contributing substantially to the osmotic pressure. The charges on the network molecules that are simultaneously formed enhance its solubility, and their repulsions strongly enhance swelling. In particular, the long-range charge interactions that result (between both the charges on the chain and the counterions) have a very strong influence on the behavior of the polyelectrolyte gel as a whole.

Most experimental results on phase transition were obtained with charged poly(acrylamide) (PAAm), poly(*N*-isopropylacrylamide) (PIPAAm), and poly(*N*,*N*-

diethylacrylamide) (PDEAAm) hydrogels (6-11). While in PAAm gels, the collapse can be brought about by the changes in the solvent composition, in PIPAAm and PDEAAm gels the transition can be induced in water by the temperature change. Both, the extent of the collapse and transition temperature increase with increasing charge concentration bound on the chain. It was also shown (9) that the polarity and structure of ionic comonomer plays an important role in the appearance and extent of the collapse. Another hydrogels which exhibit pronounced temperature transition in swelling are charged networks of poly(*N*-isopropylmethacrylamide) (PIPMAm) (12) (13).

The dimensions of network chains in mixed-solvent medium are dependent not only on interactions between polymer segments/solvents molecules but are influenced by the interactions between the solvents themselves (8). Cononsolvency phenomenon, i.e. the formation of nonsolvent medium by mixing two solvents, was found for some polymers (5) (6) (14); typical example is PIPAAm in mixtures of water with polar organic solvents, such as methanol, tetrahydrofuran, dioxane and others. Smart PIPAAm hydrogels based on this phenomenon have been proposed (9). To our knowledge no investigation of the effect of charge concentration on cononsolvency effect was done.

Most results were obtained on homogeneous one-component networks. The simplest two-component structure can be obtained by random copolymerization of two monomers; the copolymerization is an effective method for modification of physical properties of polymers and gels. Several studies (5) (6) (14) of temperature transition in uncharged PIPAAm hydrogels, reported that while incorporation of a hydrophilic comonomer leads to a higher critical temperature T_c, incorporation of a hydrophobic monomer lowers T_c. From the investigations of swelling behavior of ionized networks of random copolymers of N-vinylcaprolactam-*co*-1-vinyl-2-pyrrolidone (VCL/VP) in water/ethanol mixtures it was found that critical acetone concentration at the transition, a_c, slightly increased with increasing amount of more hydrophobic VCL component (9).

Interpenetrating polymer networks (IPNs), which are composed of two networks synthesized within each other represent another two-component system with more heterogeneous structure than in random copolymers. In general, chemical bonds do not exist between constituent networks. IPNs exhibit physical properties they are in between those of constituent networks. In such way the hydrogel systems exhibiting two transitions in dependence on composition of mixed solvent (or temperature) or IPN hydrogels with one transition in dependence on temperature and second one in dependence on solvent composition can be prepared.

This thesis is concerned with an experimental investigation of cononsolvency phenomenon of charged PIPMAm and PIPAAm networks in water/ethanol mixtures, collapse in ionized networks of random copolymers of P(AAm-*co*-DEAAm) and of interpenetrating networks of PIPMAm/PAAm in water at various temperatures and in water/acetone mixtures at room temperature. In Part 2 classification of different network structure is given. Part 3 discusses the description of mechanical and swelling behavior of uncharged and charged networks. The conditions for appearance of volume phase transition together with experimental results obtained in literature are discussed in Part 4. The aims of thesis are formulated in Part 5. Materials and methods of measurements used in thesis are described in Part 6. Main obtained results and their discussion within the scope of theory mentioned in Part 3 are shown in Part 7. Finally, conclusions, which follow from obtained results, are presented in Part 8.

2. Network Formation and Structure Characterization

The polymer networks can be formed in several ways:

- polymerization reactions of low-molecular monomers,
- reaction of the reactive groups of oligomers,
- by crosslinking of existing macromolecules.

Condition for network formation is that at least one of the reacting components is three- or more functional (acts as a crosslinker) (1) (15).

During crosslinking reaction, the molecular weight averages (number-M_n and weight M_w average) increase together with polydispersity of chains in reacting system. The increase of M_n and M_w proceeds in liquid-soluble phase until critical conversion (gel point GP), when first infinite structure in system appears, is reached. After that new insoluble (gel) phase is formed and the both, soluble phase (called sol) and gel phase coexist in system. At the gel point M_w goes to infinity. During continuation of the crosslinking reaction after the GP the sol molecules join to the network phase and the gel fraction increases.

There are direct relations between the network structure and physical network properties. The concentration of the elastically active network chains (EANCs) (chains between two crosslinks) is a basic parameter, which determines the network structure, mechanical, swelling and other physical properties. E.g. the molecular theory of rubber elasticity gives the relation between concentration of EANCs and equilibrium mechanical modulus; equilibrium swelling degree of the network is also affected by EANCs concentration (1) (15-17).

The crosslinking process is given by corresponding chemical type of reactions and depends on various factors, such as reactivity of functional groups, their concentration etc. There are several theoretical methods for description of network formation process (14) (17) (statistical, kinetic, computer simulation etc.). One of the most powerful theoretical methods is based on the theory of branching processes, which comes from tree-like model of the network growth (1) (15) (17-20). This theory allows full description of network formation process if initial information about reaction mechanism and composition of a crosslinking system is known. Theory allows description of the structure evolution in system in dependence on conversion, determines the growth of molecular weights and critical conversion at the gel point. After the GP it is possible to calculate an amount and composition of the sol and a structure of the gel (length and concentration of EANC, the length and structure of backbone and dangling chains), and in first approximation to characterize physical interactions between chains. The theory of branching processes was applied to many systems and a good agreement between measured and theoretically predicted structural characteristics was received (18-21).

It should be mentioned that real networks exhibit some structural defects. These defects can lead to the reduction of amount of EANCs (unreacted functional groups, free ends of the chains or formation of intramolecular (elastically inactive) cycles). On the other hand permanent intermolecular interactions (permanent entanglements) usually increase the EANCs concentration (1) (17).

2.1 Classification of Hydrogels

Polymeric hydrogels (swollen polymer networks in water or aqueous solutions) are classified in accord to their monomeric composition based on the method of preparation giving some important class of hydrogels namely, homopolymeric, copolymeric and interpenetrating polymer networks hydrogels. Furthermore, the chemical constituent of monomers used in the preparation of hydrogels plays an important role in classifying the hydrogels. The hydrogels are classified as either, anionic, cationic or ampholytic gels - based on the presence of charges bound on the chain. Hydrogels are also classified as an amorphous or semi-crystalline materials based on their supermolecular structure.

2.1.1. Homopolymeric hydrogels

Homopolymer hydrogels are referred to a polymer networks formed from a single monomer, which is the basic structural unit from which polymer network (22) is formed (usually with small amount of crosslinker) (23) . Homopolymer gels could have crosslinked or uncrosslinked skeletal structure depending on the nature of the monomer and polymerization technique.

Homopolymer gels, which are crosslinked, have found important applications in various areas, such as in slow drug delivery devices and contact lenses. An important category of crosslinked homopolymer hydrogels is formed by poly(hydroxyalkyl methacrylates) which include poly(3-hydroxypropyl methacrylate (PHPMA), poly(glyceryl methacrylate), (PGMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) (24) (25).

2.1.2. Copolymeric hydrogels

Copolymeric hydrogels are formed from two or more different monomers (and small amount of crosslinker) with at least one has hydrophilic character. They can be arranged in a random, block or alternating configuration along the polymer network chains (22) (24). The copolymeric hydrogel networks are generally covalently or ionically crosslinked structures (24) (26) (27). Generally, copolymers designed to function as hydrogels are confined to the combination of compatible comonomers, which will give the hydrogels the desirable properties for intended potential applications.

2.1.3. Interpenetrating polymer networks (IPNs) hydrogels

IPNs form an important class of hydrogel materials and are formed by combinations of two or more polymer networks. Several methods of synthesis, particularly sequential IPNs and simultaneous interpenetrating networks, are described in literature Similarly as with polymer blends, block copolymers and graft copolymers the phase separation can take place during IPNs formation but the rules are different. Applications of IPNs to the plastics and rubber industry are described, along with historical aspects (28).

Investigation of IPNs, as a class of heterogeneous materials, started the late 1950's - early 1960's. There had been a couple of patents on heterogeneous polymeric materials that were later identified as IPNs; in this stadium the researchers were only interested in the properties of the made materials, not understanding why these materials had the properties that they did. J. Millar was the first researcher which systematically investigated the properties of IPNs materials. He was interested in ion-exchange materials based on polyelectrolytes, like sulfonated polystyrene. Millar prepared samples of crosslinked polystyrene and swelled them in solutions of styrene and divinylbenzene. Using free radically polymerization of the monomers within the swollen network he was able to form a new polystyrene network in the first polystyrene network. This kind of IPNs is called homo-IPNs, since both networks are made of the same monomer. The IPN material displayed a lower degree of swelling than other crosslinked polystyrene ion-exchange materials, which helps the material to increase the selectively exchange ions based on ion size.

Millar was also the first person who used the term "Interpenetrating Polymer Network". The term was used to describe what he thought - the material looked like - two different networks intermeshed within each other on a molecular level. However, the name IPN was used before there was an understanding of the morphology of IPNs; now we know that there is almost never mixing of the two components on a molecular level (29).

There are several ways how to mix two kinds of polymer molecules; see *Fig. 2.1.* Simple mixing, as in an extruder, results in a polymer blend. If the chains are bonded together, graft or block copolymers result. chemical Bonding between some portion of the backbone of polymer I and the end of polymer II, the result is so called a graft copolymer. Other types of copolymers include AB-cross-linked copolymers (where two polymers make up one network (IPNs)), and also semi-IPNs (SIPNs) can be formed in which in first network some long molecules of other polymer are dissolved.

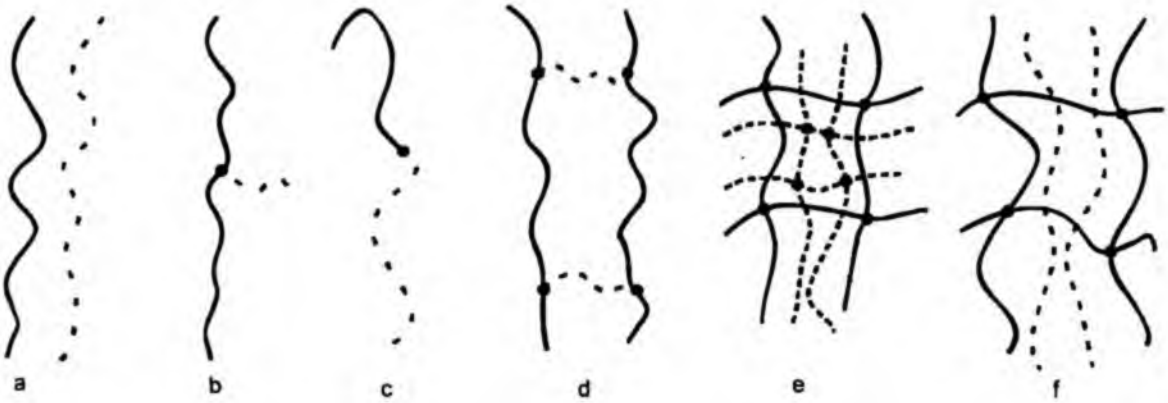

Fig. 2.1. Six basic combinations of two polymers: a-Polymer blend (no bonding between chains); b-graft copolymer; c-block copolymer; d-AB-graft copolymer; e-IPN; f-SIPN.

In many ways, IPNs are related most closely to block copolymers. In the block copolymer systems, the length of the blocks determines the size of the domains. Correspondingly, the crosslinking level (length of chain between crosslinks) plays a major role in determining the domain size of IPNs. Short blocks or short chain segments between crosslinks make small domains. However, there are some important differences. Short block lengths are important because they increase miscibility between components of polymer. For the case of IPNs, there is growing evidence that increasing crosslinking decreases the miscibility in the system relative to the corresponding blend (for systems in which the linear component polymers are miscible).

IPNs can be formed in various ways. Brief definitions of some of the more important ways of IPNs formation are (28):

- Sequential IPNs formation - Polymer network I is formed. Monomer II plus crosslinker and activator are swollen in network I and polymerized in situ (see *Fig. 2.2)*. The sequential IPNs include many possible materials where the synthesis of one network follows the other.
- Simultaneous interpenetrating network (SIN) formation - The monomers or prepolymers plus crosslinkers and activators of both networks are mixed. The reactions are carried out simultaneously, but they are noninterfering. As an example can serve chain and step polymerization character of the reaction (see *Fig.2.2*).
- Latex IPN formation - The IPNs are made in the form of latexes, frequently with a core and shell structure. A variation is to mix two different latexes and then form a film, which crosslinks both polymers. This variation is sometimes called an interpenetrating elastomer network formation (IEN).
- Gradient IPN formation - Gradient IPNs are materials in which the overall composition or crosslink density of the material varies from location to location on the macroscopic level. For example, a film can be made with network I predominantly on one surface, network II on the other surface, and a gradient in composition throughout the interior is formed.
- Thermoplastic IPNs formation - Thermoplastic IPNs materials are hybrids between polymer blends and IPNs that involve physical crosslinks rather than chemical ones. Thus, these materials can flow at elevated temperatures, similar to the thermoplastic polymers, and at used low temperature, they are crosslinked and behave like IPNs. Types of cross-links include block copolymer morphologies, ionic groups or semicrystallinity.
- Semi-IPN formation - A semi-IPNs are IPNs in which one of the components is a crosslinked networks while the other component is a noncrosslinked polymer (30), (31).

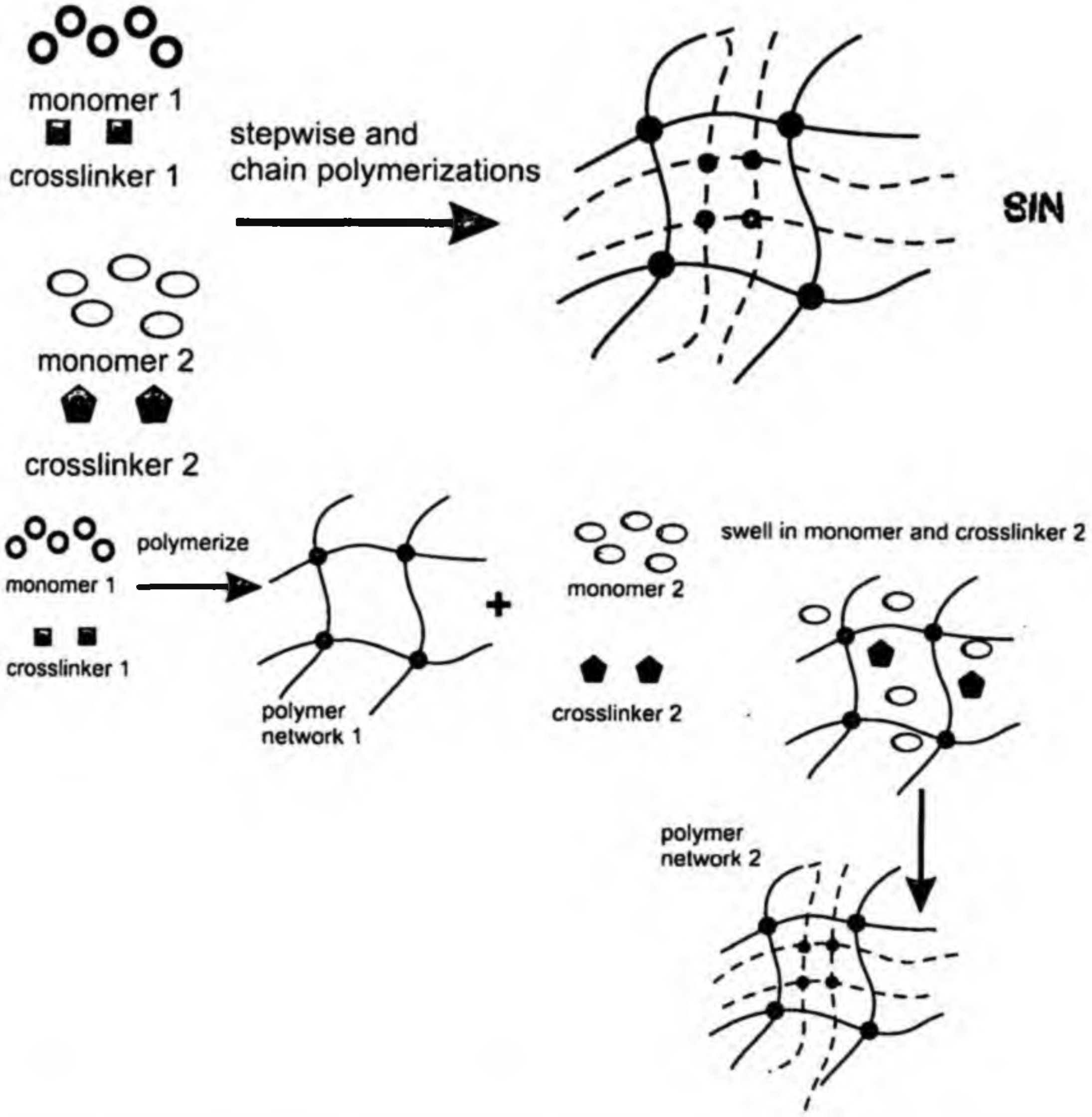

Fig.2.2. Basic synthesis methods for IPNs: Simultaneous interpenetrating polymer networks (SINs); Sequential IPNs

2.1.4. Non-ionic hydrogels

Non-ionic hydrogels, often referred to as neutral ones, are usually homopolymeric or copolymeric water swollen networks, which do not bear any charged groups on their network chains. Neutral hydrogels can be prepared by various crosslinking polymerization methods. Although generalizations can be made about hydrogels, the wide range of chemical compositions of the monomers used, give them different properties concerning biocompatibility, physical and chemical properties of the resultant gels (24).

2.1.5. Ionic hydrogels

Ionic hydrogels, usually known as polyelectrolytes, are prepared from nonionic monomers, ionic comonomers with charges and crosslinker. The charges could be positive or negative thus classing the hydrogels as cationic or anionic respectively, and furthermore, a combination of both positive and negative charges gives an ampholitic network chains (24) (32) (33). Inclusion of charges into the polymer backbone enhances the stimuli responsive properties, especially the value of degree of swelling in water, which could be controlled in dependence on the nature of charged groups thus widening possibility of hydrogels in various bioapplications areas (32-35).

3. Swelling and Deformational Behavior of Polymer Networks with Charges

3.1 Introduction

The macromolecular network structure provides the ability of these materials to undergo large strain, which leads to nonlinear elastic deformations. The knowledge of mechanical properties in a broad range of external parameters not only determines the application possibilities but also characterizes the physical structure of these materials (1) (15). In contrast to the linear polymers the networks have some special properties – they exhibit a high recoverable deformations, equilibrium swelling, high temperature stability etc.

The polymer molecule being under exposure of external force, it assumes new (the most probable under the given external conditions) conformations by diffusion motion, rate of which depends on the effective viscosity of the medium. Such time-dependent motion leads to a time-dependent (viscoelastic) mechanical behavior (16). In the low-temperature region, the polymer is in the glassy state where only local segmental motions of short parts of the main chain (usually vibrations) or of the side chains (hindered rotations) can take place. With increasing temperature, the main transition region is reached. In this region, the main chain motion is subsequently released; the beginning of this transition is given by the glass transition temperature T_g. In the relatively narrow transition temperature interval (30-50°C) the cooperative motion of main chain segments is realized and the mechanical behavior significantly changes. At still higher temperatures ($T > T_g + 50$ K), so-called rubber-like (plateau) region is reached; in this region only small dependence of mechanical behavior on time and temperature exists and practically free movement of backbone chain segments is possible. During glass-rubber transition a modulus of the polymers decreases about 3-4 orders of magnitude and time-temperature dependences of the deformation behavior becomes significantly apparent.

Introduction of chemical junctions into the system leads to the final equilibrium values of mechanical modulus. On the basis theory of rubber elasticity (1) (15), the concentration of the elastically active network chains (EANCs) can be calculated from equilibrium modulus. When such network is immersed in the low-molecular solvent, the solvent molecules diffuse into a network until swelling equilibrium is reached. This equilibrium is given by osmotic forces, which are defined by mixing of chain segments with solvent and by elastic forces originated from extended EANCs (given by the increase of network size). The suitable explanation of the mixing contribution to the swelling was done by the Flory-Huggins lattice theory (1) (14) (15) (36). Due to swelling (presence of solvent in structure), the swollen network (gel) is usually deep in the rubbery state so that time and temperature dependence of their mechanical behavior is not important. The rubber elasticity theory as well as Flory-Huggins lattice theory is discussed later. When charges are bound on network chains, the polyelectrolyte network and gel is formed and theory of swelling equilibria of such networks is also discussed latter.

3.2 Rubber Elasticity of Polymer Networks

The macromolecular network structure of in rubbery state provides the ability of these materials to undergo large strain and exhibit nonlinear elastic deformations. The structure of the network consists of long, randomly oriented molecular between the crosslinks; furthermore, the intermolecular interactions are weak. The essence of this behavior has been well-modeled by statistical mechanic treatment of the rubber elasticity (15). The early molecular-based statistical mechanical theory was developed by Flory and Rehner (14), with the simple assumption that chain segments of the network deform independently and on a microscopic scale in the same way as the whole sample (affine deformation of the individual chains). The crosslinks are assumed to be fixed in space at their positions exactly follow the specimen deformation. This model is referred to as the "affine network model". James and Guth allowed in their "phantom network model" (37) a certain fluctuation of the crosslinks about their average affine deformation positions. These two theories are in a sense the "limiting cases"with the affine network model giving an upper value of equilibrium modulus and the phantom network model gives the lower one. It is important to emphasize that both models assumes that the chains of the network behave like phantom chains, i.e. the dimensions of these chains are unperturbed by excluded-volume effects. This assumption has been confirmed by small-angle neutron scattering (SANS) of labeled (deuterated) amorphous samples. *Fig.3.1* shows schematically the difference between the affine network model and the phantom network model.

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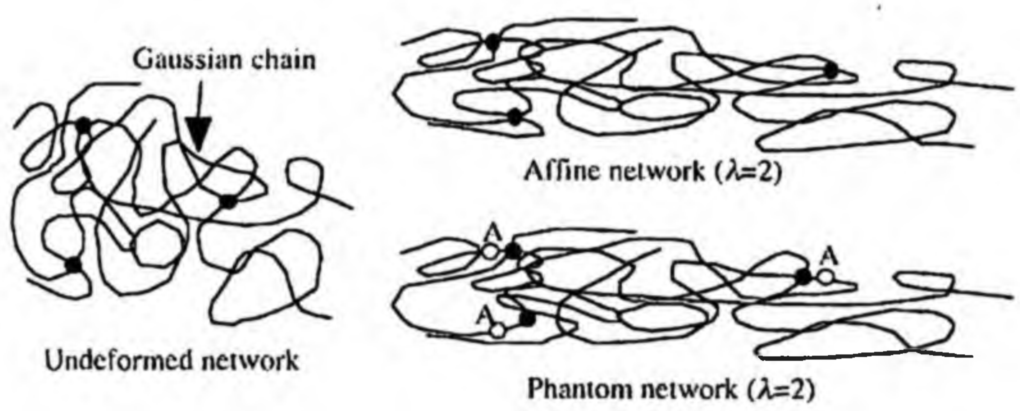

Fig. 3.1. Schematic representation of the deformation of a network according to the affine network model and the phantom network model. The unfilled circles indicate the position of the crosslinks assuming non-affine deformation (phantom network).

The affine network model assumes that the junction points (i.e. the crosslinks) have a specified fixed position defined by the specimen deformation ratio (λ). The chains between the junctions points are however free to take any of the great many possible conformations. The junction points of the phantom network are allowed to fluctuate about their mean values (shown in *Fig.3.1* by the unfilled circles) and the chains between the crosslinks to take any of the great many possible conformations. There are three necessary conditions for the occurrence of rubber-like elasticity: (a) presence of long-chain molecules, processing freely rotating links. (b) Weak secondary forces between the chains. (c) An interlocking of the molecules at a few places along their length to form a three-dimensional chemically or physically crosslinked network.

3.2.1 Conformations of chain

The discussion of the average or root-mean-square end-to-end distance of a long-chain between crosslinks shows that when the rotation about bonds is free, or only slightly hindered, the root-mean-square length is proportional to the square root of the number of bonds in the chain (1) (15) (36). Since the fully extended chain length is proportional to the number of bonds, it follows that the potential elastic extensibility of the chain is also proportional to the square root of the chain length. This deduction shows immediately that the very high elastic extensibility found in rubbery materials can only be expected to occur if the chain length is sufficiently great, and therefore leads us to expect a general

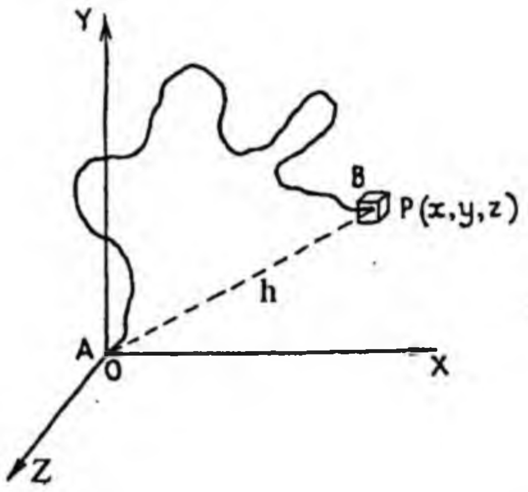

Fig. 3.2. The statistically kinked chain. Specification of probability that the end should fall in the volume element dV (= dxdydz).

relation between molecular weight and degree of extensibility which is, in fact, borne out by observation. The problem consists in evaluating the relative number of configurations of the chain, for given values of x, y, and z coordinates (*Fig. 3.2*).

The derivation of the stress-strain equation goes through some elementary steps. The Gaussian distribution function for the end-to-end distance expresses the probability of finding the end of a chain at a certain position (x,y,z) with respect to the other chain end found at (0,0,0). This equation expresses, to phrase it differently, the number of conformations a chain can take provided that the chain ends are in (0,0,0) and (x,y,z). It is then possible to calculate the Helmholtz free energy (the free energy associated with constant volume) for a single chain and by adding the contributions from all individual chains of the network, also for the network. The stress-strain equation is finally obtained by taking the derivative of the Helmholtz free energy with respect to length. Let us start by showing the Gaussian function describing the distribution of the chain end position:

$$p(x,y,z)dxdydz = \left(\mathrm{b}^3/\pi^{3/2}\right)e^{-b^2\left(x^2+y^2+z^2\right)}dxdydz \qquad (3.1)$$

$$= \left(\mathrm{b}^3/\pi^{3/2}\right)e^{-b^2h^2}dh = P(h)dh$$

where the parameter b^2 has the value $3/2nl^2$. In this formula, $p(x,y,z)$ is the density of probability and $dxdydz$ is the size of the volume element considered, so that $p(x,y,z)$ $dxdydz$ represents the probability that the components of the vector h should be between x and $x+dx$, y and $y+dy$, z and $z+dz$, respectively; $x^2+y^2+z^2 = h^2$ is the square end-to-end distance and $dh = dxdydz$. The derivation of this formula is based on certain approximations which are valid only so long as the distance between the ends of the chain is not comparable with the maximum possible extension *nl*; the formula is not applicable when the chain is nearly fully extended. The formula (3.1) is of fundamental importance in the theory of rubber elasticity. Its form is that of the Gaussian error function, which is of frequent occurrence in statistical problems, is connected with the superposition of random effects.

For the random chain the root-mean-square value of *h* may be readily calculated from the distribution function (3.1), since

$$\bar{h}^2 = \int_0^\infty h^2 P(h) dh, \tag{3.2}$$

giving $\bar{h}^2 = 3/2\, b^2 = nl^2$ or $\sqrt{\bar{h}^2} = l\sqrt{n}$

The root-mean-square length, like the most probable length, is thus proportional to the square root of the number of segments in the chain.

As has been stated already, the distribution function (3.1) is an approximation, valid only for *h*-values considerably less than the extended chain length. In practice the approximation is very close up to extensions of about one-third of the fully extended length; for higher extensions one of the more accurate distribution functions are used (15).

For a random cross-linking process the chain contour lengths (i.e. the distances between junction points measured along the chain) differ from one chain to another, but for any given chain the contour length is fixed and invariable. To calculate the entropy change corresponding to the deformation of the network it will be necessary to find the total entropy of all the chains first in the undeformed state and then in the deformed state; the difference is the entropy of deformation. For this purpose we shall assume the Gaussian statistics to apply to each chain, so that the entropy of the chain may be represented by the usual formula ($S = k.\ ln\, p(x, y, z)$)

$$S = c - kb^2\left(x^2 + y^2 + z^2\right) \tag{3.3}$$

in which the parameter *b* is a function of the chain geometry, and of the chain length; *k* is Boltzmann constant. The size of the volume element is absorbed in the constant *c*.

3.2.2 Elasticity of Gaussian network

We assume that the rubber contains a total of n_p chains per unit volume, of various contour lengths. Each chain will be characterized by a particular value of the parameter b, which will depend on its contour length. Let us now divide the whole assembly of chains into a number of groups, such that the value of chain contour length, and hence of the parameter b, is the same (within narrow limits) for all the members of each group. The total entropy of deformation for the whole assembly of chains may now be obtained by first finding the sum of the entropies for all the chains in anyone group and then summing over all the groups. Further, it was taken into account that the junction points are not fully fixed in space, but can fluctuate about certain mean positions in accordance with the random configurationally changes of the chains with which they are associated. Consequently the distances between junction points, which determine the respective end-to-end chain lengths or chain vector lengths, are also subject to statistical fluctuations. We will derive an equation relating stress and strain in a rubber on the basis of the affine network model. This model is based on the following assumptions: (1) The chains between crosslinks can be represented by Gaussian statistics of phantom chains. (2) The free energy of the network is the sum of the free energies of the individual chains. (3) The positions of the crosslinks are changed precisely according to the macroscopic deformation, i.e. deformation is affine. (4) The unstressed network is isotropic. (5) The volume remains constant during deformation.

Let us consider an individual chain (*Fig. 3.3*) having an end-to-end distance represented by the vector h, with coordinates (x, y, z), in the unstrained state of the network. After the deformation the chain may be represented by the vector h' having components $x' = \lambda_x x$, $y' = \lambda_y y$, and $z' = \lambda_z z$, the axis of coordinates being chosen with the principal axes of strain.

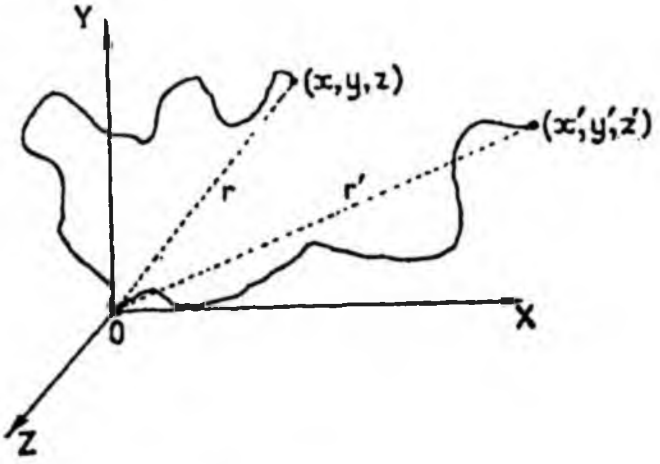

Fig.3.3. The "affine" deformation of chains

Using the formula for the entropy, we receive the total entropy of deformation (15) (1)

$$\Delta S = -\frac{1}{2} n_p k\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) \tag{3.4}$$

where λ_x, λ_y, and λ_z are deformational ratios related to undeformed state.

Usually external parameters (temperature, swelling etc.) at network formation differ from those at which external strain is applied. In such a way network formation state differs from the isotropic state in which deformation was applied to the network. In the theory of rubber elasticity, this fact was taken into account by introducing the reference state of a polymer network (17) (38) (39) one in which the mean square end-to-end distance of the chain in the network is equal to the corresponding distance of a free chain. On the average, no force acts upon the chain ends in the network in this state (generally it is supposed that network formation state is the reference one). Taking into account reference state and fact that that volume of network can change with strain, the following relation was suggested for the Helmholtz free energy $\Delta F_c = -T\Delta S$ (or work of deformation) (39-41)

$$\Delta F_c / kT = A n_p\left(\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3\right)/2 - B n_p \ln\left(\Lambda_x \Lambda_y \Lambda_z\right) \tag{3.5}$$

where Λ_x, Λ_y, Λ_z are relative deformational ratios in the direction of the main axes of strain with respect to the reference state, $A = 1$ and $B = 2/f_c$ for affine network model and

$A = (f_c - 2)/f_c$ and $B = 0$ for phantom network model; f_c is functionality of junctions. In further discussion we will use affine network model with $A = 1$ and $B = 2/f_c$..

For simple extension in x-direction we can write

$$\Lambda_x = \langle \alpha_s^2 \rangle^{1/2} \lambda \;;\; \Lambda_y = \Lambda_z = \left(\langle \alpha_s^2 \rangle v_\lambda \lambda^{-1} \right)^{1/2} \tag{3.6}$$

Here, $\lambda = L/L_s$ is the extension ratio related to isotropic state, L and L_s are deformed and initial lengths of the sample in the swollen isotropic state, $\langle \alpha_s^2 \rangle = \langle \alpha_0^2 \rangle \, v_2^{-2/3}$ is the dilation factor of chain in the swollen state, $\langle \alpha_0^2 \rangle$ is the dilation factor in the dry isotropic state, defined as the ratio of the mean-square end-to-end distance in the dry isotropic state to the same quantity in the reference state, when no force acts on the chain ends, $v_\lambda = V/V_s$ (V and V_s are deformed and initial sample volumes in isotropic state) and v_2 is the volume fraction of polymer in swollen gel: From Eq. (3.5) we obtain the relation (as $f_c \, dL = d \, \Delta F_c$)

$$\sigma = G \left(\lambda - v_\lambda \lambda^{-2} \right) \tag{3.7}$$

where σ is the stress related to initial swollen cross-section of the sample A_s ($\sigma = f_c/A_s$, f_c is the uniaxial tensile force) and G is the equilibrium shear modulus for which we have $G = \langle \alpha_s^2 \rangle n_p kT = \langle \alpha_s^2 \rangle \rho RT/M_c = \langle \alpha_s^2 \rangle v_s RT$, where ρ is the density, M_c is the number average chain molecular weight, R is the gas constant and v_s ($= n_p/N_A V_s$, N_A is Avogadro number) is the concentration of EANCs in unit isotropic volume.

3.2.3 Non-Gaussian network

Up to this point the development of the statistical theory of the network has been based upon the Gaussian distribution function (3.1) for the single chain. The results derived on this basis are therefore limited to strains, which are not too large, strains, which do not begin to approach the limiting deformability of the network. In comparing the experimental stress-strain curves with the formulae derived from the Gaussian theory one could noticed serious deviations in the region of large strains ($\lambda > 3$ *to* 4) these deviations are particularly apparent, for example, in the case of simple elongation (1) (15) (17). In the region of very large strains, where an appreciable proportion of the chains become highly extended, the Gaussian statistical treatment is no longer valid, and it is necessary to investigate the properties of the network in terms of the more accurate non-Gaussian statistical theory, which takes into account the finite extensibility of the chains, and hence of the network. Because of the high degree of swelling of polyelectrolyte gels it seems appropriate to use a distribution function taking into account the finite extensibility of polymer chains.

By employing a three-chain network model with the Langevin distribution function (15) the generalized equation for the change of the Helmholtz free energy ΔF_c, with strain was obtained (6) (15)

$$\Delta F_c = n_p kTn\left[\frac{1}{3}\left(\gamma_1 A_1 + \ln\frac{A_1}{\sinh A_1}\right) + \frac{2}{3}\left(\gamma_2 A_2 + \ln\frac{A_2}{\sinh A_2}\right) - \left(\gamma_3 A_3 + \ln\frac{A_3}{\sinh A_3}\right)\right] \quad (3.8)$$

Here the n is the number of statistical segments in the polymer chain, $\gamma_1 = \lambda\left\langle\alpha_s{}^2\right\rangle^{1/2} n^{-1/2}$, $\gamma_2 = [\ \lambda^{-1}\left\langle\alpha_s{}^2\right\rangle v_\lambda n^{-1}\ ]^{-1/2}$, $\gamma_3 = \left\langle\alpha_s{}^2\right\rangle^{1/2} n^{-1/2}$ and $A_i = L^{-1}(\gamma_i)$, where $L^{-1}(\gamma_i)$ is the inverse Langevin function of γ. Using Eq. (3.8) we obtain tensile force f_c corresponding to the change of the configurational free energy, with deformation in the form

$$f_c = \frac{n_p kT}{3L_s}\left(\ \left\langle\alpha_s{}^2\right\rangle n\ \right)^{1/2}\left[A_1 - (v_\lambda \lambda^{-3})A_2\right] \quad (3.9)$$

From expansion of the inverse Langevin function in a power series it follows that (42)

$$f_c = \frac{n_p kT}{L_s}\left\langle\alpha_s{}^2\right\rangle\left(\lambda - v_\lambda \lambda^{-2}\right)\left[\begin{array}{l} 1 + \frac{3}{5}\left\langle\alpha_s{}^2\right\rangle n^{-1}\left(\lambda^2 - v_\lambda \lambda^{-1}\right) \\ + \frac{99}{175}\left(\left\langle\alpha_s{}^2\right\rangle n^{-1}\right)^2\left(\lambda^4 + v_\lambda \lambda + v_\lambda{}^2 \lambda^{-2}\right) \\ + \frac{513}{875}\left(\left\langle\alpha_s{}^2\right\rangle n^{-1}\right)^3\left(\lambda^6 + v_\lambda \lambda^3 + v_\lambda{}^2 + v_\lambda{}^3 \lambda^{-3}\right) + \ldots \end{array}\right] \quad (3.10)$$

The overall stress σ related to undeformed cross-section of the sample A_s is given by the equation similar as Eq. (3.7)

$$\sigma = G_s\left(\lambda - v_\lambda \lambda^{-2}\right) = G\ \left(1 + \phi_N\right)\left(\lambda - v_\lambda \lambda^{-2}\right) \quad (3.11)$$

where G is modulus from Eq. (3.7) and ϕ_N is the contribution of the limited extensibility of chains (non-Gaussian term). By using Eq. (3.10), ϕ_N can be written as

$$\phi_N = \frac{3}{5}\langle \alpha_s{}^2 \rangle n^{-1}\left(\lambda^2 + v_\lambda \lambda^{-1}\right) + \frac{99}{175}\left(\langle \alpha_s{}^2 \rangle n^{-1}\right)^2\left(\lambda^4 + v_\lambda \lambda + v_\lambda{}^2 \lambda^{-2}\right) + \frac{513}{875}\left(\langle \alpha_s{}^2 \rangle n^{-1}\right)^3\left(\lambda^6 + v_\lambda \lambda^3 + v_\lambda{}^2 + v_\lambda{}^3 \lambda^{-3}\right) + \ldots \tag{3.12}$$

None of Gaussian statistical mechanical theories is adequate to describe the stress strain behavior at large strains (λ>3 to 4). The pronounced upturn in the stress-straincurve can be accounted for by the finite extensibility of the network not accounted for by the Gaussian distribution that describes the statistics of the phantom chains. In addition, some rubbers crystallize during extension and a smaller part of the increase in stiffness at high extension ratios is due to the presence of crystallites in the material.

3.3 Elasticity of Networks with Charged Groups

3.3.1 Introduction

When charges are bound on network chains, owing to their electrostatic interactions more expanded conformations can be expected. Also potential energy of charged chain will vary during the deformation, and consequently chain configurations will not be isoenergetic during the process. One cannot therefore expect a quantitative agreement between the experimental deformational behavior of polyelectrolyte gels and the kinetic theory of rubber elasticity presented in previous paragraph.

Several models have been suggested for the swelling and deformational behavior of charged gels (5) (6) (42-44). Besides spherical, ellipsoidal, and cylindrical models (1), (45-48) suited for the description of some solution properties, the random coil model has also been successfully used for polyelectrolyte gels (49). In this case the chain is regarded as an assembly of statistical segments the distances between which are controlled by an appropriate distribution function. This distribution makes it possible to know the displacement probability between any two arbitrary charges on the chain. Their mutual interactions can be calculated by means of the Debye-Hückel theory; interactions of charges on different chains are neglected. Under such assumptions, a relationship for the free energy of the electrostatic interaction of charges on the polymer chain has been derived; the theory describes titration curves fairly well, and to a lesser extent it describes also swelling equilibria (50) of polyelectrolyte gels.

In further discussion we describe generalized random coil model in which the effects of repulsion of charges on the chain and finite chain extensibility are included (42). In this model, all molecular parameters are independently accessible. This theory semiquantitatively described swelling and collapse in water/acetone mixtures of various charged gels (11) (51) (52).

3.3.2 Electrostatic contribution to rubber elasticity

In the frame of the model a polyelectrolyte network immersed in a aqueous solution of a univalent salt was considered (42). The sample will be subject to a uniaxial extension to a length L. Assuming that the overall change in free energy ΔF during deformation is given by the sum of the change ΔF_c, in the configurational free energy (see Eq. (3.8)) and in the free energy ΔF_e of electrostatic interactions with deformation, the tensile force f was defined by (42)

$$f=\left(\frac{\partial \Delta F}{\partial L}\right)_{T,V,n_i}=\left(\frac{\partial \Delta F_c}{\partial L}\right)_{T,V,n_i}+\left(\frac{\partial \Delta F_e}{\partial L}\right)_{T,V,n_i}, \tag{3.13}$$

where V is the gel volume and n_i is the number of moles of ions of the ith type in the gel.

The expression for the free energy of electrostatic interactions, F_e, has been derived (49) by applying the Gaussian distribution function to the above model of chains carrying ionized groups and immersed in a medium of a finite ionic strength. If the ionic strength of solution is not too low, the Debye radius of the ion atmosphere is small compared to the chain dimensions. On this assumption, F_e is given by (49)

$$F_e=\frac{n_p Z^2 i^2 e^2}{Dh}\ln\left(1+\frac{6h}{\kappa \overline{h_o^2}}\right), \tag{3.14}$$

where n_p is the number of polymer chains in the sample, Z is the degree of polymerization of the chain, i is the effective degree of ionization, h or $(\overline{h_o^2})^{1/2}$ is the end-to-end distance in the deformed or reference states, $\overline{h_o^2}$ is the mean square end-to-end distance in reference state and κ is the inverse of the Debye radius of the ion atmosphere ($\kappa = [4\pi e^2\Sigma(n_i/DkTV)]^{1/2}$). Eq. (3.14) was originally derived for a polyelectrolyte solution.

Assuming affine deformation, h in the deformed swollen state can be described by (42)

$$h = \left[(1/3)\bar{h}_o^2\langle\alpha_s^2\rangle(\lambda^2 + 2v_\lambda\lambda^{-1})\right]^{1/2}, \tag{3.15}$$

and h_s in the swollen isotropic undeformed state is similarly defined by

$$h_s = (\bar{h}_o^2\langle\alpha_s^2\rangle)^{1/2}. \tag{3.16}$$

By using eqs. (3.14)-(3.17), the change in the free energy ΔF_e with deformation can be expressed by

$$\Delta F_e = \frac{n_p Z^2 i^2 e^2}{D}\left[\frac{1}{h}\ln\left(1+\frac{6h}{\kappa\bar{h}_o^2}\right) - \frac{1}{h_s}\ln\left(1+\frac{6h}{\kappa\bar{h}_o^2}\right)\right]. \tag{3.17}$$

In accordance with Eq. (3.13), the force corresponding to the electrostatic interaction of charges on the chains, f_e, is given by

$$f_e = \frac{n_p Z^2 i^2 e^2(\lambda - v_\lambda\lambda^{-2})}{DhL_s(\lambda^2 + 2v_\lambda\lambda^{-1})}\left[\frac{A}{1+A} - \ln(1+A)\right], \tag{3.18}$$

where $A = 6h/\kappa\bar{h}_o^2$.

The overall stress σ related to the swollen undeformed cross section of the sample A_s is given by the sum of f_e and f_c defined by eqs. (3.18) and (3.10) in the form

$$\sigma = G_s(\lambda - v_\lambda\lambda^{-2}) = G\,(1+\phi_E+\phi_N)(\lambda - v_\lambda\lambda^{-2}) \tag{3.19}$$

where ϕ_N is the non-Gaussian contribution (given by Eq. (3.12)) and ϕ_E is the contribution of the interactions of charges on the chain. By using Eq. (3.18), ϕ_E can be expressed by

$$\phi_e = \frac{i^2e^2Z^2}{DkT}\left[\left(\frac{1}{3}\langle\alpha_s{}^2\rangle\right)^3\bar{h}_0^2(\lambda^2 + 2v_\lambda\lambda^{-1})^3\right]^{-1/2}\left[\frac{A}{1+A} - \ln(1+A)\right] \tag{3.20}$$

where $A = \{3DkT\,M_0\,\langle\alpha_s{}^2\rangle\,(\lambda^2 + 2v_\lambda\lambda^{-1})/[\pi N_A e^2\,\bar{h}_0^2\,(i\rho\, v_2 + 2\,M_0\,c_{-})]\}^{1/2}$, M_0 is the molecular weight of the monomer unit of the polyelectrolyte, ρ is the density of the dry polyelectrolyte, and c_{-} is the concentration of co-ions in the unit volume of the gel. The mean-square end-to-end distance in the reference state can be expressed by $\bar{h}_0^2 = Zsb_0^2$, where s is the number of monomer units in the statistical segment and b_0 is the length of the monomer unit.

3.4 Swelling of Polymer Networks

If we immersed polymer network in diluent of the low-molecular solvent molecules diffuse into a polymer phase; at the same time sample enlarge its size. Penetration of solvent molecules into network (swelling) is due to osmotic forces, which are defined by mixing of polymer chains with the solvent. Polymer networks can take only limited amount of solvent as elastic forces originating from deformed EANCs stop swelling process. Mixing of polymers with solvent is usually modeled with the help of lattice theory (1) (14) (15) (36) in which the separate positions are occupied by solvent molecules or polymer segments (with the same volume). The mixing entropy is equal to the combinatorial entropy of the lattice. The mixing enthalpy in this theory is included in interaction parameter χ, which reflects enthalpy changes at mixing of components. In ideal case parameter χ has only enthalpy character and it does not depend on concentration of the solvent in sample. But this condition doesn't realize in real systems.

3.4.1 Lattice model and Flory-Huggins theory

The regular solution approximation is not valid for solutions containing polymers. However, it is no great step to the Flory-Huggins mean-field theory. The theory was independently suggested by Flory (1942) and Huggins (1942). Both models are based on the idea of a lattice in which the components of the mixture are placed. They also assume that the volume is unchanged during mixing. The mixing entropy is strongly influenced by the chain-connectivity of the polymer component. The mixing enthalpy should for polymer/small-molecules mixtures have a similar form as for regular solutions. The mixing entropy and the mixing enthalpy are first calculated separately in the Flory-Huggins treatment and then brought together in the free energy of mixing as in the case of the regular solution model. *Fig. 3.4* shows schematically the lattice model used in the calculations. Each repeating unit of the polymer here denoted segment occupies one position in the lattice and so does each solvent molecule.

The lattice consists of n_L cells occupied by either solvent molecules or polymer segments. We define n_1 as the number of solvent molecules and n_2 is the number of polymer molecules; the number of segments (monomers) of each chain is N ($n_L = n_l + N n_2$). In a first step, we assume only the excluded volume condition (double occupancy of a cell is forbidden), no other interactions between solvent and polymer. In order to evaluate the partition function for this system, we are faced with the problem to calculate the number of possible confirmations of the polymers embedded on the lattice. This is not a trivial task, since the connectivity prohibits a simple calculation; this problem was solved by Flory (1) (14) (15) (mean-field approximation).

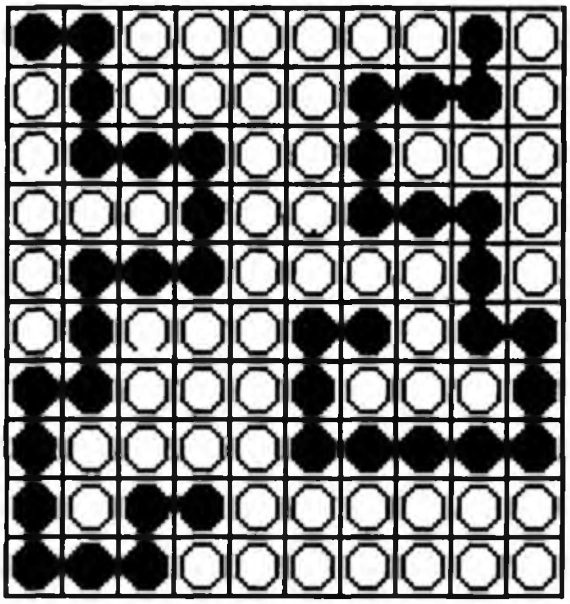

Fig. 3.4 Lattice model of the polymer solution (taken from (1))

The result for the entropy is

$$S = -k\left[n_1 \ln\frac{n_1}{n_1 + Nn_2} + n_2 \ln\frac{n_2}{n_1 + Nn_2} - n_2(N-1)\ln\frac{z-1}{e}\right] \tag{3.21}$$

where z is the coordination number of the lattice. Since we are primary interested in the contribution of mixing the polymers with the solvent molecules, one has to subtract from Eq. (3.2) the contribution S_{dis} due to the conformational disorder of the polymers. This part is obtained if there are no solvent molecules present, $n_l = 0$, and thus

$$S_{dis} = S\,(n_l = 0) = n_2 k\left[\ln N + (N-1)\ln\frac{z-1}{e}\right] \tag{3.22}$$

Therefore the "entropy of mixing" is given by

$$\Delta S = S - S_{dis} = -k\left[n_1 \ln\frac{n_1}{n_1 + Nn_2} + n_2 \ln\frac{Nn_2}{n_1 + Nn_2}\right] \qquad (3.23)$$

Using the volume fractions of solvent (v_1) and polymer (v_2)

$$v_1 = \frac{n_1}{n_1 + Nn_2}\text{ , and } v_2 = \frac{Nn_2}{n_1 + Nn_2} = 1 - v_1 \qquad (3.24)$$

we obtain

$$\Delta S_m = -k\left[v_1 \ln v_1 + \frac{v_2}{N}\ln v_2\right] \qquad (3.25)$$

In order to obtain the complete free energy of mixing we have to formulate the enthalpy of mixing. In this case one has to introduce a selective interactions between solvent molecule and polymer segment. For simplicity it was assumed that the range of interactions is restricted to nearest neighbors on the lattice. So, $\Delta E/kT = \chi v_1 v_2$; E is the energy and χ is Flory-Huggins interaction parameter. The overall change of the free enthalpy ("Gibbs free energy") per lattice site is than given by

$$\Delta G/kT = \Delta E/kT - \Delta S/k = \frac{v_1}{N_1}\ln v_1 + \frac{v_2}{N_2}\ln v_2 + \chi v_1 v_2 \qquad (3.26)$$

From Eq. (3.26) the osmotic pressure P_m is given by

$$P_m = -(RT/V_1)\,(\ln(1 - v_2) + v_2 + \chi v_2^2) \qquad (3.27)$$

where V_1 is the molar volume of the solvent. The swelling equilibrium in network, in the case of free swelling is than given by known Flory-Huggins equation (1) (14) (15) (36), which consists from osmotic and elastic contribution

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + v_d V_1(<\alpha_0^2> v_2^{1/3} - 2v_2/f_c) = P_m + P_{el} = 0 \qquad (3.28)$$

where v_d is the concentration of elastically active network chains related to dry state of network. The elastic contribution to swelling equilibrium can derived from Eq.(3.25) $P_{el} = -(\partial \Delta F_c / \partial V)_T$ taking into account that for isotropic swelling it holds

$$\Lambda_x = \Lambda_y = \Lambda_z = \left\langle \alpha_0^{\,2} \right\rangle^{1/2} v_2^{-1/3} \qquad (3.29)$$

In this equation non-Gaussian contribution to elasticity term (see Eq. (3.8)) was not taken into account.

In ideal case the interaction parameter χ has only enthalpy character. Non-ideality of the interaction parameter χ was described by introduction the entropy component, so that $\chi = \chi_H + \chi_S$, where index H belongs to the enthalpy component and S to the entropy one. In the most real systems the dependence of χ on the volume fraction of the polymer v_2 is found when Eq. (3.8) is used for swelling of networks with different EANCs concentrations (1), (17).

3.5 Swelling of Networks with Charged Groups

3.5.1 Introduction

If polyelectrolyte gel is submerged in water, it swells enormously in comparison with uncharged gel. The small, mobile counterions dissolve in the liquid phase of gel and due to electroneutrality of the sample they must stay inside the gel volume. In such a way the counterions substantially contribute to the (expansive) osmotic pressure and strongly enhance swelling.

When polyelectrolyte gel is immersed in the aqueous solution presence of the counter-ions of the charged network causes part of the ions of the added salt to be excluded from the interior of the gel, implying that the salt concentration in the internal liquid is lower than in the external medium. This effect gives rise to an excess osmotic pressure in the gel, as was first mentioned by Donnan (53). This approach can be directly employed for the case of a polyelectrolyte gel.

It was also found (48) (49) that the activity coefficient of counter-ions in aqueous solutions considerably decreases with increasing polyelectrolyte ionization. This is in agreement with the finding that only some of the counter-ions are free in polyelectrolyte solution; the rest have a limited mobility because of the formation of ion pairs or of a bond with the polyelectrolyte chain. This means that the effective degree of neutralization i (ionization) is lower than the stoichiometric degree of neutralization α ($i = \alpha\phi$, where ϕ is the osmotic coefficient (54)).

In the presence of a low molecular weight salt, the activity coefficient of the counter-ion can be determined by using the additivity rule (54) according to which

$$f_+ = \frac{\alpha Z v_s \phi + c_- f_-}{\alpha Z v_s + c_-}, \tag{3.30}$$

where Z is the degree of polymerization of the chain, v_s is the concentration of polymer chains in the swollen gel, and c_- and f_- are the concentration of co-ions and their activity coefficient, respectively. Since the probability of finding co-ions in the vicinity of a chain with the same charge is very small, the co-ions are not too much affected by the potential of the chain and their activity coefficient is usually regarded as equal to that of the same ion having the same concentration in the absence of polyelectrolyte (54).

3.5.2 Donnan equilibrium

According used model the difference between the osmotic pressure of the gel and of the solution, P_{os} can be expressed by (42) (54)

$$P_{os} = RT\left(iZv_s + 2c_- - 2\bar{c}_-\right) \tag{3.31}$$

where c_- and $\bar{c}_-$ are the respective concentrations of co-ions in gel and in solution. The relationship between c_- and $\bar{c}_-$ is described by the Donnan equilibrium in the form

$$(f_- c_- + iZv_s) f_- c_- = \bar{c}_-^{\,2} f_-^2 \tag{3.32}$$

By combining (3.31) and (3.32) we obtain

$$P_{os} = (RT / M_0)\left\{ i\rho v_2 - 2f_- c_- M_0 \left[\left(1 + \frac{i\rho v_2}{M_0 f_- c_-} \right)^{1/2} - 1 \right] \right\} \tag{3.33}$$

3.5.3 Swelling equilibrium of charged networks

As follows from preceding discussion, for charged chain immersed in a solution of a low-molecular univalent salt we have four contributions to the change of the free energy ΔF, corresponding to the volume change during swelling. During swelling the sample is subjected to the swelling pressure P given by (42) (54)

$$P = -\mu_1 / V_1 = P_m + P_{el} + P_{os} + P_{els} = -\left(\frac{\partial \Delta F}{\partial V}\right)_{T,n_j} = \sum_{i=1}^{4} -\left(\frac{\partial \Delta F_i}{\partial V}\right)_{T,n_j} , \tag{3.34}$$

and as it was already mentioned μ_1 is the chemical potential of the solvent, V_1 is the molar volume of the solvent, n_j is the number of moles of ions of the j-th type in the gel. In such way the pressure P can be separated into four individual contributions.

The contribution P_m corresponds to the mixing of polymer segments with the solvent (Flory-Huggins term, see Eq. (3.27)). The contribution P_{el} corresponds to the change of the configurational free energy with swelling (elasticity term). Owing to the high values of swelling, the finite extensibility of chain was considered (the Langevin distribution function was used to describe the end-to-end distance) and P_{el} has been divided into the Gaussian $P_{el}{}^{G}$ and non-Gaussian $P_{el}{}^{NG}$ terms (derived from ΔF_c given by Eq. (3.8))

$$P_{\mathrm{el}} = P_{\mathrm{el}}{}^{G} + P_{\mathrm{el}}{}^{NG} = -\nu_d RT\left(\langle\alpha_0^2\rangle v_2^{1/3} - v_2/2\right) - \nu_d RT\left(\frac{3}{5}\langle\alpha_0^2\rangle^2 v_2^{-1/3} n^{-1} + \frac{99}{175}\langle\alpha_0^2\rangle^3 v_2^{-1} n^{-2}\right.$$

$$\left. + \frac{513}{875}\langle\alpha_0^2\rangle^4 v_2^{-5/3} n^{-3} + \ldots\right), \tag{3.35}$$

where ν_d is the molar concentration of chain related to the dry volume, $\langle\alpha_0^2\rangle$ is the dilatation factor of the dry state (= $(v_0)^{2/3}$, where v_0 is the volume fraction of the polymer at network formation) and n is the number of statistical segments in the chain (it can be expressed by the number of monomeric units in the statistical segment s). This elasticity term P_{el} can be easily modified and more advanced theories of rubber elasticity can be used (i.e. factors $A = (f_e\text{-}2)/ f_e$ and $B = 0$ can be included in P_{el}, f_e being the average functionality of the junction, Eq. (3.5)). This modification affects collapse analysis slightly because with a high degree of swelling $v_2/2 < \langle\alpha_0^2\rangle v_2{}^{1/3}$ the experimental value of the equilibrium modulus should be used instead of $\nu_d RT \langle\alpha_0^2\rangle v_2{}^{1/3}$. The contributions P_m and P_{el} are classical terms of the Flory-Huggins equation (Eq. (3.8)) for swelling equilibria of non-ionized polymer networks (1).

The contribution P_{os}, which corresponds to the difference between the osmotic pressure in the ionized gels and in external solution (mixing of ions with the solvent), is given by Eq. (3.36). From the Donnan equilibrium we obtain

$$P_{os} = \left(RT / M_0\right)\left\{ i\rho v_2 - 2f\_c\_M_0\left[\left(1+\frac{i\rho v_2}{M_0 f\_c\_}\right)^{1/2} - 1\right]\right\}, \qquad (3.36)$$

where M_0 is the molar mass of the monomer, i is the degree of ionization given by the molar fraction of charges in the chain, ρ is the density of dry network and $c\_$, $f\_$ are the concentrations of co-ions and their activity coefficient.

The final contribution P_{els} reflects the change in the free energy of the chain due to electrostatic interaction (repulsion of charges on the chain) with swelling was derived from Eq. (3.28) in the form (54) (42)

$$P_{els} = \frac{v_d N_A Z i^2 e^2 v_2^{4/3}}{3D\left(\overline{h_0^2}\left\langle\alpha_0^2\right\rangle\right)^{1/2}}\left[\frac{2.5A}{1+A} - \ln(1+A)\right], \qquad (3.37)$$

where

$$A = 6h / \kappa\overline{h_0^2} = \left[\frac{9\left\langle\alpha_0^2\right\rangle v_2^{-2/3} DkTM_0}{\pi N_A e^2 \overline{h_0^2}\left(2M_0 c\_ + i\rho v_2\right)}\right]^{1/2}$$

and D_m is the dielectric constant of the medium, k is the Boltzmann constant, N_A is the Avogadro constant, Z is the degree of polymerization of the chain ($Z = n.s$), e is the unit charge and κ is the inverse of the Debye radius of the ion atmosphere. The terms P_{os} and P_{els} account for the effect of charges on swelling equilibria; while P_{os} is always positive, P_{els} can be positive or negative (43).

The swelling equilibrium for free swelling is given by

$$P_m + P_{el}^{G} + P_{el}^{NG} + P_{os} + P_{els} = 0. \qquad (3.38)$$

4. Volume Phase Transition of Hydrogels

4.1 Introduction

Polymeric gels absorb large amount of appropriate solvents without dissolving. During the swelling process, the network chains are forced to attain more elongated, less probable configurations. Similar to the liquid-gas transition of a fluid system, the volume of a gel can change either continuously or discontinuously upon a change of the environmental conditions such as temperature and solvent composition. The volume transition is directly related to the coil-globule transition of a dilute polymer system (55) (56).

An analysis of a classical Flory-Huggins Eq. (3.28) of swelling equilibrium of polymer networks showed (17) (33) that two polymeric phases may coexist in network with suitable structure. These phases differ in the conformation of chains and in the concentration of segments and an amount of a solvent. Small change in the polymer-solvent interactions, i.e. in value of χ parameter (given by a change in the external parameters – temperature or composition of solvent and the like) leads to a pronounced change (collapse) in the degree of swelling of the gel in free swelling conditions. In such a way, this phenomenon shows jumpwise change in the gel volume (first-order phase transition).

Such jumpwise change of volume (collapse) after a long curing time (aging) has been found by Tanaka (57) (58) in the swelling experiments of polyacrylamide (PAAm) gels in acetone-water mixtures (see *Fig. 4.1*); aging played a decisive role in the existence and in the extent of the transition. The original explanation offered by Tanaka (59) assumed a large increase in the crosslinking density with the aging. However, an investigation of the mechanical behavior of these gels led to the conclusion that crosslinking density of gels remains constant during aging and the swelling/shrinkage collapse was interpreted by the formation of pronounced heterogeneous structure (60) (apparently, formed during the aging). Later experiments on PAAm gels (6) (61) (62) demonstrated the necessity of the presence of the charges on the chain (owing to the hydrolysis of AAm) for the occurrence of the collapse. Potentiometric titration has indeed revealed (63) a small amount (~ 1 mol %) of charged carboxyl groups in aged solutions of linear PAAm.

The molecular interactions rule the macroscopic size and shape of gels. Since these interactions are functions of temperature, polymer concentration, solvent composition, pH and low molecular salt concentration, the volume phase transition can be induced by controlling one or some of these parameters. During last twenty years many papers on collapse phenomena have been published (6); collapse was achieved by a change in composition of water-acetone mixed solvent (5) (6) (9) (59-64), temperature (65-68), degree of ionization (62) (63) (69), pH of the solvent (70-72), electric field applied to the gel (73) (74), concentration of the low molecular weight salt (72) or by an external deformation (75). It was found that the discontinuous change in the gel volume is accompanied by a similar change in the other physical properties (mechanical, optical, conductivity and dielectric permittivity (11) (76-79), etc.).

The phase transition is a result of a competitive balance between a repulsive force that acts to expand the polymer network and an attractive force that acts to shrink the network. The electrostatic interaction between the polymer charges of the same kind is the most effective repulsive force. It can be imposed upon a gel by introducing ionization into the network. The osmotic pressure by counter ions adds to the expanding pressure. The attractive forces can be van der Waals, hydrophobic interaction, ion-ion interactions between opposite kinds of charges, and hydrogen bonding. The phase transition was discovered in gels induced by each of the fundamental forces.

4.2 Phase Transition at Free Swelling

A characteristic example of the coexistence of two gel phases and hence of the first-order phase transition in a swollen network consists of the van der Waals loop which appears in the dependence of the swelling pressure P (or of the chemical potential of the solvent μ_1, see Eq. (3.24)) on v_2 (or volume of the gel) (1), (6) (11) (17). The stability of phases requires $P \geq 0$. The composition of coexisting gel phases at the collapse (values v_2' and v_2'') is given by the condition of equality of the chemical potentials of the solvent μ_1 and polymer μ_2 in both phases (43):

$$\mu_1' = \mu_1'' \text{ and } \mu_2' = \mu_2''. \tag{4.1}$$

For free swelling, it holds

$$\mu_1' = \mu_1'' = 0 . \tag{4.2}$$

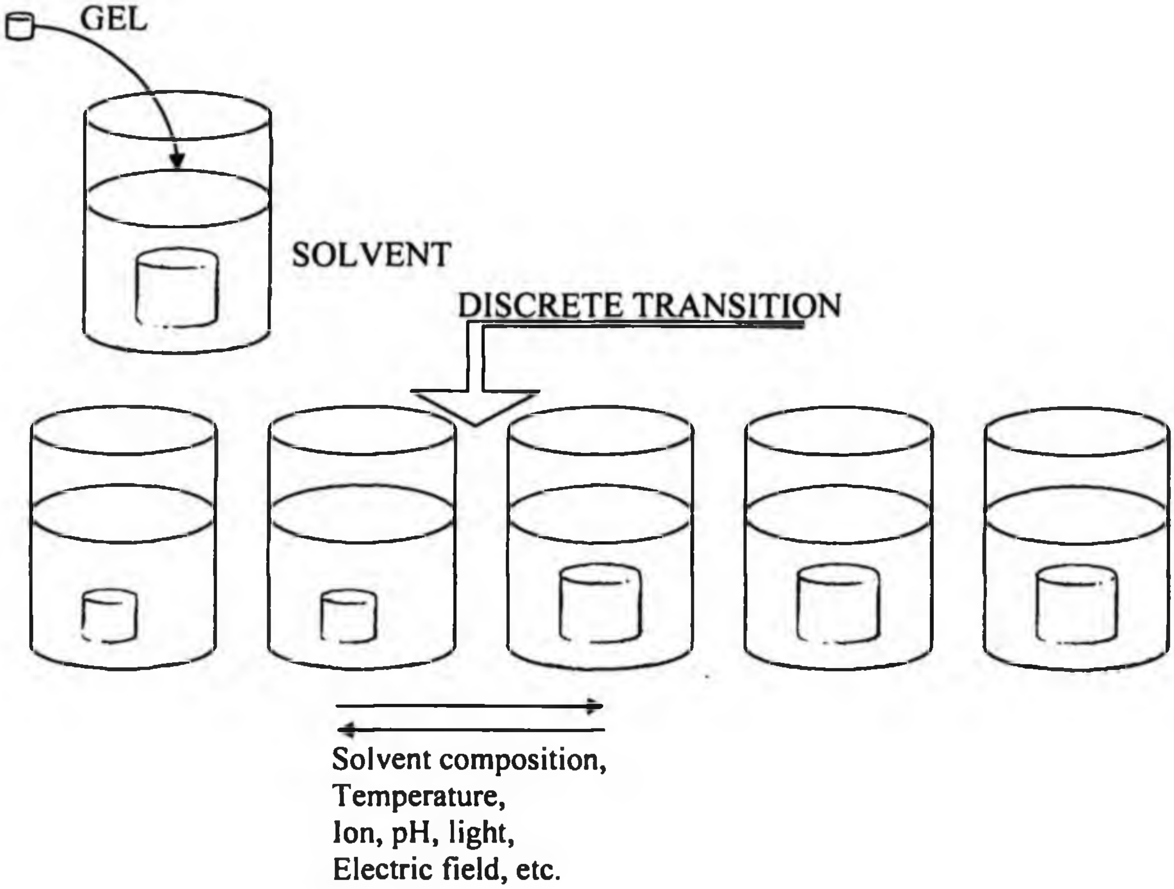

Fig. 4.1. The Phase transition of gels undergo in a solvent by changing one or some of the environmental factors, such as temperature, solvent composition, pH, etc. (taken from (5)*)*

Using the Gibbs-Dühem equation

$$(1-v_2)(\partial\mu_1/\partial v_2)+(v_2/r)(\partial\mu_2/\partial v_2)=0\ , \tag{4.3}$$

in combination with Eq. (4.1), assuming the validity (4.2) i.e. we can write (43)

$$\mu_2'' - \mu_2' = \int_{x_1'}^{x_1''}(d\mu_2)_{T,p,x_2} = rV_1\int_{v_2'}^{v_2''}\frac{1-v_2}{v_2}\left(\frac{dP}{dv_2}\right)_{T,p,x_2} dv_2 = rV_1\int_{v_2'}^{v_2''}Pv_2^{-2}dv_2 = 0\ , \tag{4.4}$$

where x_1 and x_2 are the numbers of moles of the solvent and polymer respectively, p is the external pressure and r is the number of equivalent segments of the macromolecule.

From Eq. (4.4) it follows that Maxwell's construction (in order to guarantee stability of the gel in free swelling and to determine the composition of phases v_2' and v_2'') can be performed on the dependence Pv_2^{-2} on v_2; Eq. (4.4) also demonstrates that Maxwell's construction can be carried out on the plot of P on $(1-v_2)/v_2$ because

$$\int_{v_2'}^{v_2''} \frac{1-v_2}{v_2}\left(\frac{dP}{dv_2}\right)_{T,p,x_2} dv_2 = \oint_k \frac{1-v_2}{v_2}\, dP = -\oint_k P d\left(\frac{1-v_2}{v_2}\right) = 0 \ . \qquad (4.5)$$

Eq. (3.38) allows us to calculate the dependence for free swelling of the network, of experimental determined interaction parameter $\bar{\chi}$ on the volume fraction of gel v_2 (*Fig.4.2*), if only a single molecular parameter changes (e.g. fraction of the charges *i*, *Fig. 4.3*). The dependence of the swelling pressure P (Eq. (3.34)) for a constant value $\bar{\chi} = \chi_c$ in Eq. (4.7) on v_2 may be expressed using the dependence of $\bar{\chi}$ on v_2 by subtracting Eq. (3.38) (with $\bar{\chi}$ in Eq. (4.7)) from Eq. (3.34) (with χ_c in Eq. (4.7)) which gives, eventually,

$$P = \left(RT/V_1\right)\left(\bar{\chi} - \chi_c\right)v_2^2 \ . \qquad (4.6)$$

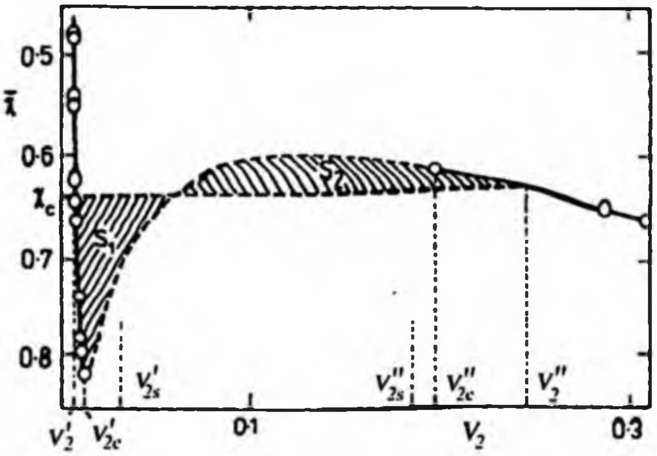

Fig. 4.2. An example of Maxwell's construction in the dependence of $\bar{\chi}$ on v_2 used in the determination of the extent of the collapse $\Delta = v_2'' - v_2'$ and critical values of the interaction parameter χ_c of networks. (o) experimental data; (---) course determined by Eq. (3.38); critical parameters χ_c and Δ defined by the condition $S_1 = S_2$ (taken from (33)*)*

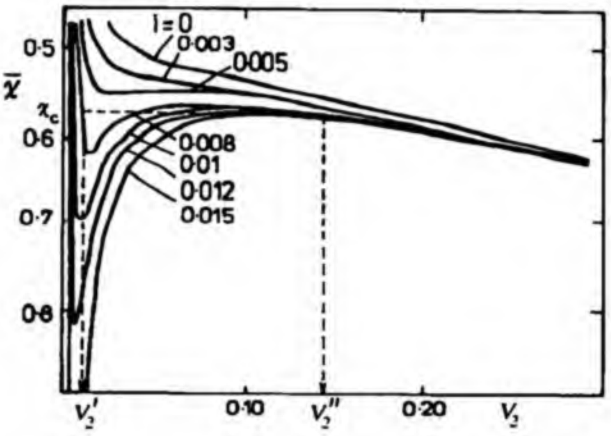

Fig. 4.3. The dependence of $\bar{\chi}$ *on the volume fraction of the dry polymer in the swollen state* v_2 *for free swelling in water for* $c\_=0$ *and* $s = 0.5$*. Numbers at curves denote the charge fractions on the chain, i. For* $i = 0.008$ *, the critical value* $\chi_c = 0.57$ *was determined using Maxwell's construction (taken from* (43)*)* .

Eq. (4.6) shows that, if the van der Waals loop exists in Pv_2^{-2} vs. v_2 dependence (Eq. (4.4)), it also exist in the $\bar{\chi}$ on v_2 dependence and its occurrence in $\bar{\chi}$ indicates the possibility of collapse of the swollen network. Substitution of Eq. (4.6) into Eq. (4.4) gives the phase transition condition

$$rRT\int_{v_2'}^{v_2''}\left(\bar{\chi}-\chi_c\right)dv_2=0\ , \qquad (4.7)$$

which means that Maxwell's construction carried out on the $\bar{\chi}$ vs. v_2 dependence determines the critical value of χ_c and hence also the composition of both phases (v_2' and v_2'') (see *Fig. 4.2*)

Theoretical calculations (see Fig. 4.3 (43)) made for PAAm network swollen in water showed that in non-ionized network no phase transition takes place; the increasing fraction of charges on the chain, *i* induces this effect. Approximately 0.5 mole % of charges on overall number of monomeric units on the chain are sufficient to induce the transition and collapse occurs for the critical value $\chi_c = 0.545$. With increasing charge fraction on the chain the beginning of the transition is shifted towards higher swelling and higher values χ_c. The jump in volume also increases with increasing *i*.

It was shown by Tanaka et al. (5) (80) (81), that the van der Waals loop in dependence of the swelling pressure P on v_2 can be predicted also by reduced form of Eq. (3.38) without electrostatic contribution ($P_m + P_{os} + P_{el}^G = 0$). It is also possible to determine the critical temperature (critical value of interaction parameter χ_c); in this case we would expect slightly different values of the critical parameters (composition of phases and χ_c).

4.3 Thermoresponsive Polymers and the Phase Transition Phenomenon

Temperature-sensitive hydrophilic polymers usually exhibit a lower critical solution temperature (LCST). Polymers of this type are soluble in a water at low temperatures but become insoluble as the temperature rises above the critical solution temperature (82) (LCST). The liquid-liquid phase diagram at constant pressure of binary polymer solutions (water/polymer) is usually determined by plotting the temperature of incipient phase separation as a function of the overall polymer concentration (*Fig. 4.4*). Although the solution is homogeneous at low temperature, a macroscopic phase separation appears when the temperature exceeds a critical value called the low critical solution temperature (LCST) or the cloud point (CP) of the mixture (83). The minimum in the phase diagram (known also as cloud point curve) is called the precipitation threshold, or LCST (lower critical solution temperature), since it denotes the extreme temperature at which phase separation can occur at all (84). At LCST the conformation of chains change from coil-like to more dense globular-like form. *Fig. 4.4* shows a typical curve of cloud point versus composition that one might find for a thermo-responsive system. The right-hand branch of the experimental phase diagram defines the composition of the polymer that precipitates at various temperatures. It can also be viewed as the equilibrium swelling ratio of the polymer solvent system as a function of the temperature. In a LCST system, a positive slope, indicating that the polymer (or gel) will precipitate (collapses) as the temperature increases, characterizes the right-hand branch of the curve.

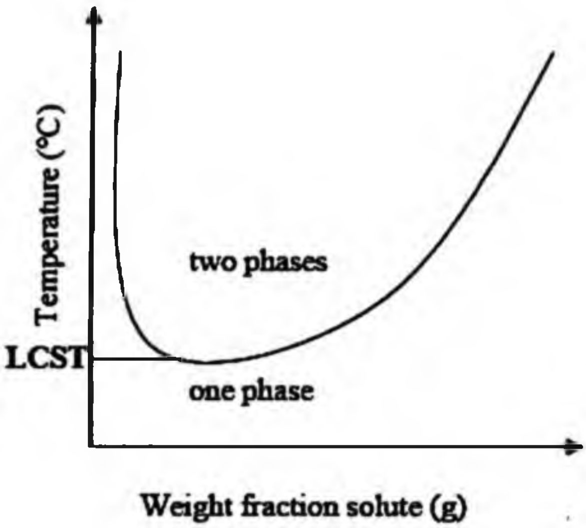

Fig. 4.4 Phase diagram of a system exhibiting lower critical solution temperature(LCST), adapted from Taylor and Gerankowski (82)

For a linear flexible polymer chain in solution, there has been extensive discussion concerning the role of various interactions contributing to the coil-to-globule transition; whether "hydrophobic effects" and/or "hydrogen bonding effects" are dominant in general in aqueous solutions (85). Some authors (86-89) favor the breakdown of polymer-water "hydrogen bonding" interactions in controlling the macromolecular contraction whereas the others (90) attribute the chain collapse to changes in the "hydrophobic effect", which induces local structure in the solvent molecules surrounding the hydrophobic substitutes of the polymer. A third group of authors (91) (64) argues that the LCST of the thermoresponsive polymers is associated with changes in both "hydrogen bonding" and "hydrophobic interactions" within the interacting polymer-solvent system. According to the last group, at the molecular level the phase transition of temperature-sensitive polymers is a change from hydrated random coil to hydrophobic globule. As the temperature rises and approaches the phase transition point, the first step of the phase separation is the breaking up of the relatively strong hydrogen bonds, formed around the polymer coil between water molecules and the NH or C=O groups of the temperature-sensitive polymers, followed by the collapse of the polymer molecule into a hydrophobic globule. Polymer-polymer interactions are responsible for the aggregation and the subsequent precipitation of the polymer out of solution is taking place since hydrogen bonding becomes weaker and breaks as the temperature is raised (92).

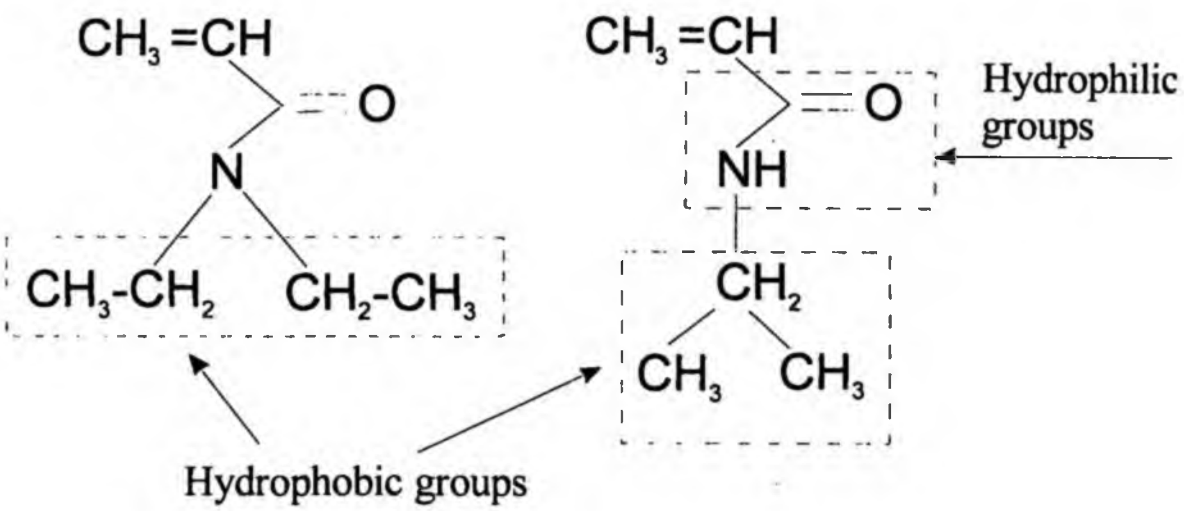

Fig. 4.5. Molecular structures of two monomers and identification of their hydrophilic and hydrophobic regions [from (93)*]*

4.3.2. Phase transition of *N*-alkylacrylamide gels in water

The unique properties of the smart hydrogels consist in the fact that very small changes in the environmental conditions caused to swell or shrink of hydrogel. The volume phase transition of gels is known to result from the interactions between the polymer chain and solvent molecules at shrunken and swollen states. Concerning interactions for gels, van der Waals interaction, hydrogen bonding, hydrophobic interaction and ionic interaction have been considered to explain this swelling behavior (76) (94). With respect to temperature dependence, three types of phase transitions have been reported:

- Thermoswelling type (or expansion) with temperature; corresponding to Upper Critical Solution Temperature (UCST) for polymer solutions (95). This behavior is usually found for hydrophobic-type polymers in organic solvent.

- Thermoshrinking type (or collapse) with temperature; corresponding to Lower Critical Solution Temperature (LCST) for water polymer solutions (95).

- "Convexo" type, a mixture of the two types mentioned above, causing firstly expansion and then shrinkage with temperature; corresponding to hour-glass type for polymer solution (64).

The main thermoshrinking hydrogels are composed of monomers like *N*-ethylacrylamide, *N,N*-diethylacrylamide and *N*-isopropylacrylamide whose hydrophobic side-chains constituents make them less hydrophilic. Gels whose monomers are composed of both hydrophobic and hydrophilic groups have the possibility of undergoing a thermoshrinking type of phase transition in water. For instance, the structure of *N*-isopropylacrylamide, which has hydrophilic groups (NH, C=O) and a hydrophobic (isopropyl) group shows that hydrophobic interaction as well as hydrophilic interaction may play an important role in the thermoshrinking transition.

4.3.3. Hydrophobic hydration/hydrophobic interactions

When hydrophobic solutes are introduced into water, two phenomena are simultaneously observed (96):

- Hydrophobic hydration, in which the water molecules form cage-like structures around the hydrophobic solutes hydrophobic hydration means the hydration of a non polar or non ionic molecule, such as a noble gas atom. The interaction is represented by the Lennard-Jones potential alone. The water molecules do not specifically reorient towards the inserted molecule; rather they try to build a net around it.
- Hydrophobic interactions, which are the association of hydrophobic solutes generally, an increase in temperature results in a reduction of the total number of water molecules structured around the hydrophobic solutes, which promotes hydrophobic interaction. As schematically shown in *Fig. 4.6*, hydrophobic hydration is an exothermic and entropically unstable process while hydrophobic interaction is endothermic and entropically stable process. Consequently, a rise in temperature strengthens the hydrophobic interaction.

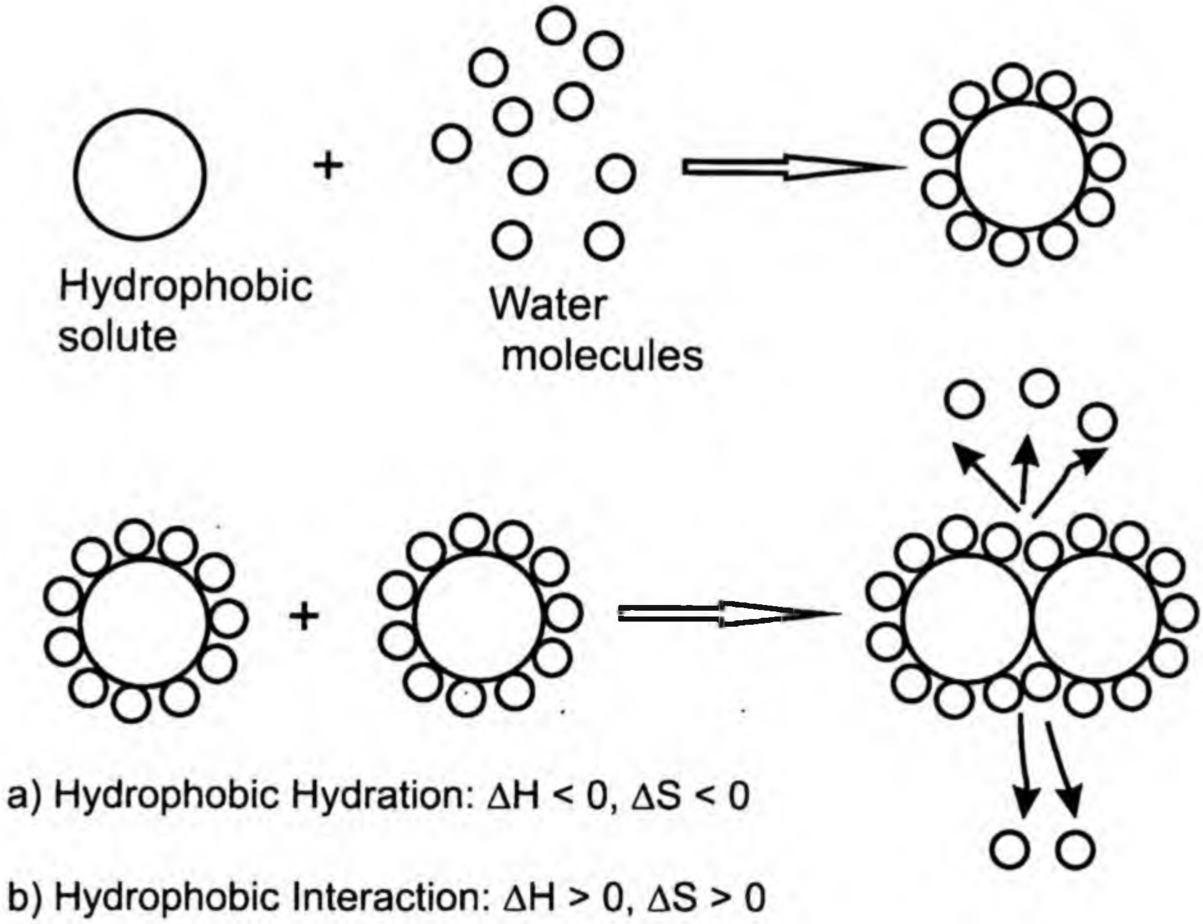

Fig. 4.6. Schematic representation of a) Hydrophobic hydration and b) Hydrophobic interaction.

4.4 Cononsolvency Effect

In past few years scientific interest and practical applications has been attracted by the cononsolvency behavior of PIPAAm in aqueous media. Cononsolvency is a phenomenon in which a mixture of two good solvents for a polymer forms a nonsolvent. Crowther and Vincent showed the swelling degree of PIPAAm microgel particles decreased to a minimum and then reswelled by the addition of methanol. (97). Hirotsu investigated the phase transition of PIPAAm gels in water-methanol mixtures. (98) He found that the interactions between PIPAAm and solvent molecules could be changed by using solvent mixtures with various compositions. Schild et al. studied the LCST of PIPAAm in the cononsolvent mixture of water and methanol by means of cloud-point and microcalorimetric measurements. (99)

There are ternary mixtures of two solvents (components 1 and 2) and a single polymer (component 3). Rather than reducing these systems to binary Flory-Huggins solutions by applying the single liquid approximation, we adopt the approach of spinodal calculations on the extended ternary mode used successfully by Tompa, (100) Patterson, (101) and others. The assumptions required to solve the complex binodal equations are avoided by exploiting the similarity of the binodal and spinodal curves. Solving the familiar expression for the free energy

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \chi_{12} n_1 v_2 + \chi_{13} n_1 v_3 + \chi_{23} n_2 v_3) \qquad (4.8)$$

where n_i the mole fraction, and v_i the volume fraction of component i, and where χ_{rs} is the binary interaction parameter between components r and s. Water is component 1, methanol is component 2, and polymer is component 3.

Flory-Huggins ternary solution theory could explain the cononsolvency results only in terms of a change in the water-ethanol interaction parameter in PIPAAm solutions. They suggested that the perturbation of the binary interaction parameter arose from local contacts between polymer and solvent. However, the Flory-Huggins theory could not appropriately predict the phase behavior of a cononsolvent system. Therefore, a ternary interaction parameter, χ_T introduced into the Flory-Huggins theory to account for the immiscibility gap in solvent-solvent-polymer system and unknown phase boundaries in the phase diagram, that could not be obtained experimentally, could be predicted.

The Gibbs free energy of mixing (ΔG), based on Flory-Huggins theory (1) including a ternary interaction parameter, χ_T(102) (103) (104) (105) for the polymer solution is

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + \chi_{12} n_1 v_2 + \chi_{13} n_1 v_3 + \chi_{23} n_2 v_3 + \chi_T n_1 v_2 v_3) \quad (4.9)$$

The role of χ_T in the last term is related to the interaction among water, methanol and PNIPAAm, and it is treated as an empirical correction parameter. The first three terms in equation correspond to the entropic contribution and the fourth to the sixth terms represent the enthalpic contribution. The role of χ_T in the last term is related to the interaction among water, methanol and PIPAAm. From Eq (4.9), the chemical potential, $\Delta\mu_i$ (μ_i - μ_i°)of the three components is given:

$$\frac{\Delta\mu_1}{RT} = \ln v_1 + 1 - v_1 - \frac{V_1}{V_2}\ln v_2 - \frac{V_1}{V_3}v_3 + (\chi_{12}v_2 + \chi_{13}v_3)(v_2 + v_3) - \frac{V_1}{V_2}v_2v_3\chi_{23} - h_1h_2v_2\frac{d\chi_{12}}{dh_2} -$$
$$- v_1v_2v_3\frac{d\chi_{13}}{dv_2} - v_1{v_3}^2\frac{d\chi_{13}}{dv_2} - v_1{v_3}^2\frac{d\chi_{13}}{dv_3} - \frac{V_1}{V_2}{v_2}^2v_3\frac{d\chi_{23}}{dv_2} - \frac{V_1}{V_2}v_2{v_3}^2\frac{d\chi_{23}}{dv_3} - v_1{v_2}^2v_3\frac{d\chi_T}{dv_2} -$$
$$- v_1v_2{v_3}^2\frac{d\chi_T}{dv_3} + \chi_T v_2v_3(1-2v_1)$$

$$\frac{\Delta\mu_2}{RT} = \ln v_2 + 1 - v_2 - \frac{V_2}{V_1}\ln v_1 - \frac{V_2}{V_3}v_3 + (\frac{V_2}{V_1}\chi_{12}v_1 + \chi_{23}v_3)(v_1 + v_3) - \frac{V_2}{V_1}v_1v_3\chi_{13} + \frac{V_2}{V_1}h_1h_2v_1\frac{d\chi_{12}}{dh_2} +$$
$$+ \frac{V_2}{V_1}v_1v_3(v_1+v_3)\frac{d\chi_{13}}{dv_2} - \frac{V_2}{V_1}v_1{v_3}^2\frac{d\chi_{13}}{dv_3} + v_2v_3(v_1+v_3)\frac{d\chi_{23}}{dv_2} - v_2{v_3}^2\frac{d\chi_{23}}{dv_3} + \frac{V_2}{V_1}v_1v_2v_3(v_1+v_3)\frac{d\chi_T}{dv_2} -$$
$$- \frac{V_2}{V_1}v_1v_2{v_3}^2\frac{d\chi_T}{dv_3} + \frac{V_2}{V_1}\chi_T v_1v_3(1-2v_2)$$

$$\frac{\Delta\mu_3}{RT} = \ln v_3 + 1 - v_3 - \frac{V_3}{V_1}\ln v_1 - \frac{V_3}{V_2}v_2 + (\frac{V_3}{V_1}\chi_{13}v_1 + \frac{V_3}{V_2}\chi_{23}v_2)(v_1 + v_2) - \frac{V_3}{V_1}v_1v_2\chi_{12} + \frac{V_3}{V_1}v_1v_2v_3\frac{d\chi_{13}}{dv_2} -$$
$$- \frac{V_3}{V_2}{v_2}^2v_3\frac{d\chi_{23}}{dv_2} + v_3(v_1+v_2)[\frac{V_3}{V_1}v_1\frac{d\chi_{13}}{dv_3} + \frac{V_3}{V_2}v_2\frac{d\chi_{23}}{dv_3}] - \frac{V_3}{V_1}v_1{v_2}^2v_3\frac{d\chi_T}{dv_2} + \frac{V_3}{V_1}v_1v_2v_3(v_1+v_2)\frac{d\chi_T}{dv_3} +$$
$$+ \frac{V_3}{V_1}\chi_T v_1v_2(1-2v_3) \tag{4.10}$$

where $h_1 = v_1/(v_1+v_2)$, $h_2 = v_2/(v_1+v_2)$

At liquid-liquid phase equilibrium at a chosen temperature and pressure, the chemical potential of each component between two phases is equal:

$$\mu_i' = \mu_i'' \qquad i = 1, 2, 3$$

where μ_i' and μ_i'' are the chemical potentials of component i in phases 1 and 2.

Wolf and Willms proposed that cononsolvency occurs when $\chi_{12} \approx +2$ or $\chi_{12} < 0.4$ (106) The mechanism of cononsolvency is proposed: this system prefers the formation of (1-2), (1-3) and (2-3) contacts rather than (1-2-3) contacts. The positive χ_T value due to rejection (1-2) pairs component (3), (1-3) pairs reject component (2) or (2-3) pairs reject component (1) to raise the free energy of the system. Indeed, the phase diagram showed that cononsolvency only occurred at lower polymer concentration, suggestion that (1-2) pairs disliking component (3) is more likely explanation of the existence of cononsolvency. When the concentration of component (3) is decreased in the system, there will be less formation of (1-3) and (2-3) contacts, which leads to the more (1-2) contacts than the polymer can tolerate, i.e., forming the unfavorable (1-2-3) contacts. Therefore, demixing occurs when a sufficient number of (1-2) contacts have formed near the vicinity of component (3) to reject to be drawn into solution. In contrast, when the polymer concentration increases, the cononsolvency phenomenon disappears because there will be more energetically favorable (1-3) and (2-3) contacts in the system. (103)

4.5 Experimental Results on Phase Transition

4.5.1 Collapse of charged networks in mixed solvents

In recent years, research has been focused to more advanced systems, the so-called stimuli-responsive, that are sensitive to various environmental conditions like temperature, pH, or solvent composition, due to expectations for novel potential applications especially in the field of biomedicine for injectable drug delivery and tissue engineering.

Majority of experimental findings on the collapse were found on the networks, which contained only the charges of one sign. Before 1982, the collapse was observed only for weakly charged polyacrylamide (PAAm) networks in the mixtures of water with acetone. Such gels undergo a first-order phase transition (collapse) reflected in a jump-wise change in the gel volume after an infinitesimal change in the composition of the solvent (57) (58). By smoothly changing the composition of the binary solvent, it is possible to vary effective value of the χ parameter and to convert the network to a collapsed state. When passing from a good (water) to a poor (acetone) solvent, the volume of PAAm gels shrinks by a factor ranging from ten to thousand. After that significant efforts were made to find out new systems, which exhibit the phase transition and to analyze the factors, which influence the specific features of the collapse.

The systematic investigation of the influence of the network formation conditions (amount of crosslinker and diluent) of weakly charged PAAm networks, containing a small number of charged groups on the chain, on the occurrence and extent of the transition in water-acetone mixtures was performed (11) (62) (63) (77) (78). Several important conclusions have been obtained during this period:

(a) phase transition could be found in various gel systems if two conditions are fulfilled: a small number of fixed charges are present on the chain and hydrogels are formed at high dilution and low crosslinking density (11) (77);

(b) transition occurs between two conformational states of the chain, i.e., Gaussian coil in the expanded state and compact globular structure in the collapsed state (76);

(c) jump-wise volume change in the transition correlates with jumpwise changes in the modulus (62), in the refractive index, in the stress-optical coefficient (78) and in the dielectric permittivity (43);

(d) polarity and chemical structure of ionic comonomer plays an important role in appearance and extent of the collapse (9);

(e) theory of swelling equilibrium of polyelectrolyte networks (discussed in details in previous sections), which includes the effect of electrostatic interactions between charges on the chain, describes the experimental swelling data in the first approximation if the effective degree of ionization was introduced (9) (11).

The PAAm networks with high charge density (with sodium methacrylate (MNa) as ionic comonomer) were studied in Khokhlov's group in the mixtures of water and acetone (107); they have demonstrated also the possibility of the occurrence of the phase transition for charged PAAm gels in the mixtures of water with alcohols and dioxane (79). Tanaka has observed discrete collapse for weakly charged networks of copolymers of *N*-isopropylacrylamide with MNa in the mixtures of water with dimethylsulfoxide (66).

Until now, mostly homogeneous slightly charged hydrogels have been studied. Interesting behavior, especially from the application point of view, can be expected in gels with multiphase structure, such as interpenetrating polymer networks (IPNs) or copolymers. In such systems, several transitions caused by the solvent composition or temperature can be expected.

In collapsed state, such hydrogels are capable of showing heterogeneous structure possibly of controlled pore size. In this direction positively charged IPNs, composed of poly(1-vinyl-2-pyrrolidone) PVP and polyacrylamide PAAm network, were investigated in water/acetone mixtures (51). Two transition regions, detected in dependence of swelling degree on acetone concentrations a, suggest that in IPNs two phase structure was formed. The first transition, located between 44 to 60 vol.% of acetone, corresponds to PAAm component, while the second transition, located at 75 vol.% of acetone, corresponds to PVP network. In dependence on amount of positive charges bound to chains both transitions exhibit continuous or jump-wise character; this fact indicates that intermolecular interactions between two components occur~~s~~ with formation of the IPNs (e.g., more polar, charged PVP component increases the extent of hydrogen bonding and makes acetone less effective solvent for IPNs at PAAm transition). V

It is well known that polymer can be dissolved in an appropriate solvent depending on chemical nature of solvent and details of experimental conditions. However, a polymer can change the mixture of two solvents to be a cononsolvent (or two nonsolvents to be a cosolvent). Recently the cononsolvency behavior of PIPAAm in aqueous media has attracted attention because of its scientific interest and practical applications. (99) (97) (98) Crowther and Vincent showed the swelling degree of PIPAAm microgel particles decreased to a minimum and then reswelled by the addition of methanol. (97) Hirotsu investigated the phase transition of PIPAAm gels in water-methanol mixtures. (98) He found the interaction between PIPAAm and solvent molecules could be changed by using solvent mixtures with various compositions. Schild et al. studied the LCST of PIPAAm in the cononsolvent mixture of water and methanol by means of cloud-point and microcalorimetric measurements. (99)

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Systematic studies of the complete phase behavior of the cononsolvent system are very scarce. In the field of ternary polymer systems, the so-called cononsolvency (or cosolvency) is an unusual phenomenon that has not been subjected to extensive investigation. (66) (106) (102).

4.5.2 Temperature collapse of charged networks in water

Temperature is one of the most significant parameters, which can affect the phase behavior of gels and polymer solutions. To observe the collapse in water on temperature requests that solubility is strongly dependent on temperature (as a rule the swelling decreases with increasing temperature (11), (12)) This condition is usually fulfilled for aqueous polymer solutions with amphiphilic polymer structure, such as is in poly(*N*–substituted acrylamides) (e.g. poly(*N,N'*-diethylacrylamide) (PDEAAm) or poly(*N*-isopropylacrylamide) (PIPAAm) (6), (11) , (108), in which, with increasing temperature, the role of hydrophobic interactions between side chains of monomeric units increases. V

Another type of amphiphilic polymers, solubility of which strongly depends on temperature, are based on poly(*N*–substituted methacrylamides) (13). In these systems, the solution phase separation temperatures in water (low critical solution temperatures (LCST)) are close to range of the human body (30 – 45 °C), so that this kind of polymers can be used in biomedical applications as basic components for biosensors, switch on/off drug release and drug delivery systems or for bioconjugated separations (74), (109) (110) (111).

It was shown that for weakly charged networks of copolymer of *N,N'*-diethylacrylamide with MNa discrete collapse is observed, when the gels of this polymer are heated in water (11) (112). Both, the extent of the collapse and transition temperature increased with increasing charge concentration. Ionized PIPAAm gels with negative charges bound to the chains (as ionic comonomer sodium acrylate was used) were extensively investigated (68) (108); the collapse was found in these networks in water in dependence on temperature. As in previous case the extent of the collapse and transition temperature increased with increasing ionization.

Poly(*N*-vinylcaprolactam) (PVCL) exhibits unique physical properties including solubility in water and organic solvents, low toxicity, high complexion ability and found application in many fields of technology, medicine and agriculture (113-115). Crosslinked poly(*N*-vinylcaprolactam) (PVCL) nonionic gels in water have shown under heating one sharp continuous shrinking region in volume (116). It was also shown that ionic PVCL hydrogels exhibited only continuous shrinking region in volume in dependence on temperature (117) (118); this was interpreted by the fact that for the uncharged PVCL network swollen in water at low temperatures the high value of the Flory-Huggins interaction parameter $\chi = 0.522$ was found while for appearance of discrete transition the value of $\chi < 0.5$ is required for network in expanded state. Further, also ionized networks of statistical copolymers of *N*-vinylcaprolactam (VC) with 1-vinyl-2-pyrrolidone (VP) were investigated in water at various temperatures (51). For all copolymers, a continuous transition was found from expanded to collapsed state; the transition temperature T_c strongly increases with increasing content of VP and increasing content of the ammonium salt (charge concentration) in gels. The shift of transition to higher T_c is caused by increasing hydrophilicity of network chains with increasing VP content.

Another type of networks for which temperature collapse in neat water was found are based on poly(vinylmethylether) (119). Recently, Ito and colleagues synthesized various polymers and gels that collapsed on temperature; they found that the transition temperature was changed using hydrophilic-hydrophobic copolymers (120). Onuki (121), (122) and Hirotsu and Onuki (123) have shown that the transition temperature is stress dependent.

Finally, also temperature collapse was studied for semi-interpenetrating polymer networks (semi-IPNs). Temperature-induced collapse was studied on semi-IPNs composed of PIPAAm network and hydrophilic polymers (124); in semi-IPNs both networks grow simultaneously. In these semi-IPNs only one transition on temperature was found; so that distinct two phase structure was not developed. Due to hydrogen bonding in gel network, the critical collapse temperatures were shifted to lower values in comparison with neat PIPAAm network. Also IPN hydrogels prepared by the sequential-IPN method composed of poly(vinyl alcohol) and poly(N-isopropylacrylamide) were studied; it was found that water uptake increase with increasing molar ratio of hydrophilic groups of PIPAAm in the IPNs. (125) The thermal behavior of cross-linked PIPAAm and poly(methacrylic acid) (PMAc) sequential interpenetrating polymer networks (IPNs) has been investigated by differential scanning calorimetry (DSC) (126). IPNs have showed higher thermal stability than the neat homopolymers and copolymers with similar compositions.

The low mechanical strength of PIPAAm hydrogels in a highly swollen state is serious limitation in many applications (108) (127). Using modifications such as copolymerization (128) or semi-IPNs formation (129) led to improved mechanical properties without affecting the gel collapsing temperature.

It should be mentioned that Amiya and Tanaka found discrete collapse for the most important representatives of biopolymers – chemically crosslinked networks formed by proteins, DNA and polysaccharides (130). Thus, it was demonstrated that discrete collapse is a general property of weakly charged gels and that the most important factor, which is responsible for the occurrence of this phenomenon, is the osmotic pressure of the counter ions.

5. The Aims of the Thesis

As it was discussed previously, many systems, which exhibit a first-order phase transition, have been already investigated. It has been shown, both experimentally and theoretically, that the conditions at network formation (concentration of crosslinker and diluent) and of the charge concentration have a great influence on the appearance and extent of the collapse. It was also shown that the polarity and structure of ionic comonomer plays an important role in the appearance and extent of the collapse. The dimensions of network chains in mixed-solvent medium are dependent not only on polymer segments-solvents molecules interactions but are influenced by the interactions between the solvents themselves. Cononsolvency phenomenon, i.e. the formation of nonsolvent by mixing two solvents, was found for some polymers.

Most results were obtained on homogeneous one-component networks, which usually exhibit one transition. Interesting swelling behavior can be expected in two- or multi-component networks, especially from the application point of view. In such systems, several transitions caused by temperature and/or by the solvent composition can be expected. In the collapsed state, such hydrogels are capable of showing heterogeneous structure possibly of controlled pore size. In this work, we investigate:

1. Swelling and mechanical behavior of ionized poly(*N*-isopropylmethacrylamide) and poly(*N*-isopropylacrylamide) networks prepared with negative and positive charges bound on network chains in water/ethanol mixtures at room temperature. As cononsolvency phenomenon can be qualitatively interpreted in terms of the interactions between polymer segments, polymer segments/solvents molecules and solvents molecules themselves we expect that introduction of charges on network chains and the change of structure of ionic comonomer will modify these interactions.
2. Effect of amount of negative bound charges and composition of random poly(acrylamide-*co*-*N*,*N*'-diethylacrylamide) networks on their swelling and mechanical behavior in water/acetone mixtures at room temperature and in water at various temperatures. One can expect that some of these networks will simultaneously exhibit the transition on solvent composition as well as on temperature, and critical values of acetone a_c and/or T_c at the transition will be affected by charge concentration and composition of copolymer.

3. Swelling and mechanical behavior of negatively charged sequential interpenetrating networks (IPNs) composed of poly(*N*-isopropylacrylamide and polyacrylamide was investigated in water at various temperatures and in water/acetone mixtures at room temperature. We expect that these IPNs will exhibit two transitions, one in dependence of swelling degree on acetone concentrations c_a and the second one in dependence on temperature *T*. While the first transition will correspond to PAAm component, the second one will correspond to PIPAAm network. Both transitions will be affected by the charge concentration, composition of IPNs and probably also the intermolecular physical interactions between components.

As in the last decade thermo-sensitive hydrogels have been used in various biotechnological application fields, we expect that investigation of the changes in the composition and ionization of random copolymer network and IPNs allow directing physical properties of hydrogels to practical applications.

6. Methods of Measurements and Preparation of Networks

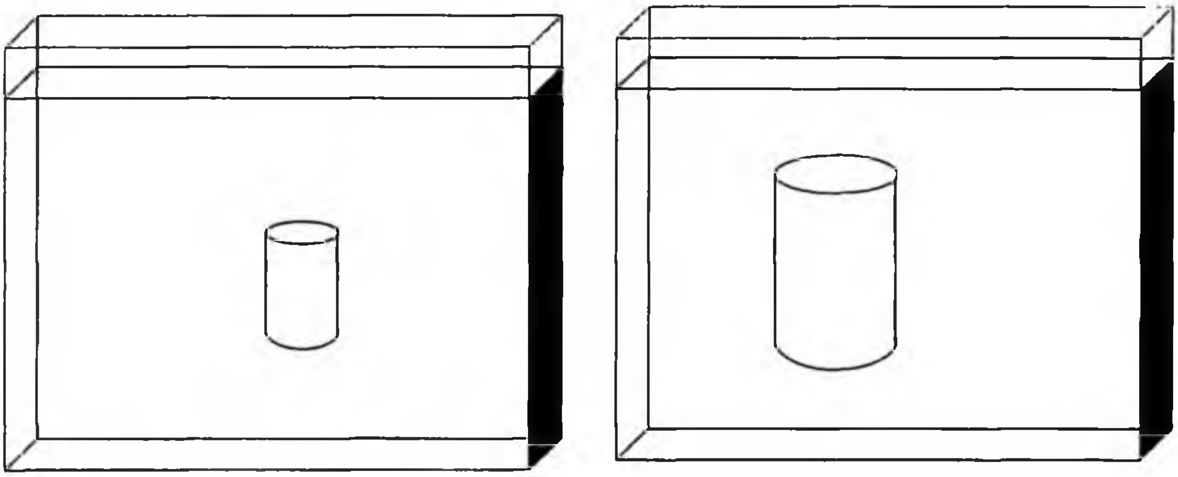
6.1 Methods of Measurements

6.1.1 Swelling

After preparation samples were extracted from the ampoules, cut into cylinders diameter ~10 mm in high; after that the samples of all networks were immersed in 100 ml of deionized water or in 100 ml of water/ethanol or water/acetone mixtures. Swelling proceeded at a chosen temperature T for four days or, in mixed solvent solutions for one month. The inverse swelling ratio X, relative to the state of network formation, was determined from (43)

$$X=(D^*/D)^3=V^*/V \tag{6.1}$$

where D^* and D, respectively, are the diameter of samples after preparation and swelling at various temperatures in water or in solutions at room temperature and V^* and V are the corresponding sample volumes.



Network formation *Equilibrium swelling*

Fig. 6.1 Schematic description of the gel swelling in a solvent

The diameters were measured with an Abbe comparator (accuracy ≈ 0.002 mm). The volume fractions of polymer in the swollen state, $v_2 = v_1 X$ were calculated from the X values, where $v_1 = v_m/\rho$ is the volume fraction of dry polymer at network formation, ρ

is the density of dry networks. The swelling degrees relative to the dry state, $Q = 1/v_2$, were also calculated.

6.1.2 Mechanical measurements

Mechanical measurements were carried out in uniaxial compression in the earlier described apparatus (11) (*Fig. 6.2*).

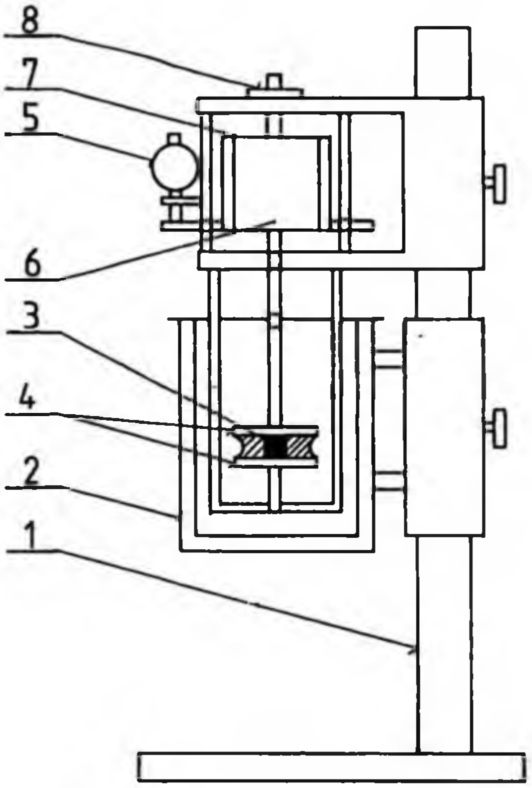


Fig. 6.2 Schematic picture of the measuring device: 1 – holder; 2, 7 – cylinders; 3 – sample; 4 – teflon surfaces; 5 – micrometric screw (strain measurement); 6 –force transducer; 8 – micrometric screw (for application of compression)

The specimen (~ 10 mm high) was compressed to a ratio λ ($\lambda = l/l_o$ where l and l_o, respectively, are compressed and initial heights) and force f was measured after 30-s relaxation (time sufficiently long for attaining equilibrium). Usually ten values of λ and f were determined ($0.8 < \lambda < 1$); the shear modulus G was calculated from

$$G=f/[S_o(\lambda^{-2}-\lambda)] \qquad (6.2)$$

where S_o is the initial cross-section of the specimen.

The mechanical experiments were done also just after networks preparation at room temperature (modulus G_l). From G_l, the concentration of elastically active network chains (EANCs) relative to the dry state v_d was determined from

$$v_d = G_l/(R\, v_l T_l) \tag{6.3}$$

where R is the gas constant and T_l = 298 K is temperature of measurement. From modulus G and G_l the reduced modulus

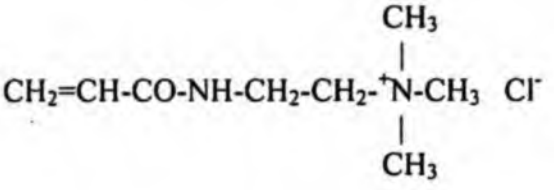
$$G_r = G/G_l \tag{6.4}$$

was also determined.

6.2 Networks Preparation

6.2.1 Preparation of PIPAAm and PIPMAm

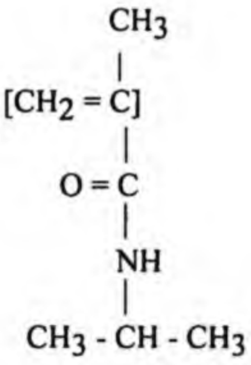
Poly(N-isopropylmethacrylamide) networks: Non-ionic monomer, N-isopropylmethacrylamide (IPMAm, Fluka) and a crosslinker (CR), N,N–methylenebisacrylamide (MBAAm, Fluka), were used as received. While for a negatively charged networks ionic comonomer - sodium methacrylate (MNa) was used, for positively charged networks quaternary salt, N–(2-acrylamidoethyl)–N,N,N–trimethylammonium chloride (QS):



$$\mathrm{CH_2{=}CH\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{{}^{+}N}}\text{-}CH_3\quad Cl^-}$$

was used. Negatively and positively charged PIPMAm networks, copolymers of IPMAm with various amounts of MNa or QS (mole fraction of sodium methacrylate x_{MNa} = 0 – 0.1 and mole fraction of quaternary salt x_{QS} = 0 – 0.075) and constant mole fraction of crosslinker (x_{CR} = 0.04) were prepared; 4,4'-azobis(4-cyanopentanoic acid) was used as initiator (mole fraction x_{I} = 0.003).

Polymerization was performed in glass ampoules, 10 mm in diameter (D^*), in ethanol/water (8/0.5 by vol.) mixture for 24 h at 70°C; the total volume fraction of all monomers in mixtures was v_m = 0.15.



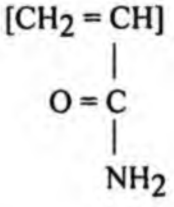
$[CH_2=C(CH_3)]-C(=O)-NH-CH(CH_3)-CH_3$

N-isopropylmethacrylamide (IPMAm)

Poly(N-isopropylacrylamide) networks: As in previous case non-ionic monomer, *N*-isopropylacrylamide (IPAAm, Fluka) and a MBAAm crosslinker, were used as received. The same ionic comonomers - MNa and QS were used for preparation of charged PIPAAm networks. Negatively and positively charged PIPAAm networks, copolymers of IPAAm with MNa and QS ($x_{MNa} = 0 - 0.1$ and $x_{QS} = 0 - 0.075$) and constant mole fraction of MBAAm ($x_{CR} = 0.006$), were prepared by radiation polymerization in water (dose $\gamma = 2$ kGy at room temperature). The total volume fraction of all monomers in mixtures was $v_m = 0.10$.

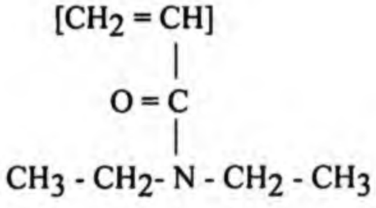
6.2.2 Preparation of random copolymers of P(AAm/DEAAm)

Materials: Commercial acrylamide (AAm, Fluka) and diethylacrylamide (DEAAm) were used:



$[CH_2=CH]-C(=O)-NH_2$

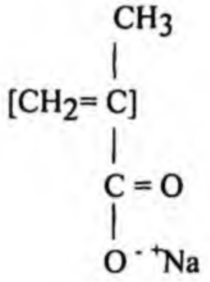
N,N'-acrylamide (AAm)



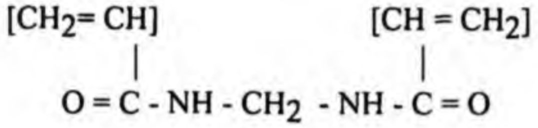
$[CH_2=CH]-C(=O)-N(CH_2-CH_3)-CH_2-CH_3$

N,N'-diethylacrylamide (DEAAm)

As negatively charged comonomer-sodium methacrylate (MNa) and a crosslinker-N,N'-methylenbisacrylamide (MBAAm) were used:



$$[CH_2{=}C(CH_3)]-C{=}O-O^{-}\,{}^{+}Na$$



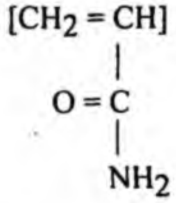
$$[CH_2{=}CH]-C({=}O)-NH-CH_2-NH-C({=}O)-[CH{=}CH_2]$$

sodium methacrylate (MNa) N,N'-methylenbisacrylamide (MBAAm)

Preparation of networks: Non-ionic monomer, N, N'-acrylamide (AAm) and N,N'-diethylacrylamide (DEAAm) and sodium methacrylate (MNa) were used for preparation of ionized networks of copolymers of P(AAm/DEAAm) with various mole fractions of AAm/DEAAm = 1/0, 0.75/0.25, 0.5/0.5, 0.30/70, 0.15/0.85, 0/1 and with various amounts of MNa (x_{MNa} = 0.0, 0.025, 0.05) Table.7.2. Networks were formed in presence of the crosslinker-N,N'-methylenbisacrylamide (MBAAm) (x_{MBAAm} = 0.003); as an initiator redox system was used (N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium persulfate). Crosslinking polymerisation of water/monomers mixtures was performed in glass ampoules (10 mm in diameter (D^*)) at room temperature for 24 h; the volume fraction of all monomers in mixtures was $v_m = 0.1$. After copolymerisation, the networks were removed from ampoules, cut into cylinders ~10 mm in height and extracted with redistilled water.

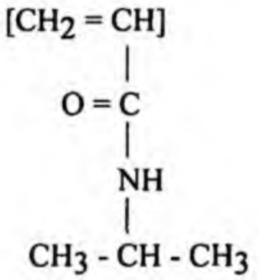
6.2.3 Preparation of interpenetrating networks of PAAm/PIPAAm

Materials: Commercial acrylamide (AAm, Fluka) and isopropylacrylamide (IPAAm) were used:



$$[CH_2{=}CH]-C({=}O)-NH_2$$

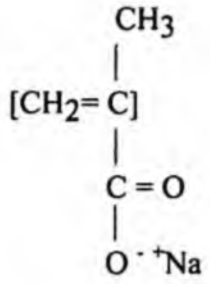
N,N'-acrylamide (AAm)



$$[CH_2{=}CH]-C({=}O)-NH-CH(CH_3)_2$$

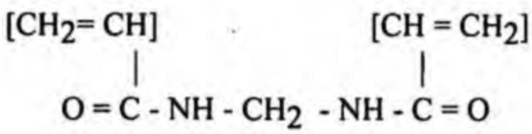
N,N'- isopropylacrylamide (IPAAm)

As negatively charged comonomer-sodium methacrylate (MNa) and a crosslinker-N,N'-methylenbisacrylamide (MBAAm) were used



$$[CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}]\underset{\underset{\displaystyle O^{-}\,{}^{+}Na}{|}}{\underset{C=O}{|}}$$

sodium methacrylate (MNa)



$$O{=}\overset{\overset{[CH_2=CH]}{|}}{C}-NH-CH_2-NH-\overset{\overset{[CH=CH_2]}{|}}{C}{=}O$$

N,N'-methylenbisacrylamide (MBAAm)

Preparation of IPNs: Non-ionic monomer, N,N'-acrylamide (AAm) and N,N'-isopropylacrylamide (IPAAm) and sodium methacrylate (MNa) as ionic comonomer were used for preparation of charged interpenetrating networks of PAAm/PIPAAm with various mole fractions of AAm/IPAAm = 1/0, 0.75/0.25, 0.5/0.5, 0.25/0.75, 0/1 and with various amounts of MNa (x_{MNa} = 0.0, 0.03, 0.05, 0.1) Table 7.3. IPNs were formed sequentional preparation method in presence of the crosslinker-N,N'-methylenbisacrylamide (MBAAm) (x_{MBAAm}). First, PAAm networks were prepared by crosslinking polymerization of water/AAm monomer/ionic MNa comonomer /MBAAm crosslinker mixtures in glass ampoules (10 mm in diameter) at room temperature for 24 h. For neat PAAm and PIPAAm networks and mole fractions AAm/IPAAm = 0.5/0.5 and 0.25/0.75, 5 g of AAm monomer and x_{MBAAm} = 0.01 was used in 100 ml solution. For 75/25 ratio 10 g AAm and amount of crosslinker MBAAm was 0.005. As an initiator redox system - (N,N,N',N'-tetramethyl ethylenediamine (TEMED) together with ammonium persulfate was used; the volume fraction of all monomers in mixtures was v_m = 0.1 (for 0.75/0.25) and v_m = 0.05 (for 1/0, 0.5/0.5 and 0.25/0.75). After polymerization, PAAm networks were removed from ampoules, and put into glass cylinders where they were left for swelling in water mixture of IPAAm with v_m = 0.05, 0.1, 0.2 with various mole fractions of MNa (x_{MNa} = 0.0, 0.03, 0.05, 0.1); The concentrations of IPAAm in water was chosen in such a way that overall ratios of AAm/IPAAm monomers in IPNs networks were 0.75/.25, 0.5/0.5, 0.25/0.75. Swelling proceeded for two months; to water mixture also the -crosslinker-N,N'-methylenbisacrylamide (MBAAm) (for ratio 0.75/0.25, 0.5/0.5 and 0.25/0.75 the values of x_{MBAAm} = 0.022, 0.01 and 0.002 were used). For crosslinking of the second, the PIPAAm network, the radiation polymerization (overall dose of γ irradiation was 2 kGy at room temperature) was used; after crosslinking the ionized interpenetrating networks of PAAm/PIPAAm were made (Table 7.3).

7. Results and Discussion

7.1 Swelling and Mechanical Behavior of Charged Poly(N-isopropylmethacrylamide) and Poly(N-isopropylacrylamide) Networks in Water/Ethanol Mixtures. Cononsolvency Effect.

7.1.1 Effect of network formation conditions on the network structure:

Both, PIPAAm and PIPMAm polymers with amphiphilic structure exhibit LCST in water (LCST~30 °C for PIPAAm and ~40 °C for PIPMAm (131)). Due to that the synthesis of PIPMAm networks was carried out in ethanol/water mixture (8/0.5 by vol.) at low initial volume fractions of monomers, $v_m = 0.15$. As follows from Table 7.1, the initial modulus of PIPMAm gels after preparation, G_I, at constant amount of crosslinker, MBAAm, slightly decreases with increasing amount of charged comonomers regardless of the sign of the charge. On the other hand, the values of G_I negatively charged gels are more than two times larger than those of positively charged ones. This finding means that efficiency of crosslinking reaction is lower for ammonium salt than sodium methacrylate comonomer. No such effect was observed for PIPAAm gels (prepared by radiation crosslinking polymerisation in water in presence of a constant amount of MBAAm) for which G_I values are virtually constant for both series (Table 7.1). In this case the efficiency of radiation crosslinking in PIPAAm gels is roughly independent of amount and structure of ionic comonomer. In such a way the decrease in the efficiency of crosslinking found for salt is probably connected with specific interactions of α-methyl group of IPMAm and long side chain of quaternary salt.

7.1.2 Swelling and mechanical behavior

As can be seen from *Figs 7.1a* and *7.1b* all uncharged and negatively charged PIPAAm and PIPMAm gels exhibit the "reentrant" swelling behavior in the water/ethanol (w/eth) mixtures; after abrupt deswelling, swelling minimum and reswelling with increase of ethanol content in mixture is observed. Ethanol can interacts with polymer through the polar and unpolar groups, while water lacks the nonpolar group. A drastic shrinkage of gels is caused dehydration of chains due to competition of hydrophobic hydration between alcohol and polymer. The steepness of transition is indicative of cooperative effects; once alcohol molecules destroy a part of hydration shell, the damage quickly propagates through entire hydration structure and dehydrated chains associate to form a collapsed structure. In this state, ethanol molecules are adsorbed on collapsed structure. On further increase of ethanol content, the solvent power of the mixture overcomes polymer cohesion and gels begin to swell again.

Table 7.1. Composition, mechanical, and swelling parameters of hydrogels

x_S	G_I g cm^{-2}	$\nu_d \times 10^{-5}$ mol cm^{-3}	Q_w	Q_{min}	$c_{eth.\,min}$	ϕ
poly(N-isopropylacrylamide)						
0	54.3	2.34	17.0	1.50	30	-
0.025^a	61.5	2.65	28.8	1.9	33	0.29
0.050^a	65.7	2.83	85.1	2.6	38	0.23
0.075^a	63.2	2.72	112.0	11.3	60	0.18
0.100^a	67.4	2.90	123.0	14.8	60	0.15
0.025^b	60.8	2.62	95.5	-	-	0.46
0.050^b	53.0	2.28	154.9	-	-	0.28
0.075^b	62.2	2.68	199.5	-	-	0.25
poly(N-isopropylmethacrylamide)						
0	146.7	4.38	13.2	2.6	36	-
0.025^a	145.3	4.34	21.8	2.6	36	0.47
0.050^a	134.4	4.01	37.5	3.9	37	0.46
0.075^a	124.6	3.72	41.8	5.8	40	0.28
0.100^a	120.2	3.59	50.1	7.7	44	0.13
0.025^b	57.4	1.71	75.9	-	-	0.29
0.050^b	47.2	1.41	128.8	-	-	0.18
0.075^b	40.0	1.19	148.9	-	-	0.11

$^a x_S = x_{MNa}$; $^b x_S = x_{QS}$

For uncharged PIPAAm and PIPMAm networks the swelling minima are observed at $c_{eth.m}$~33 vol.% of ethanol (Table 7.1). It is important to mention that the swelling minima roughly coincide with maximum of the mixing enthalpy, ΔH, of w/eth mixtures (c_{eth}=35 vol.%, ΔH=-180 cal/mol, ref. (132)); this $c_{eth,m}$ value corresponds also to the maximum of w/eth interactions. From *Figs 7.1a* and *7.1b*, it further follows that the swelling degree Q of PIPAAm and PIPMAm gels in water and ethanol are roughly the same, which means that swelling power of both neat solvents is similar.

The swelling degree in water Q_w increases with increasing content of charged groups on chains for all four networks series (*Figs 7.1a* and *7.1b*, Table 7.1); generally higher swelling values are observed for more hydrophilic PIPAAm than for PIPMAm gels and for positively charged gels in comparison with those negatively charged ones. Pronounced swelling minima in dependence on w/eth compositions are observed for gels with negative charge; with increasing ionic comonomer content the ethanol concentration in the minimum, $c_{eth,m}$ as well as degree of swelling in the minimum, Q_m, increase (Table 7.1). The shift of minimum to higher ethanol content indicates that charges stabilize the hydrogen bonding between water molecules and chains segments and make alcohol molecules to destroy the hydration shell more difficult. Increasing Q_m values with MNa content mean that amount of mixed solvent in collapsed structures increases with increasing ionisation. Generally, higher changes in $c_{eth,m}$ and Q_m with x_{MNa} are observed for more polar PIPAAm gels in comparison with PIPMAm ones. For charged gels of both network series water is better solvent than neat ethanol.

From *Figs 7.1a* and *7.1b* also follows that at low ethanol concentrations second, less pronounced, swelling minimum exists on w/eth composition for negatively charged gels of both series; the increase in ethanol concentration and swelling degree in the minimum with charge content can be seen as in previous case of the main minimum. As larger changes in Q values are observed for less polar PIPMAm gels (with α-methyl group), we believe that this minimum is connected with interactions of alkyl groups of ethanol with nonpolar groups of polymer main chain.

Unexpected swelling results were found for positively charged gels of both network series (*Figs 7.1a* and *7.1b*). In this case roughly no minima on Q vs. w/a dependences were found. This means that 2.5 mol% of quaternary ammonium salt is sufficient for stabilization of hydration of polymer chains. We believe that this behavior is caused by the presence of alkyl groups in side chain of ammonium salt. In such a case the structure of ionic comonomer plays an important role in cononsolvency behavior of charged gels in mixed solvents.

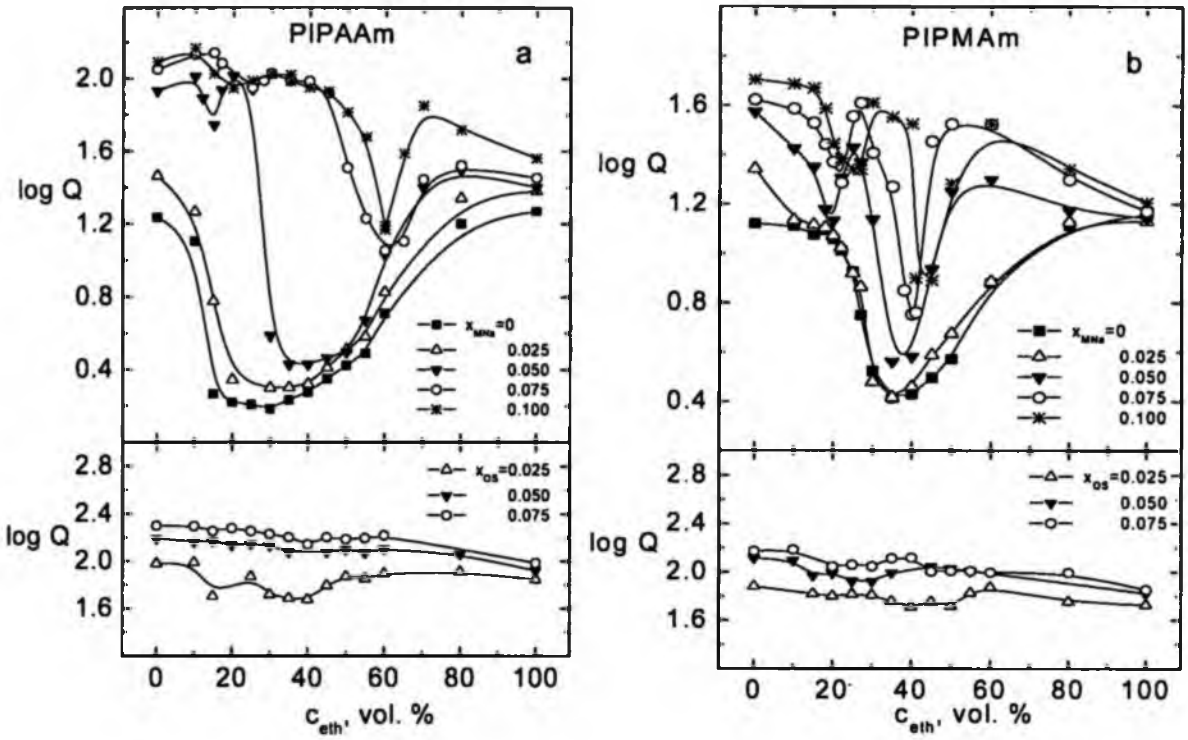


Fig. 7.1. Dependence of the swelling ratio Q on ethanol concentration c_{eth} in water/ethanol mixtures for PIPAAm (a) and PIPMAm (b) gels with different content of ionic comonomers

An example of the measured dependences of the reduced modulus, $G_r = G/G_l$ (Eq. (6.4)) on ethanol concentration in w/eth mixtures are shown in *Fig. 7.2* for PIPAAm gels. As expected, minima found in Q vs. c_{eth} dependences (*Fig. 7.1a*) for uncharged and negatively charged gels are reflected in maxims in dependences of G_r vs. c_{eth}. For positively charged PIPAAm gels G_r values roughly independent of c_{eth} were observed. The dependences of the *log* G_r on *log* Q of PIPAAm gels are plotted in *Fig. 7.3*. For comparison, the predicted rubber elasticity slope (17) for the dependence of *log* G_r vs. *log* Q, $s = -0.33$, is also shown. In the range of high swelling (*log* $Q > 2$), the increase in modulus G_r from expected dependence with increasing swelling can be seen for all gels; this increase is probably due to the finite extensibility of the chains. Departures from the straight line in the region of low swelling (*log* $Q < 0.3$) are probably due to the influence of the main transition region (vitrification) at low swelling degrees (11). The value of s = 0.33 independent of charge concentration was found (52) for poly(1-vinyl-2-pyrrolidone)

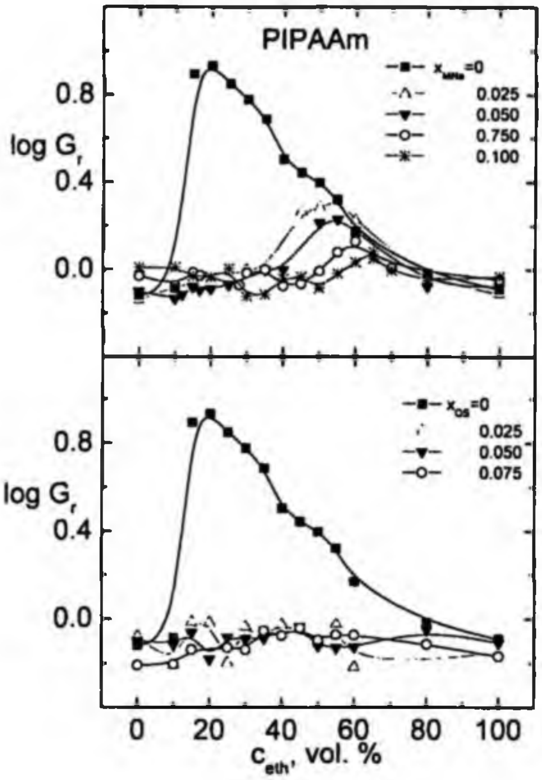


Fig. 7.2. *Dependence of the reduced modulus G_r on the ethanol concentration c_{eth} in w/eth mixtures for PIPAAm gels*

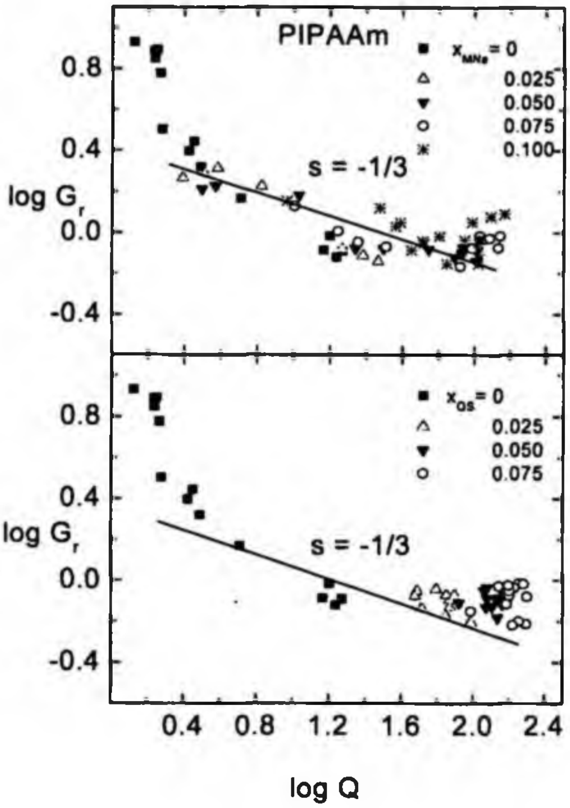


Fig. 7.3. *Dependence of the reduced modulus G_r on the swelling degree Q for PIPAAm gels*

networks. On the other hand, a high value of s = 0.7 independent of charge concentration, was found (9) for charged polyacrylamide (PAAm) networks in water/acetone mixtures. The swelling dependence of the modulus with the slope s = 5/6 was recently suggested by the theory of Rubinstein et al. (133) based on the scaling concept of the polyelectrolyte chain. Qualitatively similar results were obtained also for PIPMAm gels. Universal correlation between *log G_r* and *log Q* means that mechanical behavior is predominantly determined by the degree of swelling regardless of charge concentration and its polarity for both network systems.

7.1.3. Comparison of the theory of swelling equilibrium and experiment

For comparison of experimental swelling data with theoretical prediction, we apply the theory discussed above (paragraphs 3 and 4) based on single liquid approximation and we will have use Eqs (3.38), (4.6) and (4.7). In the theory the swelling pressure P is given as a sum of four terms (see Eq. (3.38)): the mixing term P_m - given by mixing of solvent with chain segments (Flory-Huggins equation with interaction parameter χ), the elastic term P_{el} - given by the change in elastic energy with swelling in which the finite chain extensibility was included, the osmotic term P_{os} - given by mixing of network ions with the solvent and the electrostatic term P_{els} - determined by the interactions (repulsion) of charges on the chain. For uncharged gel, only two first terms in Eq. (3.38) remain as the degree of ionization $\alpha = x_{MNa} = x_{QS} = 0$ i.e., $P_{os} = P_{els} = 0$. From the knowledge of network parameters (crosslinking density ν_d, density of dry network ρ, volume fraction of polymer at network formation v_l, molecular weight of monomer units M_{IPAAm} or M_{IPMAm}, permittivity of mixed solvent D and molar volume of mixed solvent w/eth V_1 - determined independently), and using Eq. (3.38), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, v_2, could be calculated from experimental $v_2 = 1/Q$ values of the uncharged networks measured in w/eth mixtures (*Fig. 7.4*). As swelling data were collected for free swelling, $P = 0$ in Eq. (3.38) was used at calculations. In such way, the values of $\chi = 0.497$ and 0.515 were found for PIPAAm and PIPMAm gels in water. As expected, with increasing v_2 (increasing ethanol concentration), χ values of uncharged networks first increase (deswelling region) and after that they decrease (reswelling region). It is interesting to note that χ values determined from all w/eth mixtures lay on the same χ on v_2 dependence for both PIPAAm and PIPMAm gels, regardless of cononsolvency effect (*Fig. 7.4*).

As can be seen from Table 7.1, the swelling degree in water at room temperature, Q_w, increases with charge concentrations; the Q_w values are always higher for ammonium salt in comparison with MNa. As we know all network parameters (ν_d, ρ, v_l, M, D and V_1), and if we further assume that the degree of ionization $\alpha = x_S$ ($x_S = x_{MNa}$ or $x_S = x_{QS}$), we could use full Eq. (3.38) for the description of dependence of Q_w on x_S. We have obtained unrealistic high χ values (ranging from 0.6 to 10). As it was introduced into the used theory (11) (6) χ is a measure of polymer–solvent interactions when all charges are screened. It is therefore reasonable to require the same value of $\chi = 0.497$ for all PIPAAm and $\chi = 0.515$ for all PIPMAm charged networks in water. This requirement is possible to fulfill by the assumption that the effective degree of ionization α^* is lower than the sodium or ammonium salt concentration i.e., $\alpha^* = \phi\alpha = \phi x_S$, where ϕ is the correction factor; in such a way the values ϕ in the range ~ 0.47–0.11 were found (Table 7.1). Due to higher Q_w values found for gels with ammonium salt, their ϕ vales are always higher than those of gels with MNa. The ϕ factor is related to the osmotic coefficient of counter-ions and to the clustering of counter-ions due to possible heterogeneity of highly dilute networks and accounts for the effects, which were not

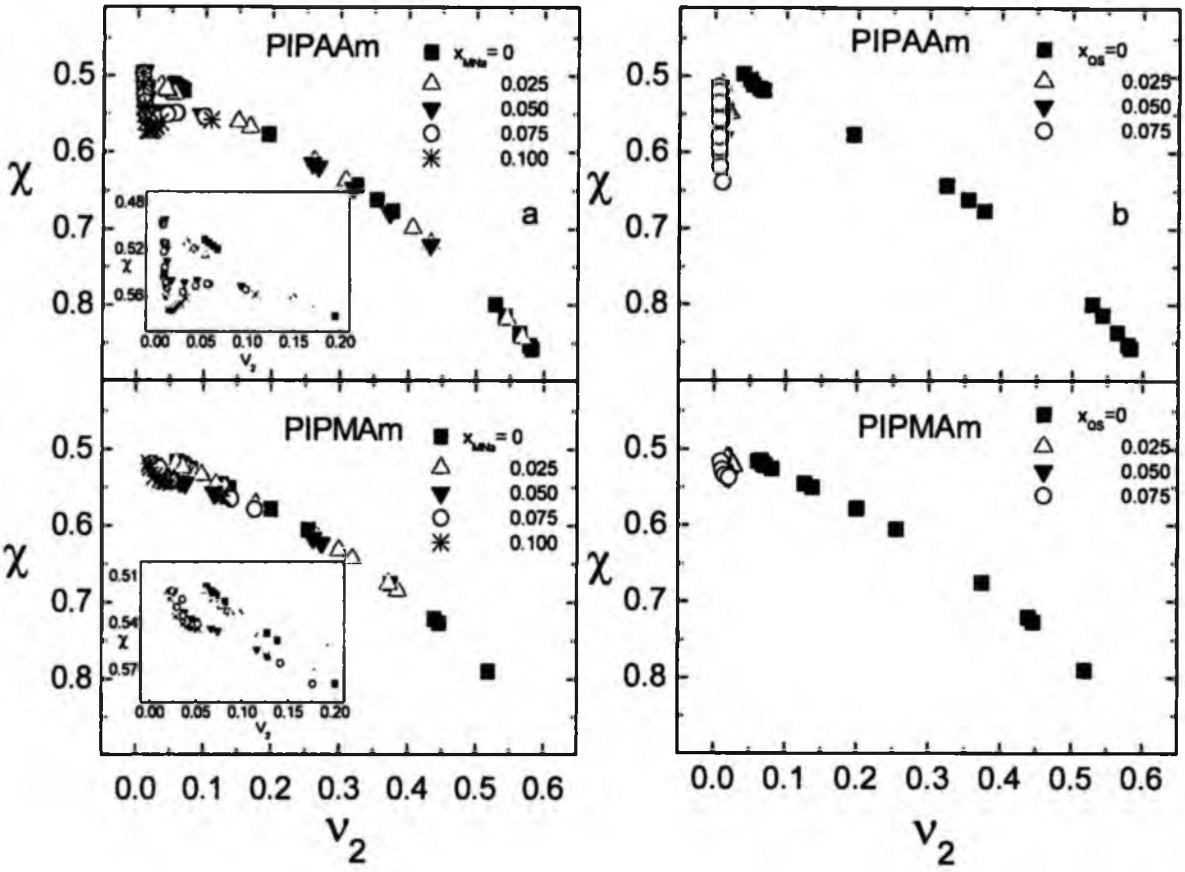


Fig. 7.4. Dependence of interaction parameter, χ, on volume fraction of dry network in the swollen state, v_2, measured in water/acetone mixtures with indicated ionic comonomers (a) negatively charged gels and (b) positively charged gels

considered in the used theory. Similar ϕ values were found earlier (11) for charged poly(*N,N*-diethylacrylamide) hydrogels with sodium methacrylate (MNa) (ϕ = 0.56–0.28 for x_{MNa} = 0.005–0.07).

Using known molecular parameters and the effective degree of ionization $\alpha^* = \phi x_S$, the dependences of χ on v_2 were calculated from Q values measured at various w/eth compositions (*Fig. 7.1*) for all ionized networks (*Fig. 7.4*). As follows from *Fig. 7.4a* for negatively charged PIPAAm and PIPMAm gels universal χ vs. v_2 dependences, independent of charge concentration, were found in region of lower swelling (v_2>0.1). Such universal dependences were observed earlier for variously charged gels of different systems (11). As follows from the insets in *Fig. 7.4a*, in the region of high swelling (v_2< 0.1), χ vs. v_2 dependences depend on amount of charges; such results were not earlier observed. Also for positively charged networks χ vs v_2 dependences are different from those of uncharged ones (*Fig. 7.4b*). Both two latest facts mean that Eq. (3.38) gives only qualitative description of the swelling results. It is worthwhile to mention that a van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump-change in the gel volume (1st-order phase transition (43) (11)); the critical value of the interaction parameter χ_c and compositions of the coexisting phases are determined by Eq. (4.7). Only negatively charged PIPAAm gels with $x_S \geq 0.075$ show the tendency to exhibit such type behavior (*Fig. 7.4a*).

7.2 Swelling and Mechanical Behavior of Ionized Poly(N,N'-acrylamide-co-N,N'-diethylacrylamide) Gels in Water/Acetone Mixtures and in Water at Various Temperatures

7.2.1 Effect of network formation conditions on the network structure

As follows from Table 7.2 at roughly constant network formation conditions (amount of water and crosslinker) the equilibrium modulus G_l after network formation is in the first approximation independent of the copolymer composition and of the charge concentration. From that it follows that also crosslinking density v_d related to dry gel volume is constant; at calculation of v_d the differences in dry densities of PAAm and PDEAAm were taken into account. As expected, with increasing amount of charges on the chain, x_{MNa}, swelling degree at room temperature Q_w increases for all three network series. On the other hand increasing amount of DEAAm in copolymers decreases the swelling degree; this fact means that amphiphilic DEAAm, due to two ethyl groups attached to nitrogen, is more hydrophobic than AAm.

7.2.2. Swelling and Mechanical Behavior in Water/Acetone Mixtures at Room Temperature

A continuous or jump-wise change in the volume of the gel (in the degree of swelling Q) with increasing volume fraction of acetone, c_a, in the w/a mixtures can be seen in

Fig.7.5. Incorporation of more hydrophobic DEAAm component into networks results in shifting of the transition region from expanded (low c_a values) to collapsed (high c_a values) state to higher acetone concentrations in all three series. While for uncharged networks acetone interval lies in the range from ~40 to 95 vol. %, for charged

Table 7.2 Composition, mechanical and swelling parameters of poly(N-acrylamide-co-N-diethylacrylamide)P(AAm/DEAAm) hydrogels

AAm/ DEAAm	x_{MNa}	G_l g cm^{-2}	$\nu_d.10^5$ mol cm^{-3}	Q_{w}- 25°C	χ	Φ
1.00/0.00	0	98	5.23	20.7	0.492	–
0.75/0.25	0	111	5.59	19.3	0.498	–
0.50/0.50	0	108	5.12	17.5	0.500	–
0.30/0.70	0	96	4.33	16.2	0.510	–
0.15/0.85	0	93	4.04	14.4	0.507	–
0.00/1.00	0	97	4.06	12.6	0.512	–
1.00/0.00	0.025	98	5.23	70.1	–	0.36
0.75/0.25	0.025	108	5.44	51.1	–	0.31
0.50/0.50	0.025	112	5.31	41.3	–	0.20
0.30/0.70	0.025	111	5.00	34.1	–	0.21
0.15/0.85	0.025	104	4.52	33.3	–	0.15
0.00/1.00	0.025	103	4.32	31.2	–	0.13
1.00/0.00	0.05	101	5.39	111.9	–	0.28
0.75/0.25	0.05	114	5.75	100.5	–	0.25
0.50/0.50	0.05	118	5.60	80.3	–	0.21
0.30/0.70	0.05	111	5.00	79.7	–	0.18
0.15/0.85	0.05	105	4.57	66.2	–	0.15
0.00/1.00	0.05	118	4.94	61.6	–	0.14

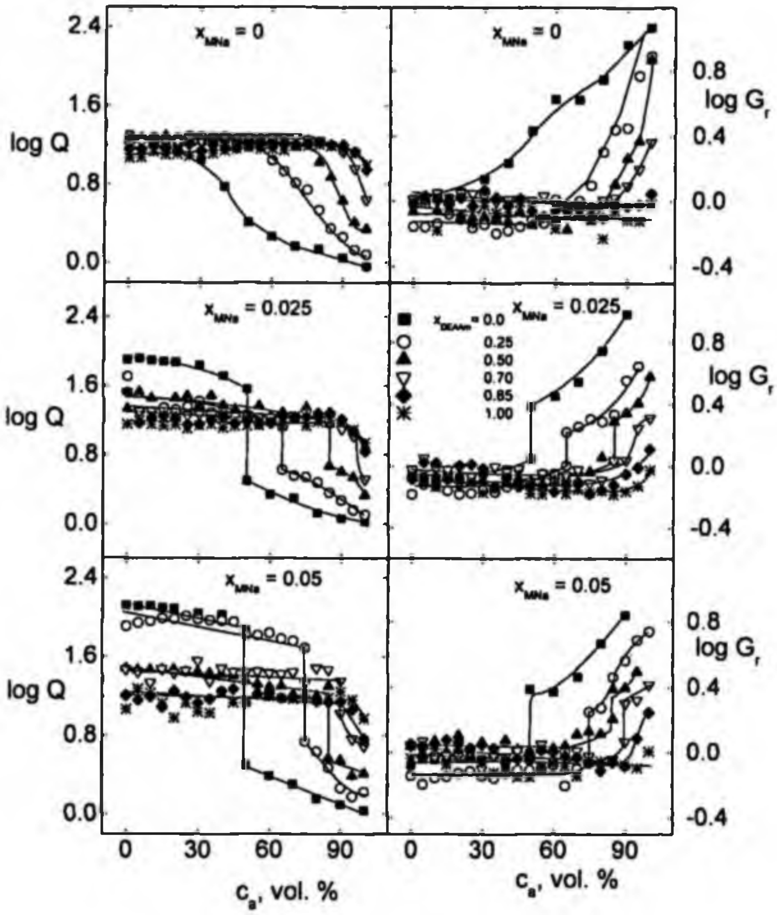


Fig.7.5 Dependence of the swelling degree, log Q, and reduce modulus log G_r on acetone conncentrations c_a, for gels with indicated mole fractions of DEAAm, x_{DEAAm} and for indicated mole ratios of sodium methacrylate, x_{MNa}

copolymers this interval is in range from ~50 to 95 vol. %. This indicates that with increasing DEAAm content in networks the extent of hydrogen bonding decreases, as chains are more hydrophobic and acetone becomes better solvent for gels.

As follows from *Fig. 7.5* the jump-wise change in Q in dependence on c_a takes place in most networks with $x_{MNa} \geq 0.025$; for two highest DEAAm contents only small decrease in Q at c_a~95-100 vol. % is observed. *Fig. 7.6* shows that the critical acetone concentrations, at which transition appeared, a_c, only slightly depend on the charge concentration and increase with DEAAm content; for uncharged networks the a_c values were determined as acetone concentrations where slope $d(\log Q)/dc_a$ has a maximum.

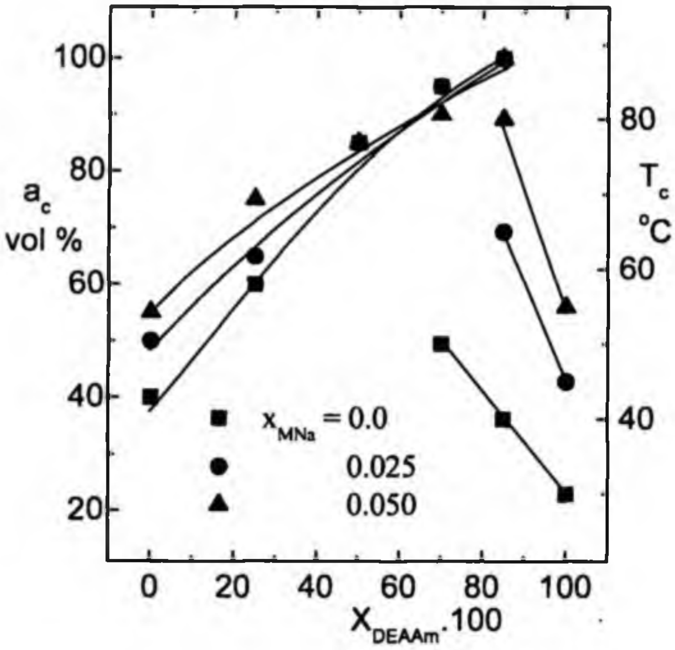


Fig. 7.6 Dependence of the critical acetone concentrations, c_c, and transition temperature T_c, at which transition from expanded to collapsed state appeared on composition of copolymers

The dependences of the reduced modulus, $G_r = G/G_l$ (Eq. (6.4)) on c_a in w/a mixtures are also shown in *Fig. 7.7.* As expected, a jump in the volume of the gel is reflected also in a jump-wise change in the reduced modulus. For copolymers with $x_{MNa} = 0$ continuous dependences of Q on c_a are accompanied by continuous dependences of modulus G_r on c_a. The dependences of *log* G_r on *log* Q of all three series copolymers measured in w/a mixture are plotted in *Fig. 7.7.* For comparison, the predicted rubber elasticity slope (15) for the dependence of *log* G_r vs *log* Q, $s = - 0.33$, is also shown. Departures from the straight line in the region of low swelling (*log* $Q < 0.2$) are probably due to the influence of the main transition region (vitrification) at high acetone concentrations. (135). Swelling dependence of the modulus with the slope $s = - 5/6$ was suggested by the theory of Rubinstein et. al (133) based on the scaling concept of the polyelectrolyte chain.

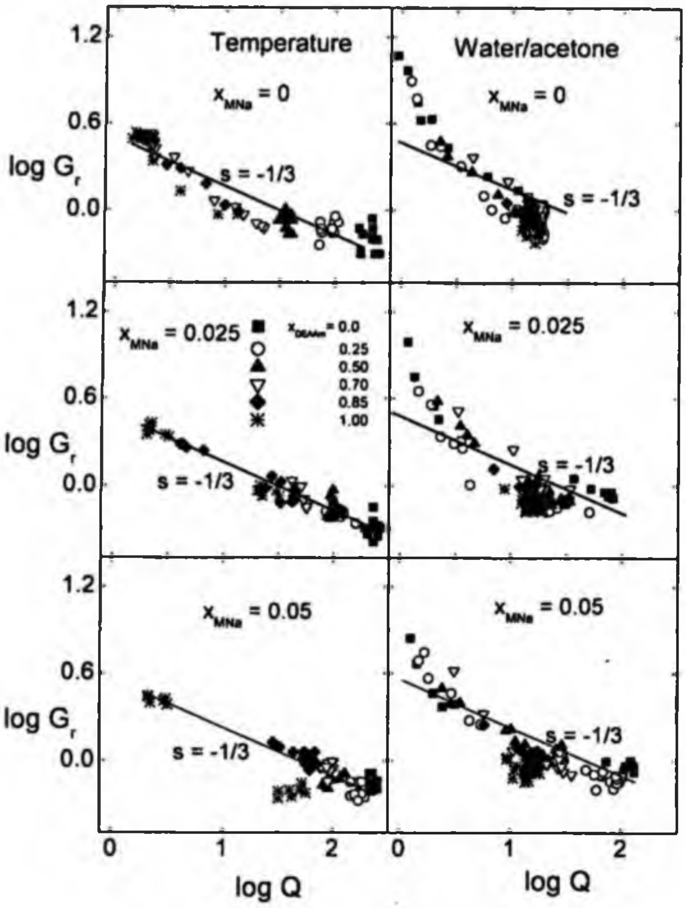


Fig. 7.7 Dependence of reduce shear modulus log G_r on log Q for variously ionized gels with different fractions of DEAAm in copolymers measured in w/a mixtures and in water

7.2.3 Swelling and mechanical behavior in water at various temperatures

The dependences of swelling ratio in water, *Q*, and reduce modulus G_r, on temperature, *T*, are shown in *Fig. 7.8*. A continuous change in *Q* from the expanded (low temperatures) to collapsed (high temperatures) state with increasing temperature can be seen for three uncharged networks with the highest contents of DEAAm (x_{DEAAm} = 1, 0.85 and 0.70). On the other hand only two charged networks with x_{DEAAm} = 1 and 0.85 exhibit the jumpwise change in volume at temperature T_c. The copolymers with higher content of AAm exhibit *Q* values independent of *T*. Incorporation of AAm, the more hydrophilic component, into copolymers results in pronounced shift of T_c to higher temperatures in all three series (*Fig. 7.6*); for uncharged networks the T_c values were determined as a temperatures where slope *d(log Q)/dT* has a maximum.

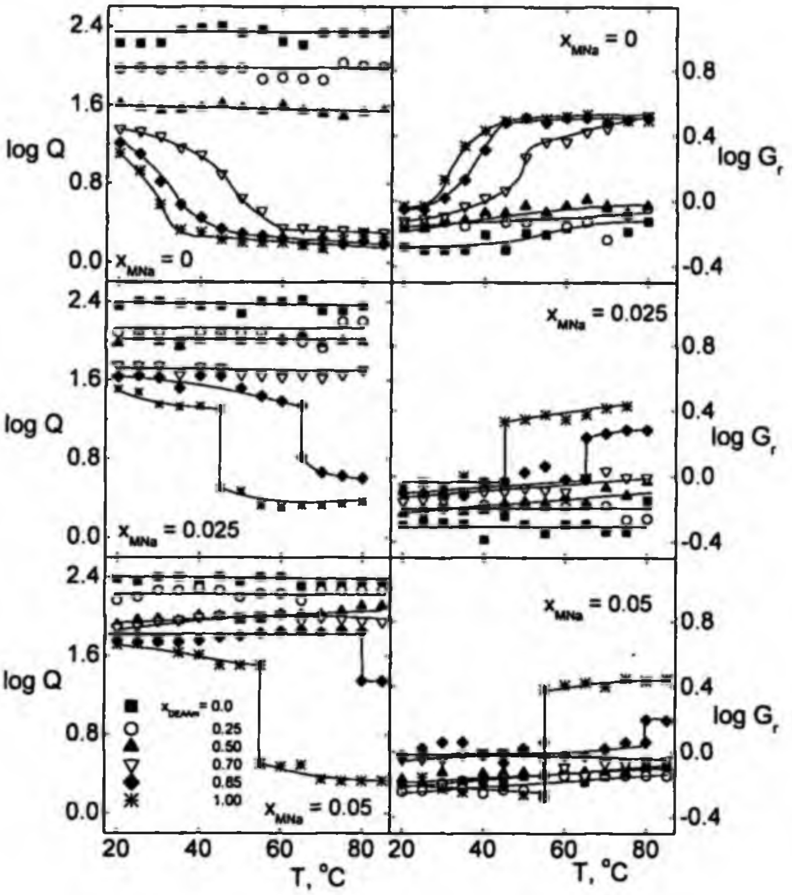


Fig.7.8 Dependence of the swelling degree, log Q, and reduce modulus log G_r *on temperature, T for gels with indicated mole fractions of DEAAm,* x_{DEAAm} *and for indicated mole ratios of sodium methacrylate,* x_{MNa}

From *Fig. 7.8* it can be seen that the both, increasing AAm and x_{MNa} values shift the transition to higher temperatures very efficiently (more than 20°C). This indicates that with increasing AAm as well as charge content in networks, the extent of hydrogen bonding increases and water becomes a better solvent for gels. These results can be helpful in practical applications of hydrogels as they show the possibility of adjusting T_c by composition of copolymer to the required values.

The dependences of the reduced shear modulus, $G_r = G/G_l$ (Eq. 6.4) on temperature are also shown in *Fig. 7.8*. As expected, a decrease in the volume of the gel is reflected in an increase of the G_r and continuous or jumpwise dependences of G_r on T are observed for network with continuous or jumpwise dependences of Q on T. The dependences of the *log* G_r on *log Q* for three series of copolymers with x_{MNa} are plotted in *Fig. 7.7*. As in previous case, the predicted rubber elasticity slope (15) for the dependence of *log* G_r vs *log Q*, $s = -0.33$, is also shown; one can see that theory describes quite well experimental data for all network. For hydrogels measured in water at various temperatures no vitrification effect is seen in *Fig. 7.7* at low swelling ($\log Q < 0.2$) as in the case in w/a mixtures; we believe that high temperatures compensate low swelling so that all copolymers are deeply in the rubbery region. As good correlation exist between the Q and the G_r we can conclude that mechanical behavior of all hydrogels is predominantly determined by the swelling degree.

7.2.4 Comparison of Swelling Data with the Theory of Polyelectrolyte Networks

As in previous case for comparison of swelling results obtained on gels of random P(AAm/DEAAm) copolymer networks with theory, we will use our generalized model (Eqs (3.38) and (4.6)); in this model, all molecular parameters are independently accessible. The individual terms P_i of Eq. (3.38) are expressed in network molecular parameters - concentration of network chains ν_d (Table 7.2), density of dry networks ρ, an average molecular weight of monomer units in this case M ($= x_{AAm} \cdot M_{AAm} + x_{DEAAm} \cdot M_{DEAAm}$), molar volume of w/a mixtures V_1 (determined earlier (60)) or water ($V_1 = 18.1 \text{cm}^3/\text{mol}$), volume fraction of dry polymer at network formation v_i and the permittivity of mixed solvent w/a ($D = 80$ for water and 21 for acetone; for w/a mixtures the linear dependence of D on c_a was used). A low fractions of MNa were used and pH of external solvents were higher than pK_0 of methacrylic acid we assumed, in the first approximation, that the degree of ionization $\alpha = x_{MNa}$. Using Eq. (3.38), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, $v_2 = 1/Q$, can be calculated from experimental equilibrium Q values measured at w/a mixtures or various temperatures (as the data were collected for free swelling, $P = 0$ in Eq. 3.38) by employing the same procedure described earlier (see 7.1).

The application of Eq. (3.38) for the uncharged network series ($\alpha = x_{MNa} = 0$, $P_{os} = P_{els} = 0$, the classical Flory-Huggins equation is restored) and using the swelling degrees Q_w measured at room temperature (expanded state of gels, Table 7.2), leads to the values of interaction parameters χ shown in Table 7.2. As expected with increasing DEAAm content χ slightly increases due to an decrease in Q_w values; for all copolymers these values are higher than 0.5. The increase of χ means that increasing content of hydrophobic DEAAm in copolymers slightly decreases the overall hydration

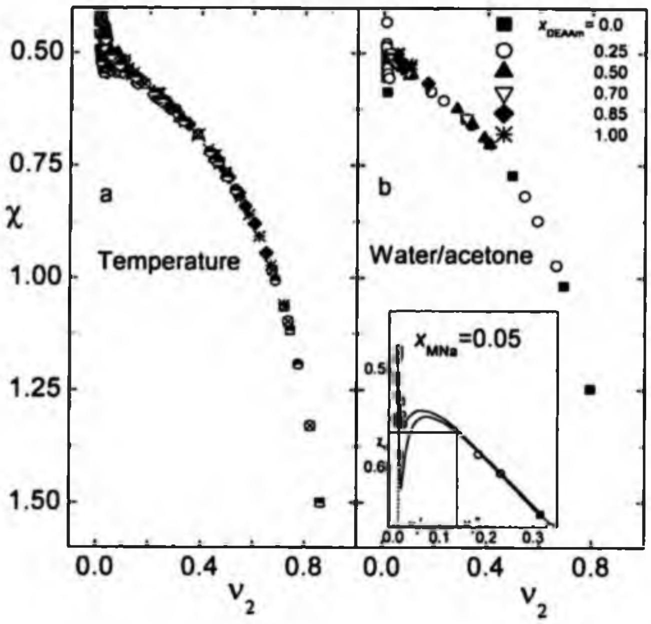


Fig 7.9 Dependence of the interaction parameter, χ, on volume fraction of dry network in the swollen state, υ_2, in water measured on heating (a) and w/a mixtures (b) for gels with indicated AAm/DEAAm mole fractions and various ionic comonomer concentrations

of P(AAm/DEAAm) chains in water. Finally, from Q_w data of uncharged networks measured at various w/a compositions and temperatures (*Fig. 7.9*), the universal increase of χ with increasing v_2 shown in *Fig. 7.9a*, independent of AAm content in hydrogels was obtained. Such universal dependences were observed earlier (11).

As expected, the swelling degree in water Q_w measured at room temperature increases with increasing content of charged groups on the chain x_{MNa} (Table 7.2). Similarly to previous cases (see 7.1), the use of Eq. (3.38) for ionic networks with the degree of ionization $\alpha = x_{\mathrm{MNa}} > 0$ gives unrealistically high χ values calculated from Q_w values (for networks of various compositions with x_{MNa} = 0.025, 0.05, the χ values in the region 0.55 – 0.85 were obtained). Since, as was already mentioned in the used theory, χ is a measure of polymer-water interactions when all charges are screened (the effect of charges is included in P_{os} and P_{els} terms), χ values shown in Table 7.2 for uncharged networks may be, in the first approximation, required also for corresponding ionic hydrogels swollen in water at room temperature. With this requirement, the Q_w data shown in Table 7.2 can be described by Eq. (3.38) assuming that the effective degree of ionization α^* is lower than the x_{MNa}, i.e., $\alpha^* = \alpha \cdot \Phi = \Phi x_{MNa}$, where Φ is the correction factor. This factor, as it was mentioned, is related to the activity coefficient of counter-ions, and to clustering of counter-ions due to possible heterogeneity of highly dilute networks. The Φ values thus calculated lie in the range 0.1-0.4 (Table 7.2) and are dependent on the content of charges and DEAAm in hydrogels (with increasing x_{MNa} and DEAAm the Φ values decrease). Higher Φ values were found earlier (137) for charged poly(N,N'-isopropylacrylamide) hydrogels with MNa ($\Phi = 0.67 - 0.20$ for $x_{MNa} = 0.01–0.10$).

Finally, using known molecular parameters and the effective degree of ionization $\alpha^* = \Phi x_{MNa}$, the dependence of χ on v_2 was calculated from Q values measured at various w/a mixtures and temperatures (*Figs 7.5* and *7.8*) for all copolymers (*Fig. 7.9a,b*). As was discussed previously (11), (43), the van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump in the gel volume (collapse). If the van der Waals loop in the dependence of χ on v_2 is experimentally found than the critical then
interaction parameter χ_c and compositions of coexisting phases (the values v_2' and v_2'') at the transition are given by Eq. (4.7).

In the inset of *Fig. 7.9b*, the van der Waals loops are shown for neat PAAm and copolymer (x_{DEAAm}-0.25) networks with $x_{MNa} = 0.05$ measured in w/a mixtures together with the application of Eq. (4.7) for neat PAAm network (Maxwell's construction is applied to the χ vs v_2 dependence, i.e., χ_c is determined by the requirement that the areas above and below the line are equal). In such way, the values χ_c and the extents of the collapse, $\Delta v_{2,t} = v_2'' - v_2'$ can be determined using Eq. (4.7). As the v_2 vs c_a dependences for nonionic networks are known, the dependences of χ vs. v_2 can be transformed to the dependences of χ vs c_a and the critical acetone compositions a_c can be determined from χ_c values.

The phase state of our P(AAm/DEAAm) copolymer gels in water and w/a mixtures is determined by interactions of polar and non-polar groups on the chain with water and/or acetone molecules. As the $\chi = 0.490$ and $\chi = 0.510$ was found for the PAAm and PDEAAm uncharged networks in water (Table 7.2) means that increasing amount of ethyl side groups in copolymers decreases the overall hydration of the P(AAm/DEAAm) chains. In PDEAAm networks swollen in water the SAXS measurements have revealed (138) that network chains adopt more or less dense conformations with hydrophobic micelle-like structure near LCST.

7.3. Swelling and Mechanical Behavior of Interpenetrating Networks of Poly(N-isopropylmethacrylamide) /Poly(acrylamide) in Water/Acetone Mixtures and in Water at Various Temperatures

7.3.1 Effect of network formation conditions on the network structure

As follows from Table 7.3 crosslinking density v_d related to dry gel decreases with increasing amount of PIPAAm component and is roughly independent of the charge concentration; at calculation of v_d the differences in dry densities of PAAm and PIPAAm were taken into account. As expected, with increasing amount of charges on the chain, x_{MNa}, equilibrium swelling degree at room temperature Q_w increases for all five network series. On the other hand increasing amount of PIPAAm component in IPNs decreases the swelling degree; this fact means that amphiphilic PIPAAm component, due to presence of isopropyl group attached to nitrogen, is more hydrophobic than PAAm one. The χ parameter of uncharged IPNs changes in expected range from 0.465 to 0.509 and correction factor Φ strongly decreases with increasing ionization of neat IPNs component, similarly to the results shown in Table 7.1.

Table 7.3 Composition, mechanical and swelling parameters of IPNs of PAAm/PIPAAm hydrogels

PAAm/PIPAA mole/mole	x_{MNa}	G_l g cm^{-2}	10^{-5} v_d mol cm^{-3}	Q_w. 23°C	χ	Φ
1/0	0	73.0	3.97	109	0.490	-
1/0	0.03	84.5	4.59	210	-	0.950
1/0	0.05	87.6	4.73	376	-	0.671
1/0	0.10	85.2	4.63	418	-	0.220
0/1	0	40.0	1.71	22	0.497	-
0/1	0.03	57.0	2.44	63	-	0.371
0/1	0.05	62.4	2.67	99	-	0.303
0/1	0.10	85.2	3.64	141	-	0.196
0.75/0.25	0-0	75.2	4.77	47	0.465	-
0.50/0.50	0-0	51.5	2.80	12	0.488	-
0.30/0.70	0-0	52.1	0.96	11	0.509	-
0.75/0.25	0-0.03	67.8	4.33	71	-	0.800
0.50/0.50	0-0.03	52.0	2.80	19	-	0.515
0.75/0.25	0-0.05	78.4	5.43	98	-	0.500
0.50/0.50	0-0.05	56.5	2.86	24		0.386
0.75/0.25	0-0.1	78.2	5.34	101	-	0.430
0.50/0.50	0-0.1	63.0	3.39	28	-	0.236
0.75/0.25	0.03-0	83.4	5.86	101	-	0.460
0.50/0.50	0.03-0	40.5	3.03	43.9	-	0.520
0.25/0.75	0.03-0	95.0	1.74	23	-	0.450
0.75/0.25	0.03-0.03	80.6	5.33	104	-	0.410

0.50/0.50	0.03-0.03	43.0	3.33	76	-	0.368
0.30/0.70	0.03-0.03	90.0	1.66	47	-	0.230
0.75/0.25	0.03-0.05	73.3	4.90	113	-	0.340
0.50/0.50	0.03-0.05	42.5	3.33	96	-	0.322
0.33/0.67	0.03-0.05	68.0	1.31	83	-	0.135
0.75/0.25	0.03-0.1	71.5	4.55	138	-	0.330
0.50/0.50	0.03-0.1	48.3	3.79	108	-	0.213
0.75/0.25	0.05-0	77.5	5.05	123	-	0.290
0.50/0.50	0.05-0	32.5	1.90	54	-	0.352
0.25/0.75	0.05-0	95.0	1.76	21	-	0.100
0.75/0.25	0.05-0.03	75.9	4.73	124	-	0.350
0.50/0.50	0.05-0.03	30.0	1.90	64	-	0.244
0.25/0.75	0.05-0.03	103	1.90	58	-	0.283
0.75/0.25	0.05-0.05	65.8	3.99	163	-	0.197
0.50/0.50	0.05-0.05	33.5	2.02	85	-	0.231
0.33/0.67	0.05-0.05	85.0	1.71	74	-	0.222
0.75/0.25	0.05-0.1	74.0	5.12	159	-	0.300
0.50/0.50	0.05-0.1	33.0	2.20	117	-	0.188
0.75/0.25	0.1-0	65.9	3.97	162	-	0.230
0.50/0.50	0.1-0	37.6	2.26	59	-	0.185
0.75/0.25	0.1-0.03	69.9	3.90	165	-	0.210
0.50/0.50	0.1-0.03	37.4	2.14	66	-	0.125
0.25/0.75	0.1-0.03	112.0	2.04	43	-	0.163
0.75/0.25	0.1-0.05	72.5	4.36	186	-	0.135
0.50/0.50	0.1-0.05	38.1	2.32	72	-	0.139
0.25/0.75	0.1-0.05	82.0	1.47	58	-	0.106
0.75/0.25	0.1-0.1	70.2	4.32	191	-	0.115
0.50/0.50	0.1-0.1	45.9	2.50	71	-	0.102
0.35/0.65	0.1-0.1	85.0	1.64	72	-	0.095

x_{MNa} is mole fraction of sodium methacrylate, G_I is the modulus after preparation, ν_d is the concentration of elastically active network chains, Q_w is equilibrium swelling degree.

7.3.3. Swelling and mechanical behavior in water/acetone mixtures at room temperature

Measured experimental dependences of swelling degree Q on solvent composition are shown in *Fig. 7.10* for all IPNs regardless a compositions and charge concentrations. A continuous decrease of the gel volume (degrease of swelling Q) with increasing volume fraction of acetone, c_a, in the w/a mixtures can be seen for all IPNs series (transition has continuous character); transition corresponds to PAAm networks. Increasing mole fraction of charge groups results in slight shift of the transition region from expanded (low c_a values) to collapsed (high c_a values) state to higher acetone concentrations in all series; the effect of the composition of IPNs is less clear. For IPNs with PIPAAm component equal to 0.75 (and to some extent also 0.50) one can observed faster decrease in Q values in the range of the lowest acetone concentrations (0.09-0.2) than for other IPNs. We believe that this effect is associated with the cononsolvency phenomenon of PIPAA in w/a mixture as was discussed earlier in the part 7.1.

As in the case of statistical copolymers the critical acetone concentrations a_c values were determined as acetone concentrations where the slope $d(\log Q)/dc_a$ has a maximum. *Figs.7.11* a,b,c,d show the composition dependences of the critical parameters - a_c and the extent of the transition ΔQ for various ionizations of IPNs components. Generally, it can be seen that the a_c values for several IPNs series depend on the charge concentration. As follows from *Fig. 7.11a* for IPNs formed from uncharged components the a_c values are roughly constant independent of the composition; this fact indicates that intermolecular interactions between uncharged components practically do not exist at PAAm transition. With increasing charged comonomer concentration in PIPAAm network the a_c firstly increases with increasing amount of PIPAAm component in IPNs and after that is almost constant; constant a_c values again suggest week intermolecular interactions between uncharged PAAm (formed as the first network) and charged PIPAAm components. Extent of the PAAm transition ΔQ decreases with increasing participation of PIPAAm component in IPNs; this decrease is practically unaffected by the charge concentration in PIPAAm component. *Fig. 7.11b* shows the a_c and ΔQ values for IPNs formed uncharged PIPAAm component and charged PAAm ones. As expected, a_c values increase with charge concentration in PAAm network; at the same time, the decrease of a_c was found with increasing amount of uncharged PIPAAm network. The decrease of a_c with composition indicates that in this case, intermolecular interactions between variously charged PAAm networks (formed as the first) and uncharged PIPAAm network occurs at formation of the IPNs. The extent of the PAAm transition ΔQ strongly increases with charge content in PAAm network and decreases with increasing participation of PIPAAm component in IPNs. Suppression of PAAm transition with composition is probably due to incorporation of more hydrophobic PIPAAm component into IPNs, which makes acetone more effective solvent at PAAm transition. The maximum in a_c and decrease in ΔQ with increasing participation of charged PIPAAm networks in IPNs, shown in *Fig. 7.11c,* indicates that also between charged PAAm and PIPAAm networks intermolecular interactions exists at IPNs formation.

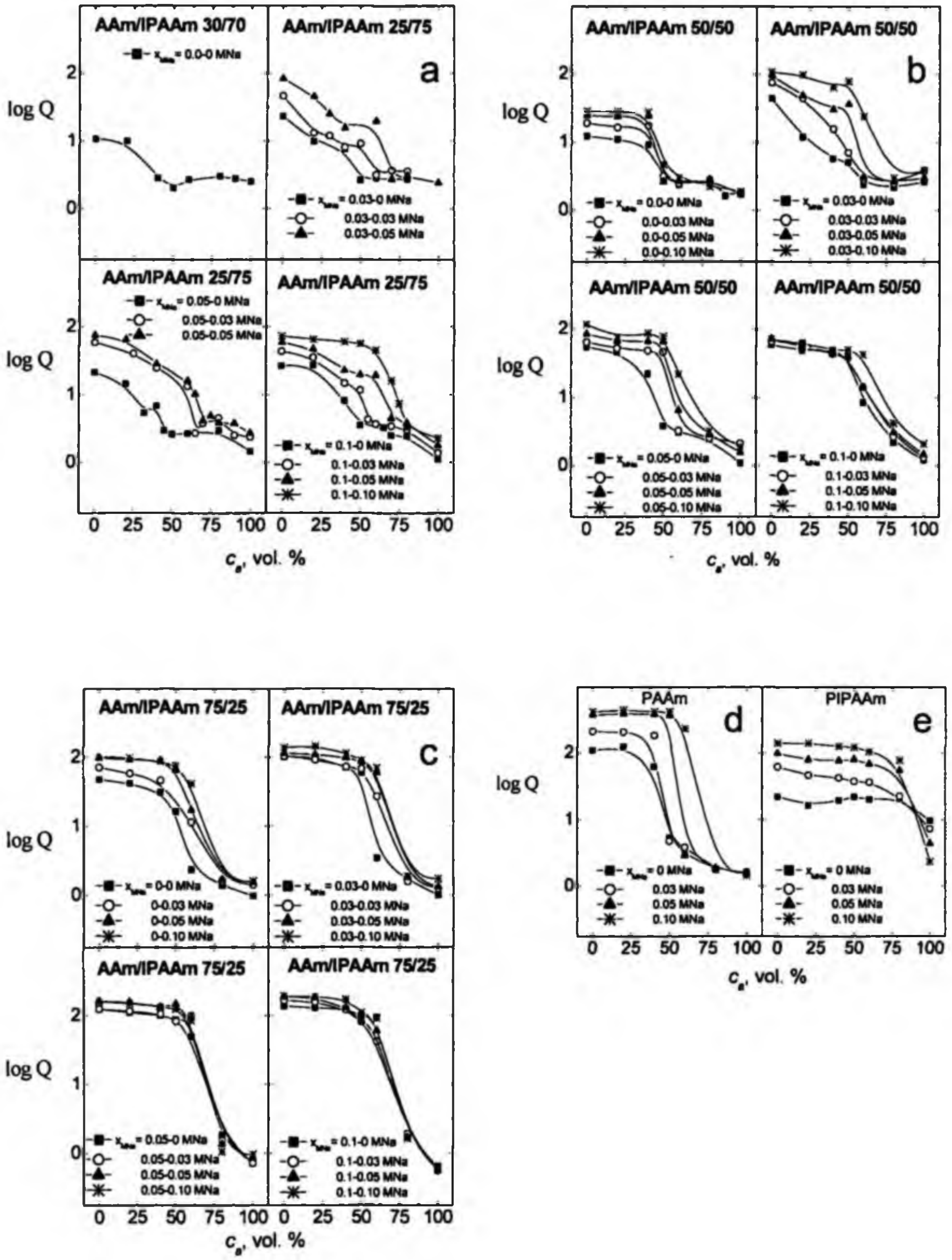


Fig. 7.10 Dependence of the swelling degree log Q on acetone concentrations c_a for gels with mole fractions of PAAm component: a – 0.25 (resp. 30); b – 0.50; c – 0.75; d – 0.0; e – 1.0 and for indicated mole ratios of sodium methacrylate, x_{MNa}

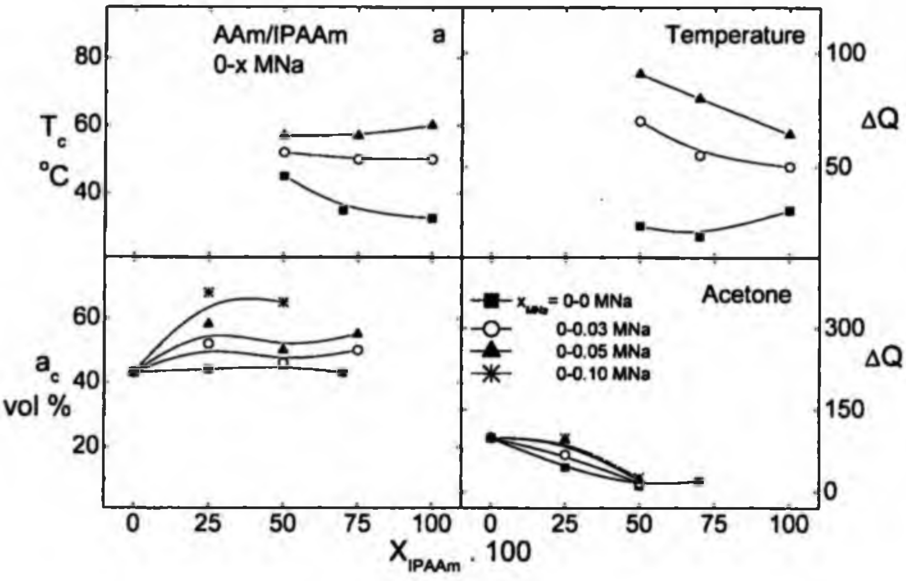


Fig. 7.11a Dependence of the critical acetone concentrations a_c, critical transition temperature T_c, and extent of the transition ΔQ, on composition for IPNs with uncharged PAAm component and charged PIPAAm component with indicated charge concentrations

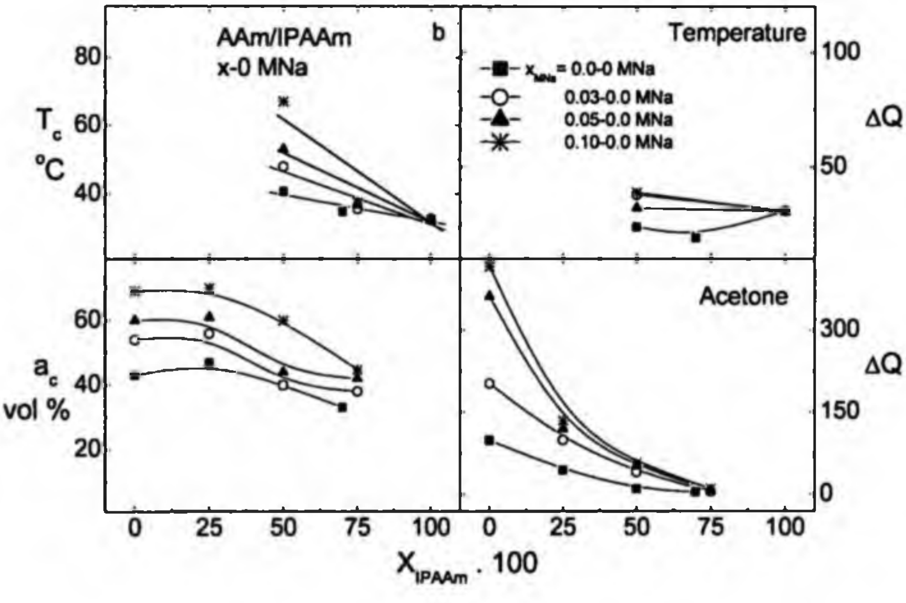


Fig. 7.11b Dependence of the critical acetone concentrations a_c, critical transition temperature T_c, and extent of the transition ΔQ, on composition for IPNs with charged PAAm and PIPAAm components with indicated charge concentrations

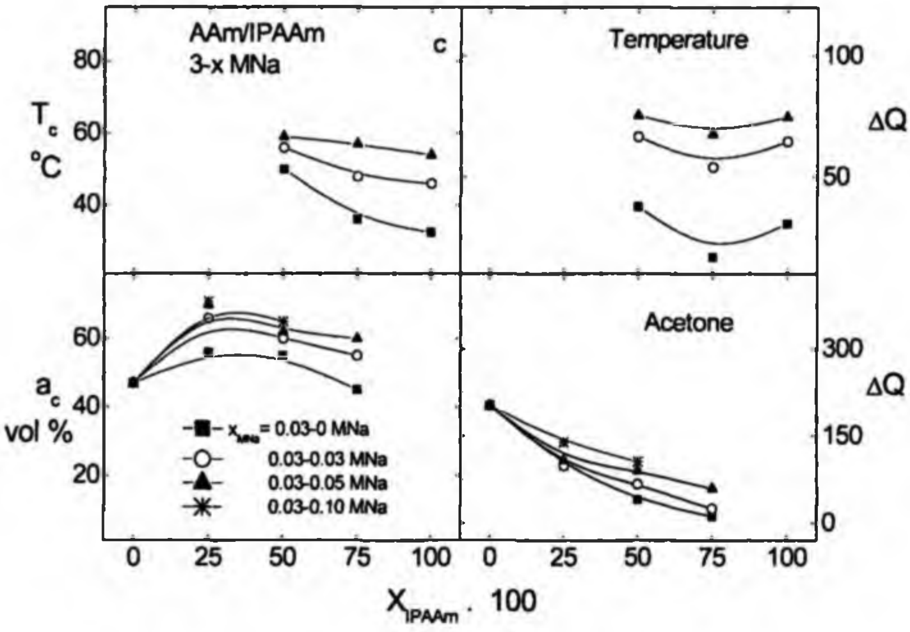


Fig. 7.11c Dependence of the critical acetone concentrations a_c, critical transition temperature T_c, and extent of the transition ΔQ, on composition for IPNs with uncharged PIPAAm component and charged PAAm component with indicated charge concentrations

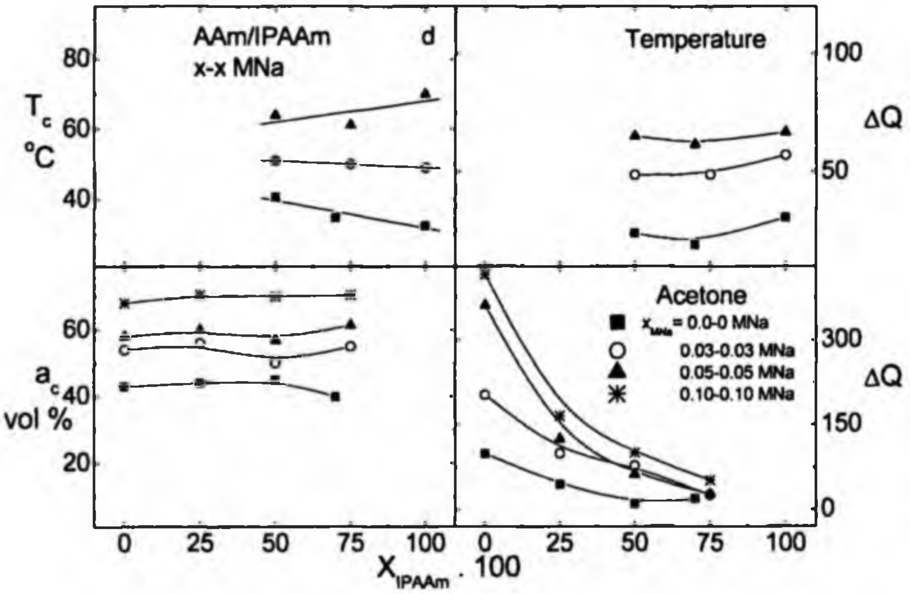


Fig. 7.11d Dependence of the critical acetone concentrations a_c, critical transition temperature T_c, and extent of the transition ΔQ, on composition for IPNs with charged PAAm and PIPAAm components with indicated charge concentrations

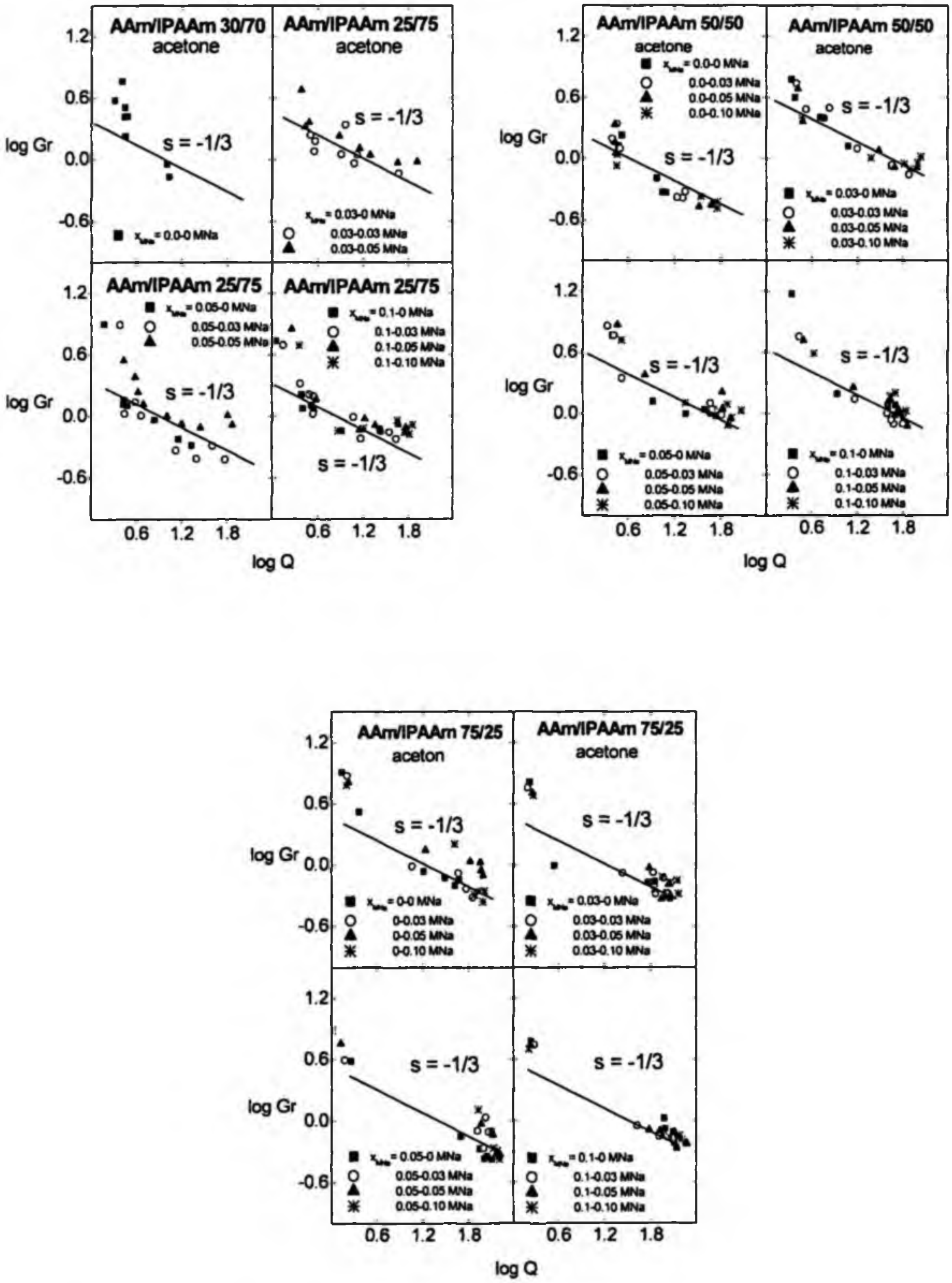


Fig. 7.12 Dependence of reduce shear modulus log G_r on log Q for variously ionized gels with different fractions of PIPAAm in IPNs measured in w/a mixtures

Very interesting results are shown in *Fig. 7.11d* for IPNs formed from PAAm and PIPAAm networks with the same charge concentrations. Expected increase of a_c values with ionization was found; on the other hand, the a_c values of PAAm transition are roughly constant, independent of composition. This finding means that intermolecular interactions between components are predominantly associated with charge concentration of individual networks. From *Figs 7.11* a,b,c,d it can be concluded that neat PAAm network as well as all three compositions of IPNs exhibit transition in w/a mixtures.

The dependences of $log\ G_r$ on $log\ Q$ of all three series IPNs regardless the ionization and composition measured in w/a mixtures are plotted in *Fig. 7.12*. For comparison, the predicted rubber elasticity slope for the dependence of $log\ G_r$ vs $log\ Q$, $s = - 0.33$, is also shown. Departures from the straight line in the region of low swelling ($log\ Q < 0.5$) are probably due to the influence of the main transition region (vitrification) at high acetone concentrations. The dependences of $log\ G_r$ on $log\ Q$ are roughly the same regardless of charge concentrations and composition of IPNs; this means that the mechanical behavior is predominantly determined by the degree of swelling for all gels.

7.3.4. Swelling and mechanical behavior in water at various temperatures

The dependences of swelling ratio in water $log\ Q$ on temperature, T, for IPNs on heating are shown in *Fig.7.13*. The decrease in swelling with increasing temperature correspond to expected PIPAAm transition; as in previous case of PAAm transition in w/a mixture, this transition exhibits continuous character. It was observed that in the expanded state (at low temperatures) all gels were transparent while in the collapsed state all gels were turbid. The transparent structure is characteristic for an ordinary homogeneous three-dimensional network, the turbid one is typical for heterogeneous structure; heterogeneous structure is usually due to formation of microsegregates inside the gel (69). In all cases, increasing ionization shifts the transition to higher temperatures. Incorporation of PAAm, the more hydrophilic component, into IPNs results in shift of the transition to higher temperatures. It can be also seen that for IPNs with the highest content of PAAm network ($x_{AAm} = 0.25$) temperature transition does not exist more. On cooling modified swelling results, with transition temperatures shifted to lower values, were obtained (see *Fig.7.14*).

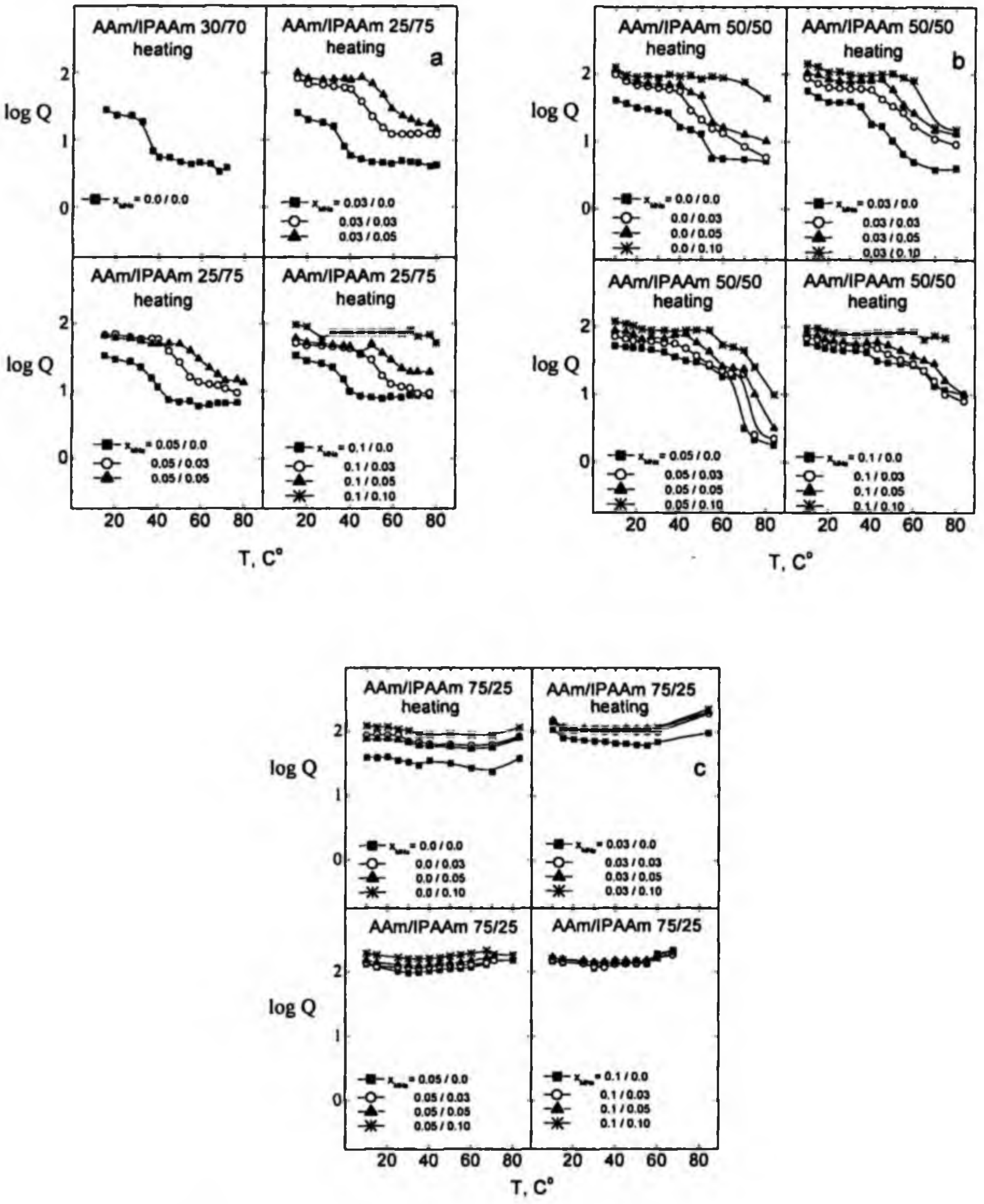


Fig. 7.13 Dependence of the swelling degree log Q on temperature for variously ionized gels with different fractions of PIPAAm in IPNs measured in water on heating for indicated ionizations

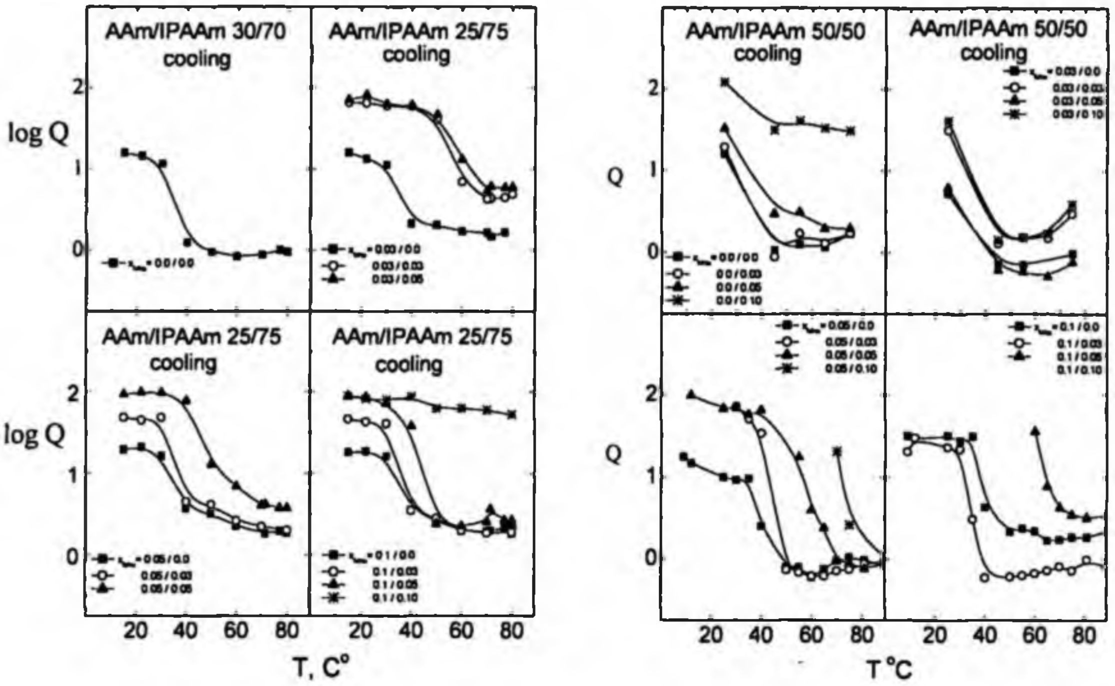


Fig.7.14 Dependence of the swelling degree log Q on temperature for variously ionized gels with different fractions of PIPAAm in IPNs measured in water on cooling for indicated ionizations

As in previous case the transition temperatures T_c were determined as a temperatures where the slope *d(log Q)/dT* has a maximum; the T_c temperatures together with extents of the temperature transition ΔQ in dependence on composition are shown in *Fig.7.11a,b,c,d.* As expected for all IPNs series the T_c temperatures increase with increasing charge concentration in both component; this means that charges increase the extent of hydrogen bonding in networks and make water a better solvent for gels. For IPNs which were prepared from uncharged PAAm network (first network) and variously charged PIPAAm networks and IPNs formed from PAAm and PIPAAm networks with the same charge concentrations the T_c values are roughly independent of the composition (see *Fig. 7.11a,d).* On the other hand, for IPNs prepared from uncharged PIPAAm network and variously charged PAAm networks and IPNs prepared from variously charged PAAm and PIPAAm components an increase of T_c with increasing amount of PAAm component was found (*Fig. 7.11b,c*); similar results were found for IPNs in the case of PAAm transition in w/a mixed solvent. Similar molecular interpretation can be offered; while for the first two IPNs series only week intermolecular interactions exist, for second two series interactions are formed and they are mainly associated with charge

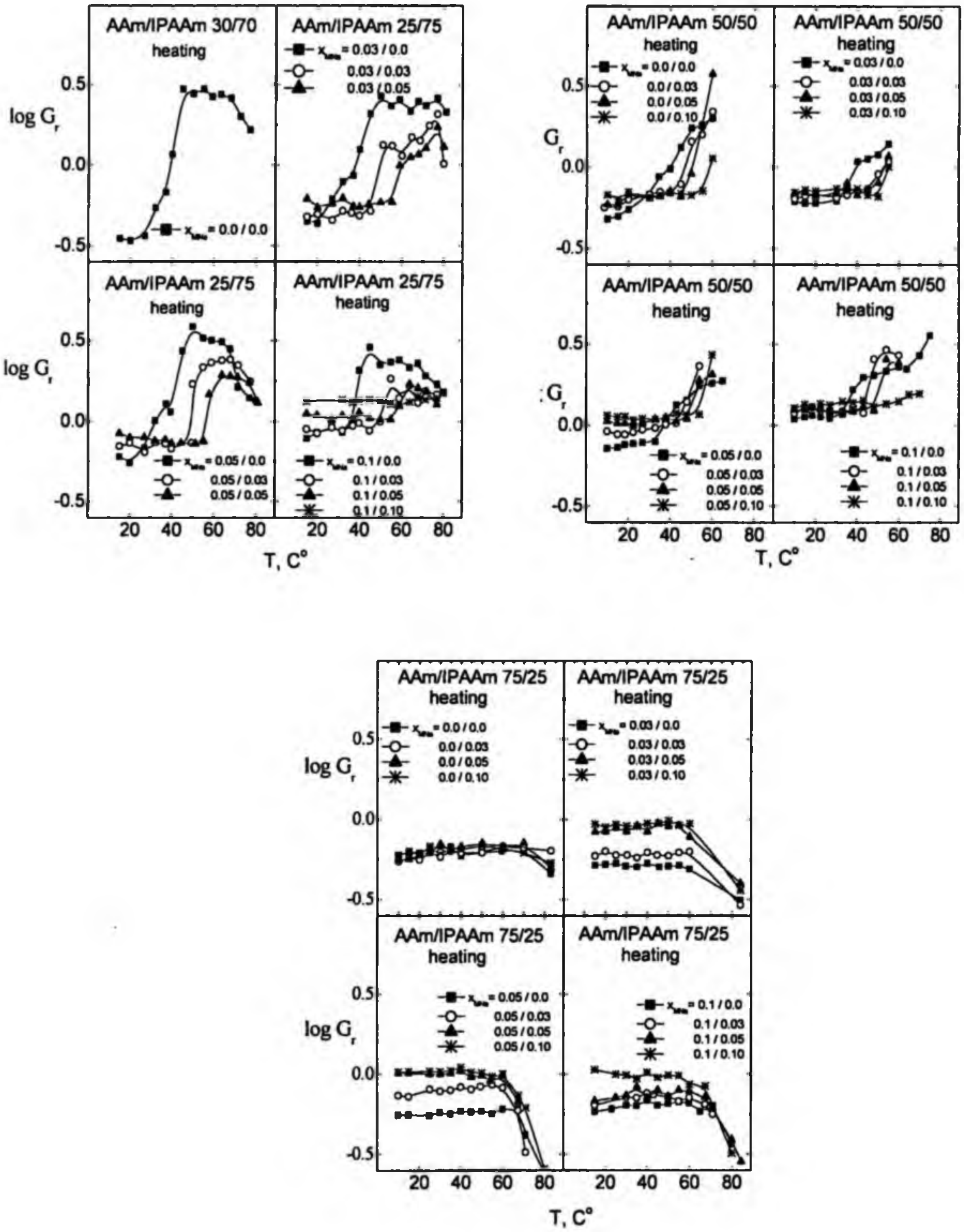


Fig. 7.15 Dependence of the reduce modulus log G_r on temperature for variously ionized gels with different fractions of PIPAAm in IPNs measured in water on heating for indicated ionizations

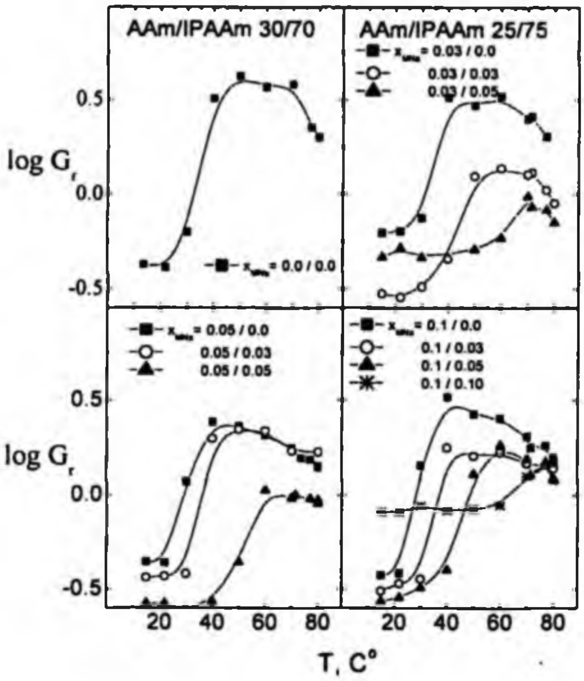


Fig. 7.16 Dependence of the reduce modulus log G_r on temperature for variously ionized gels with different fractions of PIPAAm in IPNs measured in water on cooling for indicated ionizations

concentration of individual networks. Neat PIPAAm networks and two IPNs with the highest participation of PIPAAm component show temperature transition.The dependences of the reduced shear modulus, G_r (Eq. (6.4)) of IPNs on temperature are shown in *Fig. 7.15* on heating and in *Fig. 7.16* on cooling regime. As expected, a decrease in the volume of the gel (temperature transition) is generally reflected in an increase of the G_r so that increase of *log* G_r on T observed for IPNs correlate with decrease of *log* Q on T. Increasing amount of charges in IPNs shifts the G_r values to higher temperatures; the largest increase of log G_r is observed for gels with the lowest ionizations. As it was mention earlier, the turbid, heterogeneous structure was found for gels in collapsed state (at high temperatures) and was interpreted by formation of microsegregates. The decrease in *log* G_r with increasing ionization in the collapse region suggests that the repulsion of charges bound on chains decreases the two-phase character of hydrogels. From small decrease of the *log* G_r values with increasing T, found at the highest temperatures ($T > 60°C$, *Fig. 7.15 and 7.16*), it follows that increasing temperature decreases the two-phase character of hydrogels similarly as ionization.

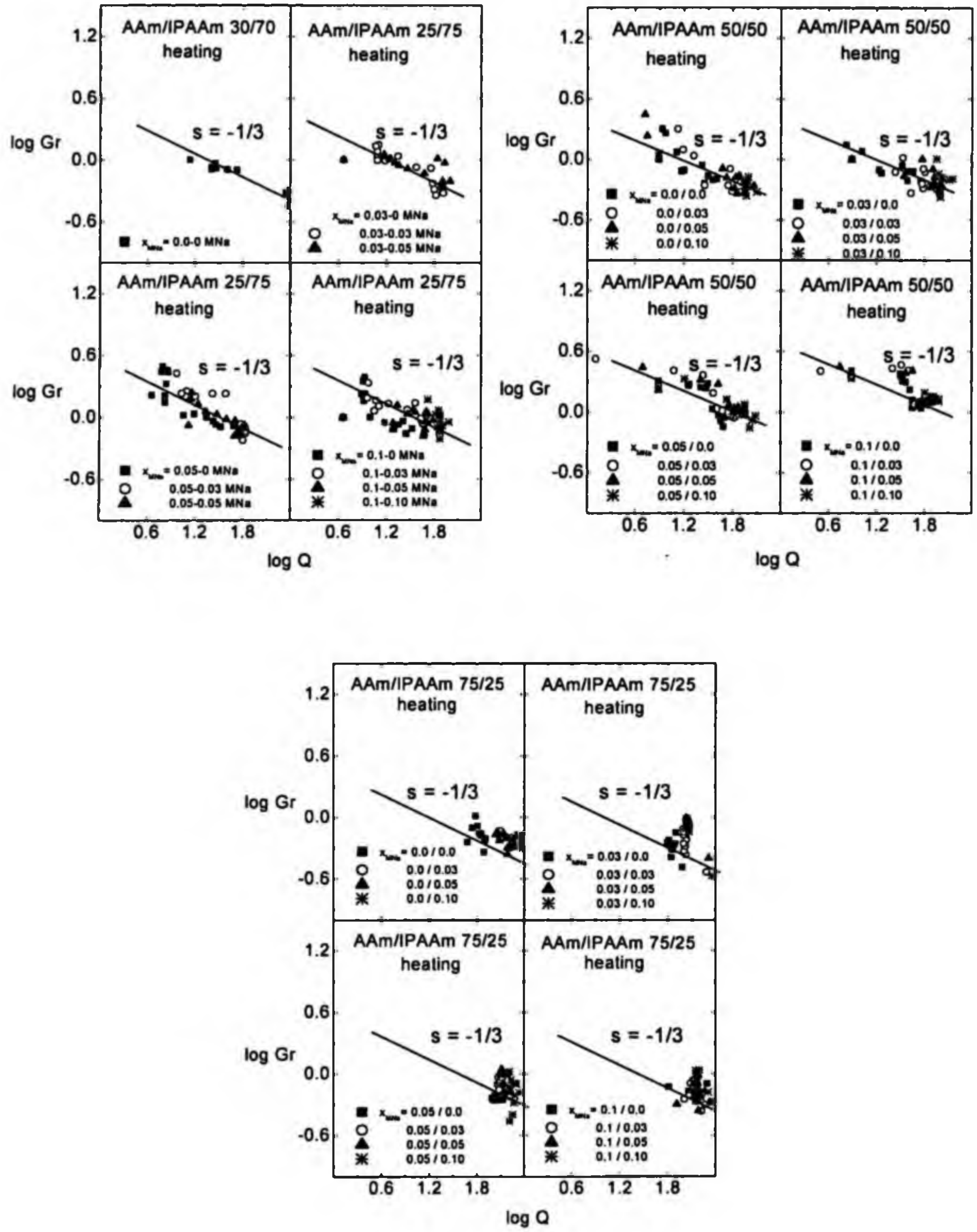


Fig. 7.17 Dependence of the reduce modulus log G_r on log Q for gels with different fractions of PIPAAm in IPNs measured in water at various temperatures on heating for indicated ionizations

The *log* G_r vs. T dependences of IPNs were transformed to the *log* G_r vs. *log* Q dependences and are shown in *Fig. 7.17.* As in previous case, the predicted rubber elasticity slope for the dependence of *log* G_r vs *log* Q, $s = -0.33$, is also shown. An universal dependences of *log* G_r on *log* Q were found regardless of ionizations and compositions of IPNs; this means that the mechanical behavior, as in all previous cases, is predominantly determined by the degree of swelling.

7.3.5. Comparison of swelling data with the theory of polyelectrolyte networks

As in previous cases for comparison of swelling results of IPNs with theory, we will use our generalized model (Eqs (3.38) and (4.6)). In this IPNs case individual terms P_i of Eq. (3.38) were expressed in network molecular parameters: concentration of network chains v_d (Table 7.3), density of dry networks ρ (= $x_{AAm} \cdot \rho_{AAm} + x_{IPAAm} \cdot \rho_{IPAAm}$), average molecular weight of monomer units M (= $x_{AAm} \cdot M_{AAm} + x_{IPAAm} \cdot M_{IPAAm}$), molar volumes of w/a mixtures V_1 (determined as earlier), volume fraction of dry polymer at network formation v_l and the permittivity of mixed solvent or water ($D = 80$ for water and 21 for acetone; for w/a mixtures the linear dependence of D on c_a was used). As low fractions of MNa were used we assumed, in the first approximation, that the degree of ionization $\alpha = x_{AAm} \cdot x_{MNa} + x_{IPAAm} \cdot x_{MNa}$. Using Eqs (3.38) and (4.6), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, $v_2 = 1/Q$, can be calculated from experimental equilibrium Q values measured at w/a mixtures or at various temperatures (as the data were collected for free swelling, $P = 0$ in Eq. (3.38) and (4.6)) by employing the same procedure described in detail earlier.

The application of Eq. (3.38) for uncharged series ($\alpha = x_{MNa} = 0$, $P_{os} = P_{els} = 0$, classical Flory-Huggins equation is restored) and using the swelling degrees Q_w measured at room temperature (expanded state of gels, Table 7.3), leads to the values of interaction parameters χ shown in Table 7.3. As expected, with increasing amount of PIPAAm network in uncharged IPNs χ slightly increases due to decrease in Q_w values; for all uncharged IPNs the values are close to 0.5. The increase of χ means that increasing amount of hydrophobic PIPAAm network in IPNs slightly decreases the overall hydration of IPNs, which leads to lower swelling in water.

As expected, the swelling degree in water Q_w measured at room temperature increases with increasing content of charged groups in neat networks and IPNs (Table 7.3). If we assume that the degree of ionization is $\alpha = x_{MNa}$ (see above) and use Eq. (3.38) for the description of dependence of Q_w on ionization x_{MNa} for all networks we obtain unrealistic high χ values (ranging from 0.6 to 10). As χ was introduced into the used theory as a measure of polymer–solvent interactions when all charges are screened, it is reasonable to require the same χ values, which were found for uncharged neat networks and IPNs (Table 7.3), also for all charged networks in water. This requirement is possible to fulfill by the assumption that the effective degree of ionization α^* is lower than the fraction of charges x_{MNa} i.e., $\alpha^* = x_{MNa}\ \Phi$, where Φ is the correction factor. With this requirement, the Q_w data shown in Table 7.3 were described by Eq. (3.38); the Φ values thus calculated lie in the range 0.095-0.95 and are dependent on the content of charges and composition of IPNs. The Φ factor, as was mentioned earlier, is related to the activity coefficient of counter-ions, and to clustering of counter-ions due to heterogeneity of highly dilute networks.

Finally, using known molecular parameters and the effective degree of ionization α^*, the dependence of χ on v_2 was calculated from Q values measured at various w/a mixtures and temperatures (*Fig 7.18* and *7.19*) for all IPNs. As was discussed previously, the van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump in the gel volume (collapse). If the van der Waals loop in the dependence of χ on v_2 is experimentally found than the critical interaction parameter χ_c and compositions of coexisting phases (the values v_2' and v_2'') at the transition are given by the Eq. (4.7).

In the inset of *Fig 7.18*, the van der Waals loops are shown and Maxwell's construction is applied to the χ vs v_2 dependences which allows to determine χ_c by the requirement that the areas above and below the line are equal; also the extents of the collapse, $\Delta v_{2,t} = v_2'' - v_2'$can be determined.

The phase state of PAAm/PIPAAm IPNs gels in water and w/a mixtures is determined by interactions of polar and non-polar groups on the chains of both networks with water and/or acetone molecules. As the $\chi = 0.490$ and $\chi = 0.497$ was found for the PAAm and PIPAAm uncharged networks in water (Table 7.3), the presence of isopropyl side groups in IPAAm has decreased the overall hydration of the IPNs as the number of hydrophobic groups in the side chain of the PIPAAm network increased. Van der Waals loops were not observed for uncharged and slightly charged IPNs so the transitions from expanded to collapsed state are continuous.

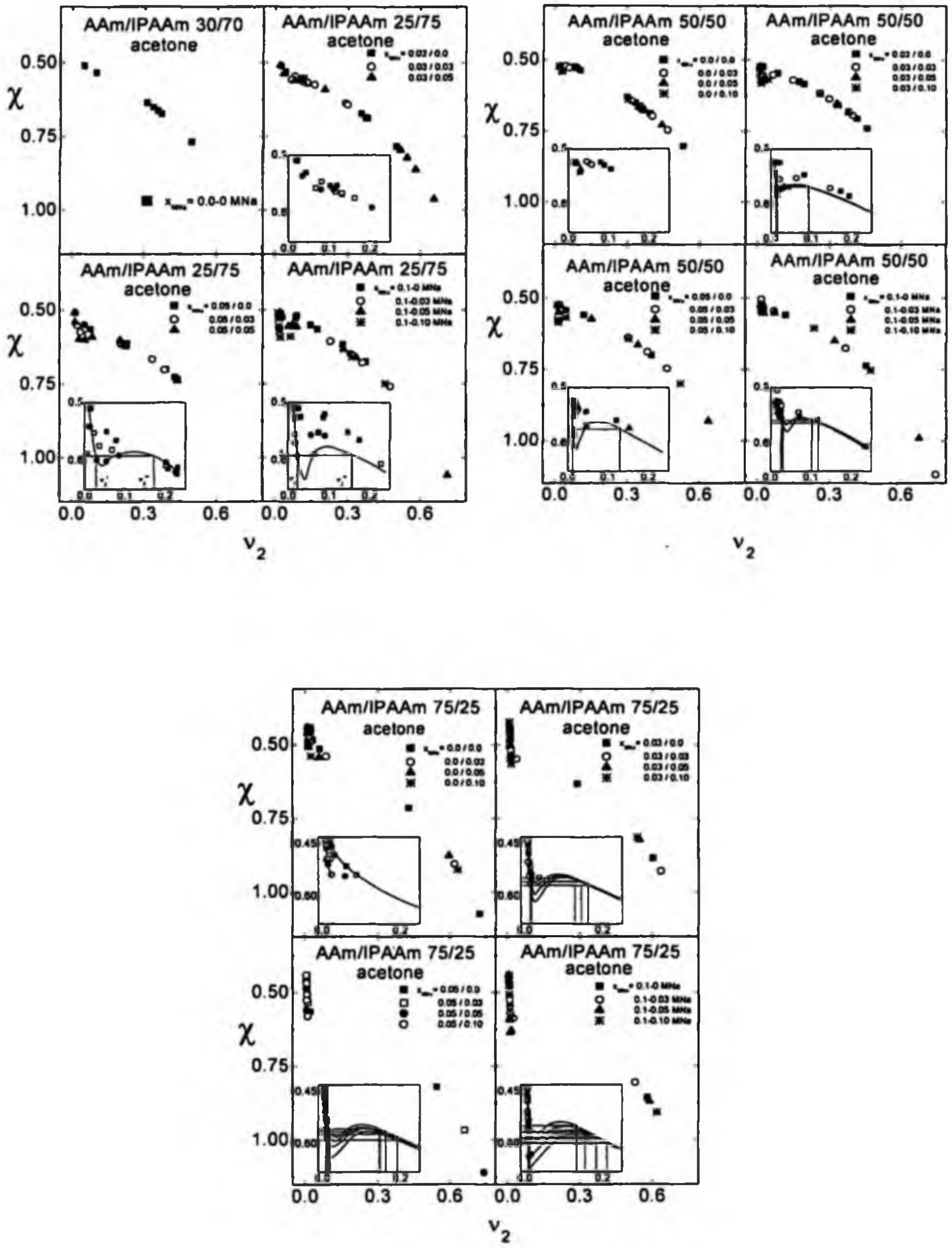


Fig 7.18 Dependence of the interaction parameter, χ, on volume fraction of dry network in the swollen state, v_2, in water measured w/a mixtures for gels with 0.25/0.75, 0.50/0.50 and 0.75/0.25 indicated AAm/IPAAm mole fractions and various ionic comonomer concentrations

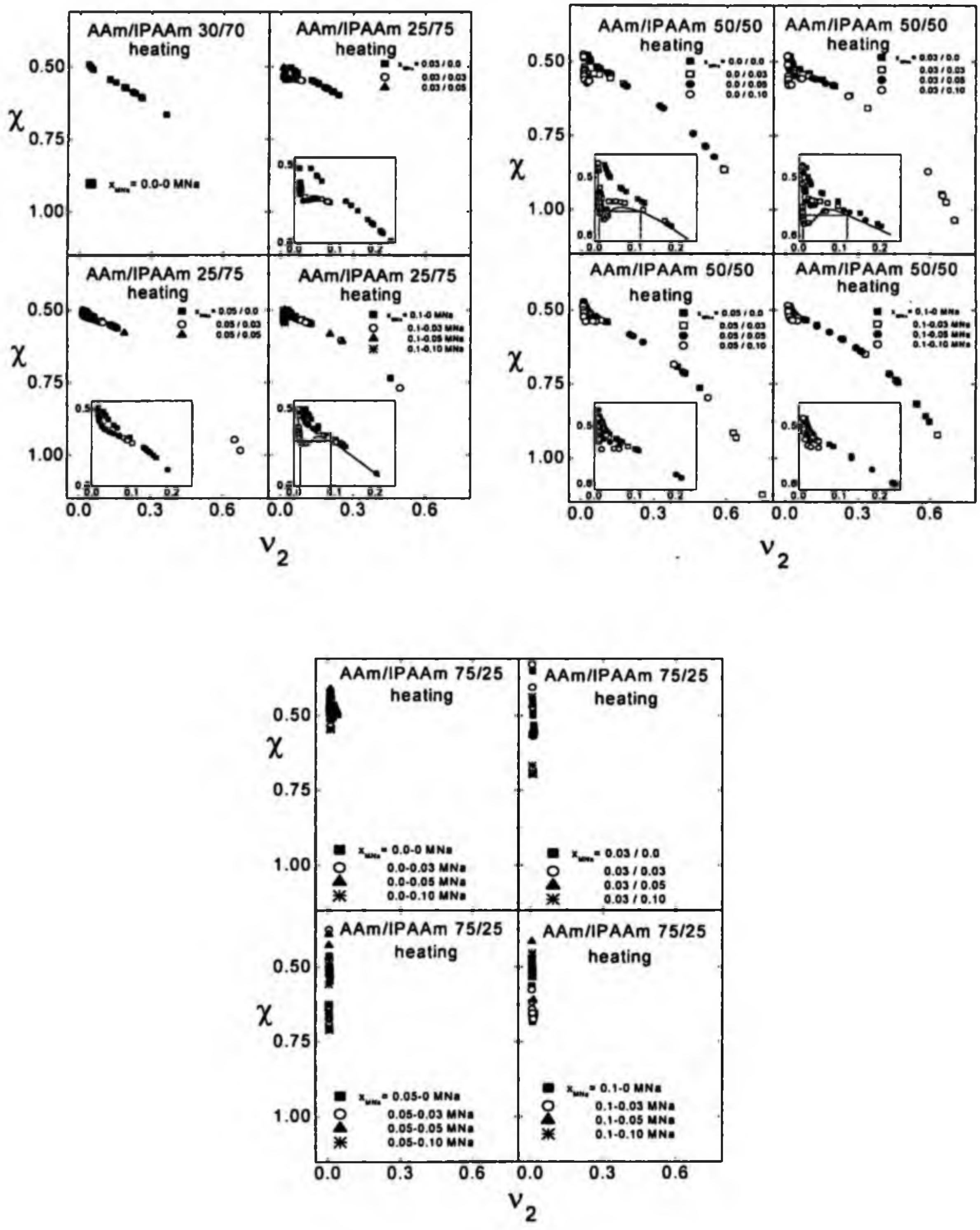


Fig 7.19 Dependence of the interaction parameter, χ, on volume fraction of dry network in the swollen state, v_2, in water measured on heating for gels with 0.25/0.75, 0.50/0.50 and 0.75/0.25 indicated AAm/IPAAm mole fractions and various ionic comonomer concentrations

In Table 7.4 the critical values of interaction parameter χ_c and extents of the transtion ΔQ_{teor} ($=1/v_2' - 1/v_2''$) are shown for IPNs with different contents of AAm in water/acetone mixture. As expected, the values of interaction parameters as well as the extents of the transition increase with increasing mole fraction of MNa, x_{MNa}.

Tabl.7.4 Composition, critical value of interaction parameter χ_c and extent of collapse ΔQ_{teor} ($=1/v_2' - 1/v_2''$) and ΔQ (from experiment) of IPNs of (PAAm/PIPAAm) hydrogels measured in water/acetone mixtures

x_{IPAAm} mole %	x_{MNa} mole %	χ_c	ΔQ_{teor}	ΔQ
0.75	0.05-0.05	0.591	32	26
	0.10-0.10	0.587	28	51
0.50	0.03-0.05	0.566	51	62
	0.03-0.10	0.568	73	65
	0.05-0.05	0.565	49	61
	0.05-0.10	0.569	91	87
	0.10-0.05	0.558	23	40
	0.10-0.10	0.562	76	100
0.25	0.03-0.0	0.592	50	56
	0.03-0.05	0.603	68	70
	0.03-0.10	0.613	69	71
	0.05-0.0	0.558	44	100
	0.05-0.03	0.565	52	104
	0.05-0.05	0.572	96	124
	0.05-0.10	0.589	124	150
	0.10-0.0	0.548	62	126
	0.10-0.03	0.566	83	157
	0.10-0.05	0.584	98	158
	0.10-0.10	0.599	135	165
0.0	0.03	0.549	63	47
	0.05	0.563	104	361
	0.10	1.039	248	415

The dependences of the critical values of interaction parameter χ_c and extents of the collapse *ΔQ* on amount of PIAAm component in IPNs for the highest ionization of both components are shown in *Fig. 7.20* The value of χ_c and ΔQ_{teor} decrease with increasing amount of the PIPAAm network which is incorporated in IPNs (with increasing amount of more hydrophobic of network).

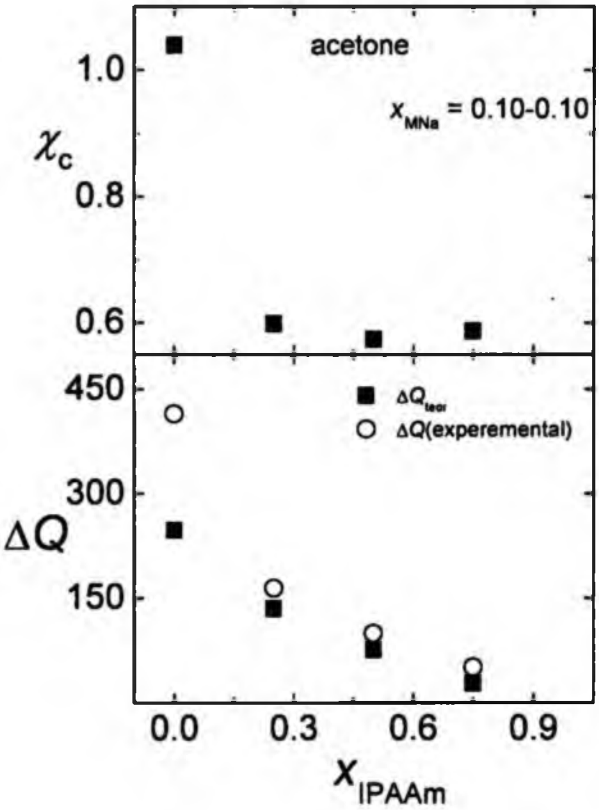


Fig. 7.20 Dependence of the extent of the collapse ΔQ_{teor}, experimental ΔQ and critical values of the interaction parameter χ_c on the concentration of AAm in P(AAm/IPAAm) networks in water/acetone mixture.

8. Conclusions

1. We have investigated the swelling and mechanical behavior of negatively ((mole fraction of sodium methacrylate $x_{MNa} = 0 - 0.1$) and positively (mole fraction of quaternary salt-(2-acrylamidoethyl)trimethyl ammonium chloride $x_{QS} = 0 - 0$) charged networks of poly(*N*-isopropylmethacrylamide) (PIPMAm) and poly(*N*-isopropylacrylamide) (PIPAAm) in water/ethanol mixtures at room temperature. Networks were prepared by radical polymerization and at networks synthesis the constant mole fraction of crosslinker-N,N'-methylenbisacrylamide ($x_{CR} = 0.04$) was used. From our investigation following conclusions can be made:

a) Strong cononsolvency effect was observed for uncharged and negatively charged gels in both PIPAAm and PIPMAm systems; while for neat solvents high degree of swelling Q was observed, for solvent mixtures pronounced minima in swelling were found. Swelling minima are connected with the coil-to-globule transition of network chains and their characteristic parameters-concentration of ethanol at the minimum, $c_{eth,m}$, and corresponding swelling degree, Q_m, were determined. With increasing amount of negatively charged ionic comonomer the minimum in swelling shifts to higher $c_{eth,m}$ values and Q_m increase. We believe that this minimum is connected with interactions of alkyl groups of ethanol with nonpolar groups of polymer main chain.

b) On the other hand, positively charged networks of both systems exhibit roughly constant Q values practically independent of solvent mixtures compositions. We believe that this behavior is caused by the presence of alkyl groups in side chain of ammonium salt. In such a case the structure of ionic comonomer plays an important role in cononsolvency behavior of charged gels in mixed solvents.

2. Ionized networks of random copolymers of acrylamide (AAm) and N,N'-diethylacrylamide (DEAAm) (mole ratios of x_{AAm}/x_{DEAAm} = 1/0, 0.75/0.25, 0.5/0.5, 0.30/70, 0.15/0.85, 0/1) with various amounts of ionic comonomer-sodium methacrylate (MNa) (mole ratios to all monomers x_{MNa} = 0.0, 0.025, 0.05) and crosslinker - N,N'-methylenbisacrylamide were prepared at high dilution in water. Their swelling and mechanical behavior was investigated in water at various temperatures (from 10 to

90°C) and in water/acetone (w/a) mixtures at room temperature. Following conclusions can be made:

a) For some copolymers the transition region from expanded to collapsed state was observed at critical concentration of acetone, a_c, in w/a mixtures or at critical temperature, T_c, in water. It was found that for AAm-reach copolymers with increasing content of DEAAm component the a_c values increase; the similar increase was observed with increasing x_{MNa}. This indicates that both increasing DEAAm and charge content in networks stabilizes hydration of chains. Acetone can interact with polymer segments through the polar and unpolar groups, while water lacks the non-polar group. With increasing hydrophobic DEAAm content in networks, acetone becomes a better solvent for gels. Shrinkage of gels is caused by dehydration of chains due to stronger hydrophobic interactions between acetone and polymer; once acetone molecules destroy a part of hydration shell, the damage propagates through entire hydration structure and dehydrated chains associate to form a collapsed structure. In this state, acetone molecules are adsorbed on collapsed structure.

b) Neat PDEAAm and copolymers with the highest DEAAm content exhibit temperature transition; both increasing amount of AAm and charges bound on the chains in copolymers shifts the T_c temperatures to higher values very efficiently (for more than 20°C). This means that with increasing fraction of AAm as well as charge content in networks, the extent of hydrogen bonding increases and water becomes a better solvent for gels. These results can be helpful in practical applications of hydrogels as they show the possibility of adjusting T_c by composition of copolymer to the required values.

3. Swelling and mechanical behavior of sequentially prepared interpenetrating negatively charged polymer networks (IPNs), composed of poly(*N*-isopropylacrylamide) (PIPAAm) and polyacrylamide (PAAm) networks, was investigated in water at various temperatures and in water/acetone (w/a) mixtures at room temperature. While the first - PAAm networks were prepared by thermal radical copolymerization at 65 °C, PIPAAm networks were subsequently prepared by radiation polymerization at room temperature. PAAm/PIPAAm IPNs with various mole fractions of AAm/IPAAm = 1/0, 0.75/0.25, 0.5/0.5, 0.25/0.75, 0/1 and with various amounts of charges - MNa (mole fractions x_{MNa} = 0.0, 0.03, 0.05, 0.1) were prepared in presence of the crosslinker-N,N'-methylenbisacrylamide (MBAAm) in water. Following conclusions can be made:

a) Two transitions, one – corresponding to PAAm component - in dependence of swelling degree on w/a composition at room temperature and second one – corresponding to PIPAAm component - in dependence of swelling degree on temperature, were detected in IPNs. As expected, for reach-PAAm IPNs a_c as well as extent of the collapse ΔQ increase with increasing ionization; on the other hand both a_c and ΔQ slightly decrease with increasing content of PIPAAm networks in IPNs. Unpronounced dependences of a_c on composition suggest that only weak intermolecular interactions between two networks occur for uncharged networks; stronger intermolecular interactions between two components occur in IPNs when networks are formed in presence of charges. It was found that more hydrophobic PIPAAm component makes acetone more effective solvent for IPNs at PAAm transition.

b) For reach - PIPAAm IPNs the temperature transition was found. An increase of transition temperature T_c with increasing amount of PAAm network in IPNs was found. As expected, the T_c values increase with ionization. Generally, a small increase of ΔQ with increasing amount of PAAm component was observed. These results suggest that intermolecular interactions between networks in IPNs prepared with various charge concentrations exist. Found increase of T_c and ΔQ means that PAAm networks acts as more hydrophylic components in IPNs.

4. For all measured systems it was found that mechanical behavior is predominantly determined by the degree of swelling regardless of charge concentration.

5. A comparison of experimental swelling results of all measured systems with the theory of polyelectrolyte gels shows that agreement is reasonably good if the effective degree of ionization (correction factor $\Phi < 1$) is introduced.

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