

Electroresponsive Acrylic Gels

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ABSTRACT: *This article is comprised of two parts: a) an experimental investigation on the behavior of an acrylic gel under DC electric field and b) a physico - mathematical description.*

a) Gel rods made of poly [acrylamide-co-bisacrylamide] were partially hydrolyzed to different extents at pH 12 by tetramethylethylene diamine. Equilibrium properties of the resulting gels rods (water content, number of carboxyl groups and pore size) were determined. Gel rods were then placed in water parallel to planar platinum electrodes. Under the field strengths greater than 2 V/cm the gels gradually bend towards cathode and after reaching a maximum, they traverse a smooth reverse deformation, finally bending towards anode. The speed and extent of these deformations depend on the electric field strength; length, diameter, charge density (extent of hydrolysis) of the gel rods; temperature, and the pH of the bathing medium. In all cases the bending behavior follows the relation for the three – point mechanical bending of solid rods. Anodic swelling and bending towards cathode is attributed to the difference in the osmotic pressure between the anodic and the cathodic sides of the gel, while the reverse deformation and bending towards anode is assigned to the migration of H⁺ ions from the anolyte into the gel and neutralization of COO⁻ groups.

b) Theoretical analysis: These attributes are quantitatively represented by a proper theoretical formulation based on Donnan and Flory-Huggins theories. The relation obtained for the osmotic pressure within the gels, in the absence of an electric field, is modified to include the ionic flux in response to concentration and electric field gradients. Considering the ionization of water and the network carboxyl groups, together with the principle of charge neutrality, and assuming Donnan equilibrium at the gel boundaries under the applied electric fields, the equations for ionic fluxes are derived and solved by Laplace transform. It is found that the concentration of cations decreases in the anodic side of the gel while it increases in the cathodic side, leading to an osmotic swelling gradient in the gel causing it to bend.

KEY WORDS: *Intelligent, Electroresponsive, Gels, Acrylic, Acrylamide, Donnan-Flory theories, Bending.*

INTRODUCTION

The gel is defined here as a crosslinked polymeric network whose matrix is filled with an imbedded

low molecular weight fluid. The network may be electrically neutral or possess ionizable groups (i. e. a

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1021-9986/04/1/13

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polyelectrolyte). The properties and behavior of a gel are intrinsically determined by the network as well as its interactions with the liquid. The liquid prevents the full contraction and collapse of the network while the latter in turn prevents the free flow of the liquid. The, "gel" is thus a state of equilibrium intermediate between the liquid and solid states, with properties that can fall anywhere between the two extremes. Besides, the gel structure can be easily influenced by the external stimuli, e. g. some gels can change their volume by a thousand fold by a change of pH [1].

Gels may be classified in several different ways: a) according to their electric charge [2], b) profiles of their physical structure [4], c) structural and mechanical properties [5]; and d) the nature and strength of the crosslinks (covalent, van der Waals, hydrogen bonding, Coulombic, hydrophobic, etc.) [6,7].

Despite the long history of existence and use of gels, only in recent years have their unique properties so widely attracted the attention of investigators. This is because it has gradually been recognized that gels readily and remarkably respond to the tiniest of stimuli in the form of variations in: temperature [8-11], solvent [12,13], pH [14-16], ionic strength [17], electric field [18,19], mechanical pressure [20], light [21-23], biochemicals [24], etc. Thus, it has become fashionable to use the term "intelligent gels" to convey these responsive characters [25,26].

Investigation of these properties have not only expanded our fundamental knowledge of the material properties and their governing laws, but have paved the ways for extending their promising novel applications in various fields (chemical, medical, pharmaceutical, food, petrochemical, biotechnological,...) [27-35].

Among the different stimuli mentioned, electric field is probably one of the simplest and the most convenient, because it can easily be applied, varied, and controlled [36,37]. Under the influence of a DC field the gels usually swell, contract or bend [38]. The type and the extent of such deformations depend on factors like shape and dimensions of the gel; its molecular composition and architecture, its position and orientation in the field, intensity and duration of the field, composition of the internal and the bathing media, temperature, etc. [39-41].

An attempt is made here to investigate the bending behavior of the partially hydrolyzed acrylamide gel rods

and develop a suitable physico-mathematical model for quantitative description of their behaviors.

EXPERIMENTAL

MATERIALS AND METHODS

Materials

Acrylamide, bisacrylamide, N,N,N',N'-tetramethylethylene diamine (TEMED), ammonium persulfate, dichlorodimethylsilane, sulfuric acid, sodium hydroxide, and ethanol were all chemically pure grade purchased from Merck (Darmstadt, Germany) and used without further purification.

Method

Gel preparation

Internal surfaces of glass capillaries (1.2 mm ID) were silanized with dichlorodimethylsilane following the standard procedures and washed thoroughly with distilled water [42]. Acrylamide-bisacrylamide gels were prepared via free radical polymerization in these capillaries using ammonium persulfate and TEMED initiators according to the well known procedures [43,44]. After their formation (≈ 30 min) the gels were carefully removed from capillaries using a gentle water pressure and washed with large quantities of water to removed residual unreacted monomers additives and other soluble components. Gels were then placed in a solution of TEMED (pH=12) for two months or longer for their gradual hydrolysis (conversion of $-\text{CONH}_2$ to $-\text{COOH}$ and $\text{COO}^- \text{NH}_4^+$ groups) [45,46].

Characterization of gels

For each gel prepared the following properties were determined: density, swelling ratio, carboxyl content, and the average pore size.

Density: Gel densities were determined by placing gel samples in a gelatin density gradient column. The value obtained was 1.034 g/cm^3 .

Swelling ratio: After hydrolysis gels were placed in distilled water until they reached their equilibrium swelling and their diameters were then measured under a microscope. The extent of swelling is expressed as:

$$V^*/V = (D^*/D)^3 \quad (1)$$

where V and V*, D and D* respectively represent volumes

and diameters before, and after swelling. The value obtained was 37.

Carboxyl content: This was determined by titrating the -COO^- groups on the gel with 10^{-2}M sodium hydroxide for which a value of 10^{-3}M/cm^3 was found.

Average pore size: For a 5% acrylamide gel which is hydrolyzed for 2 months, a value of 25 nm. was found in the literature [47].

Gel deformation under D.C electric field

A $3\text{cm}\times 3\text{mm}$ piece of the gel rod that had reached equilibrium swelling was placed in a glass cell filled with distilled water parallel to identical platinum electrodes ($1\times 4\text{ cm}\times \text{cm}$, 3 cm apart), Fig. 1. In experiments reported here an electric field of 10 V cm^{-1} at a current density of 10^{-4} A cm^{-2} was applied, and the gel was free and unbound, except for a few cases wherein it was kept fixed by two tiny pins on the sides near the middle to prevent its migration towards any of the electrodes, but allow it to bend in either direction. The extent of bending, is defined as the distance the end of the gel deflects from its initial position. The sign is considered positive if bending takes place towards the negative electrode (cathode) and negative if it occurs towards the anode.

RESULTS

The speed and extent of bending under the electric field was found to depend on the following internal and external parameters:

1. Charge density: This was found to be an increasing function of the hydrolysis time. Nonhydrolyzed gels, as expected do not respond to electric field, but as the hydrolysis time increases the charge density and swelling capacity of the gel increases (up to the 80 days that was studied).

2. Gel thickness (diameter): Fig. 2 shows that bending is an inverse function of the gel diameter.

3. Gel length: Bending was found to be directly proportional to the length and inversely related to the square of diameter, Figs. 3-4.

4. pH of bathing solution: As the pH increases from 7 to 11, the number of cycles the gel would bend towards anode/cathode increases, Figs. 5-7.

5. Intensity of the electric field: The onset of bending occurs at 1 V/cm , Fig. 8.

6. Duration of the Electric field: Gels begin, at first to

bend towards cathode but gradually unbend and reach their initial straight parallel position and later bend in the opposite direction, Fig. 9.

7. Elasticity of deformation: A gel deformed under a field of 10 V/cm for 2 min. gradually retracts to its original shape after removal of the field, Fig. 10.

DISCUSSION

As can be seen from Fig. 2 the extent of deformation is dependent on the number of the -COO^- groups on the gel. It has been reported that when such a gel bends toward cathode it swells and when towards anode, it contracts [40-48]. The swelling behavior of polymeric gels under electric fields can be adequately described by the Flory-Huggins theory [49]. For a neutral gel, deformation is governed principally by two opposing forces: a) solvent-polymer interaction tending to swell the gel, b) elasticity of the polymer network comprising the gel matrix [50-51]. In gels with fixed charges, according to Donnan equilibrium, the concentrations of mobile ions inside and outside the gel are not equal. This in turn leads to an excess osmotic pressure and swelling of the gel [52-54] (ionic osmotic pressure):

$$\Delta\Pi = RT \sum (C_{ig} - C_{is}) \quad (2)$$

Where C_{ig} and C_{is} respectively are ionic concentrations in the gel and the bathing solution. It is this excess pressure that is affected by the applied electric field, ie. When it increases, it causes swelling and when decreases it leads to contraction.

In gels under consideration the fixed ions are the negatively charged -COO^- groups while the mobile counterions involved are H^+ and NH_4^+ . Under the electric field, these mobile cations within the gel move towards the cathode, while ions in the bathing solution which move in different speeds towards their respective electrodes, enter into the gel in opposite directions. With time, the concentration of NH_4^+ in the anodic side of the gel decreases while that of the cathodic side increases, Fig. 11. Consequently the osmotic pressure in the two sides of the gel become unbalanced ($\Delta\Pi_{\text{anodic}} > \Delta\Pi_{\text{cathodic}}$) and the gel bends accordingly, Fig. 11. The situation in the anodic side is schematically depicted in Fig. 12.

The dependence of osmotic pressure in acrylic gels on the internal concentration of the cation has been studied by others [55]. It has been shown that at low cation

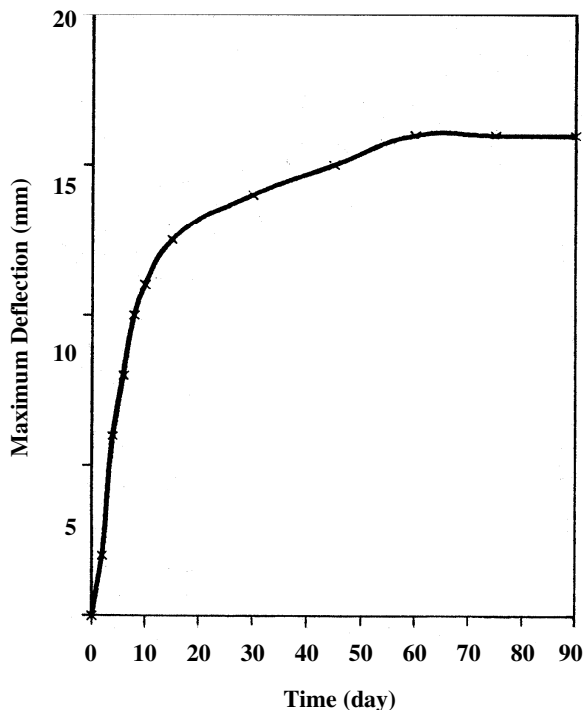


Fig. 1: Maximum deflection of the gel rod as a function of the hydrolysis period (network charge density). Gel length 3 cm, diam. 4 mm, electrodes 3 cm a part, electric field: 10 V/cm.

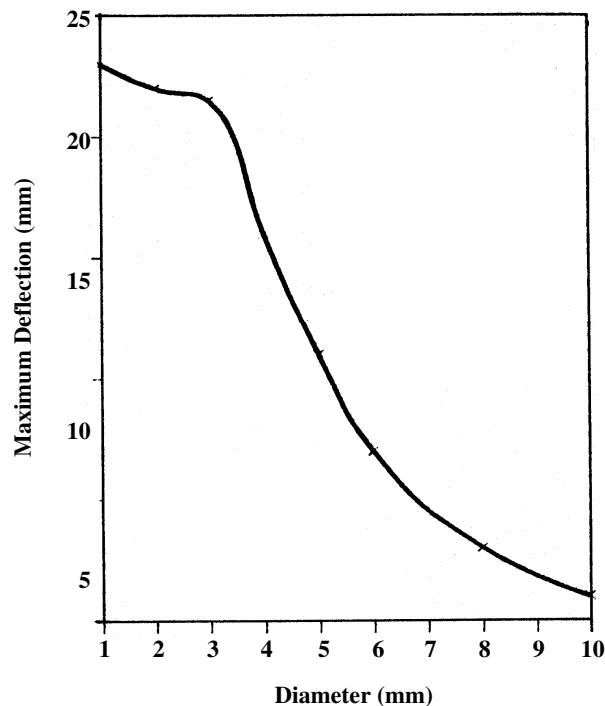


Fig. 3: Bending behavior as a function of gel rod diameter (hydrolysis time: 2 months, sample length 3cm, diam 4 mm, electric field 10 V/cm, electrodes 3 cm apart).

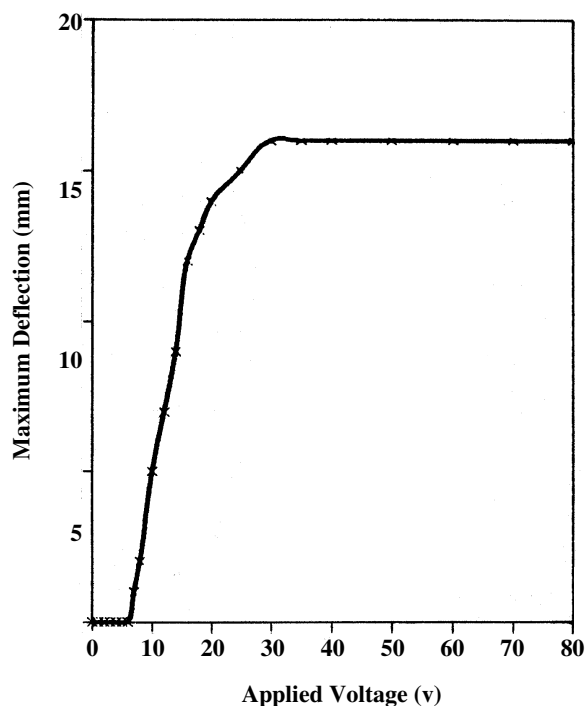


Fig. 2: Bending behavior of the gel rod (after 2 months hydrolysis) as a function of applied electric field (other conditions same as in Fig. (1)).

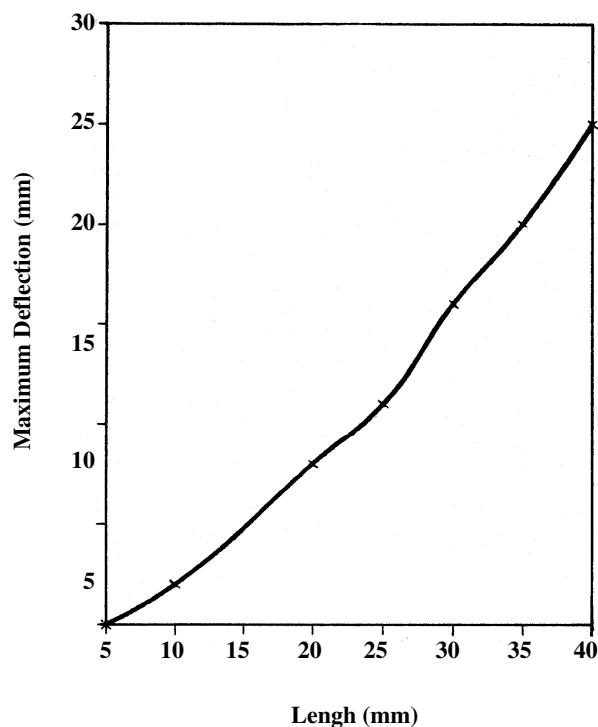


Fig. 4: Bending as a function of length of gel rod (conditions as in Fig. (3)).

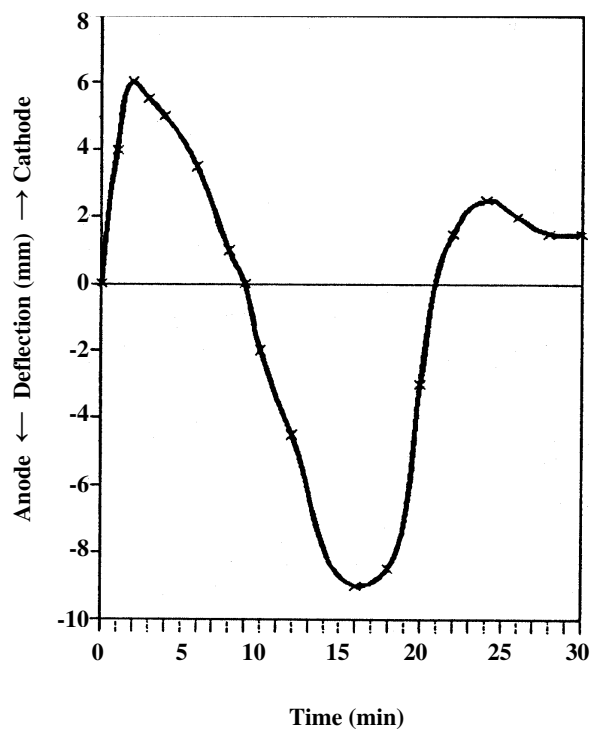


Fig. 5: Bending cycles of the gel rod at pH 7.5 (conditions as in Fig. (3)).

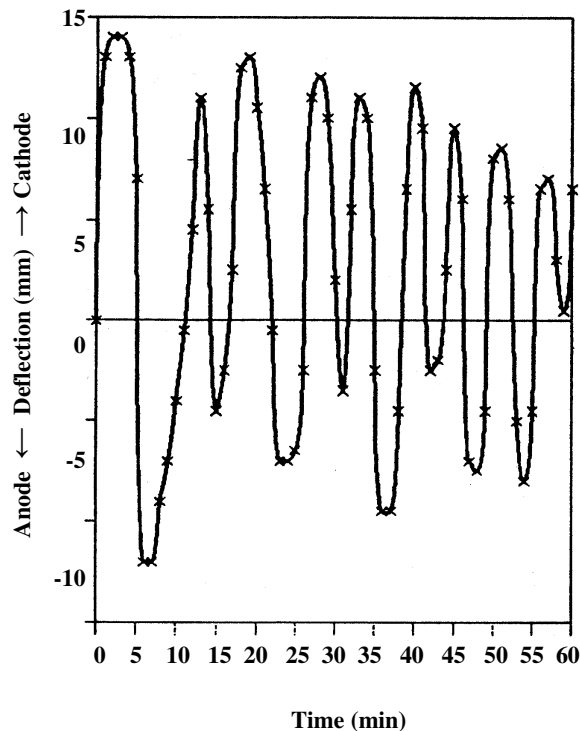


Fig. 7: Bending cycles of the gel rod at pH 11.0 (conditions as in Fig. (3)).

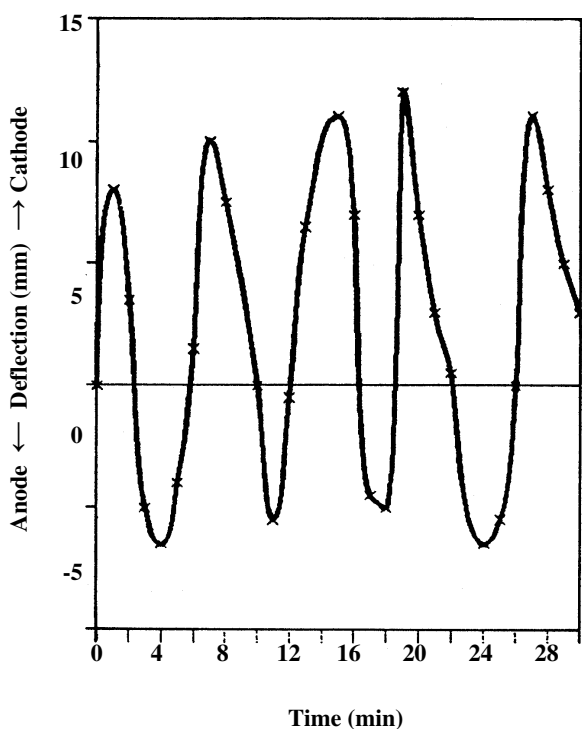


Fig. 6: Bending cycles of the gel rod at pH 9.5 (conditions as in Fig. (3)).

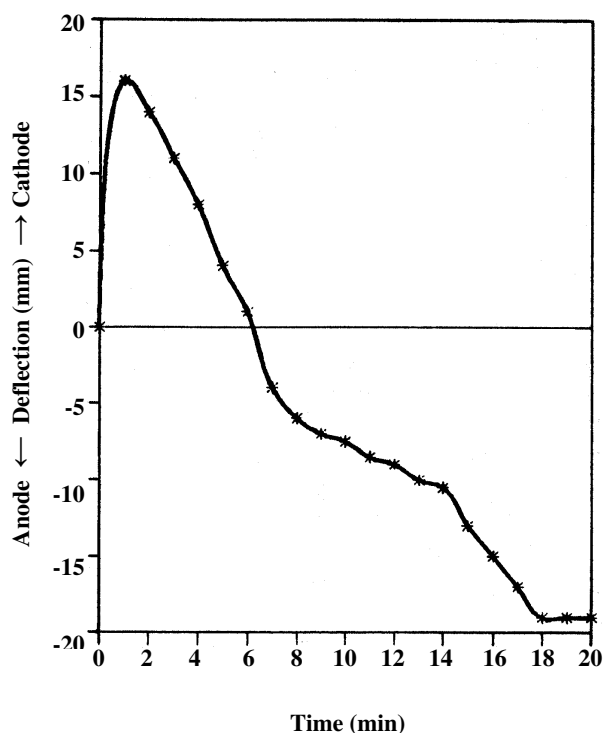


Fig. 8: Bending behavior of the gel rod under sustained electric field (conditions as in Fig. (3)).

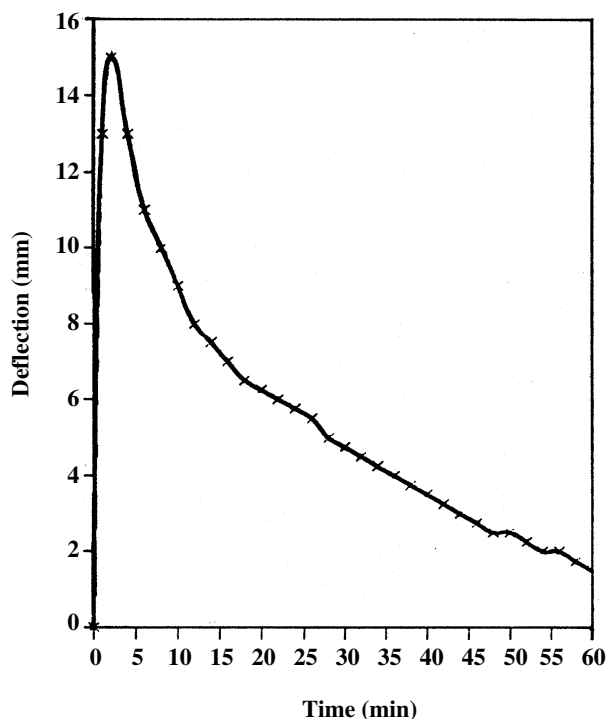


Fig. 9: Retraction of deflected gel rod after removal of the electric field (conditions as in Fig. (3)).

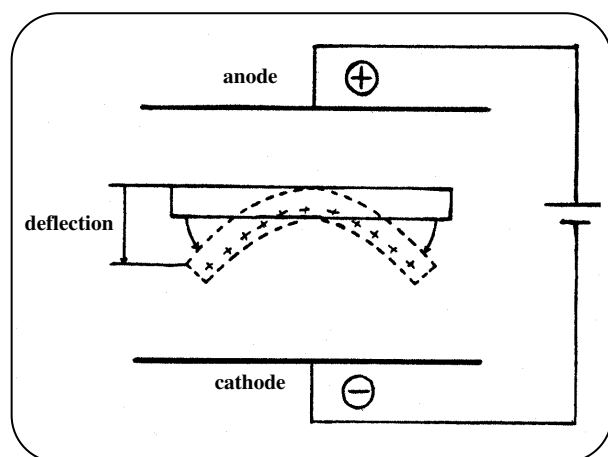


Fig. 10: Schematic diagram of gel deflection towards cathode.

concentrations, the $-\text{COOH}$ groups undergo partial dissociation. With the increase in cation concentration the degree of dissociation increases towards a maximum. Thereafter, a decrease in osmotic pressure occurs because the cations can leave the fully ionized gel, lessening the difference in osmotic pressure between the gel and the bathing solution. Due to similarity of those gels with the ones studied here, their data is directly applicable. Since the concentration of NH_4^+ in the anodic region of the gel

tends to decrease as a function of time from its initial value of 10^{-3}M , while the negative fixed charges increase, i.e. the anodic side must swell, thereby causing bending towards the cathode.

On the other hand due to electrolysis of water there is a gradual build up of concentration H^+ in the anode and of OH^- in the cathode. The former may enter the anodic region of the gel where it can replace NH_4^+ ions on the gel, owing to its preferred selection by the $-\text{COO}^-$ groups, [37] thereby producing neutral $-\text{COOH}$ groups, and reducing repulsion between the fixed charges which in turn leads to lowering of $\Delta\Pi_{\text{anodic}}$. At the same time the electrostatic repulsion between the $-\text{COO}^-$ groups diminishes. These all cause the subsequent contraction of the anodic region and bending of the gel rod towards the anode, Fig. 12.

In every point during bending, the osmotic pressure difference between the anodic and cathodic regions of the gel, $\Delta\Pi$, is balanced by the corresponding deformational stress, σ . Assuming $\Delta\Pi$ is equivalent to σ_{max} in a three-point mechanical bending of solid rods, one can write: [56,57].

$$\Delta\Pi = \sigma_{\text{max}} = \frac{6DEY}{L^2} \quad (3)$$

$$Y = \text{const} \cdot \Delta\Pi \quad (4)$$

where E is the Young (elastic modulus), Y the extent of bending, D gel diameter, and L is the gel length prior to bending. Differentiating the above equation with respect to time allows one to calculate the rate of bending. Data depicted in Fig. 6 and 7 are in good agreement with the above relation.

THEORETICAL ANALYSIS

Swelling of Ionic Polymer Networks

When a polymer network is in contact with a solvent medium, the solvent is absorbed due to its interaction with the polar, ionic or other special groups causing it to swell while at the same time the network opposes expansion of its structure as a consequence of going from a high entropy state to lower ones [49,5]. In the absence of electrical charges these two forces balance each other and at equilibrium,

$$(\Delta\mu)_t = (\Delta\mu)_{\text{mix}} + (\Delta\mu)_{\text{el}} = 0 \quad (5)$$

where $(\Delta\mu)_{\text{mix}}$ is the change in chemical potential due

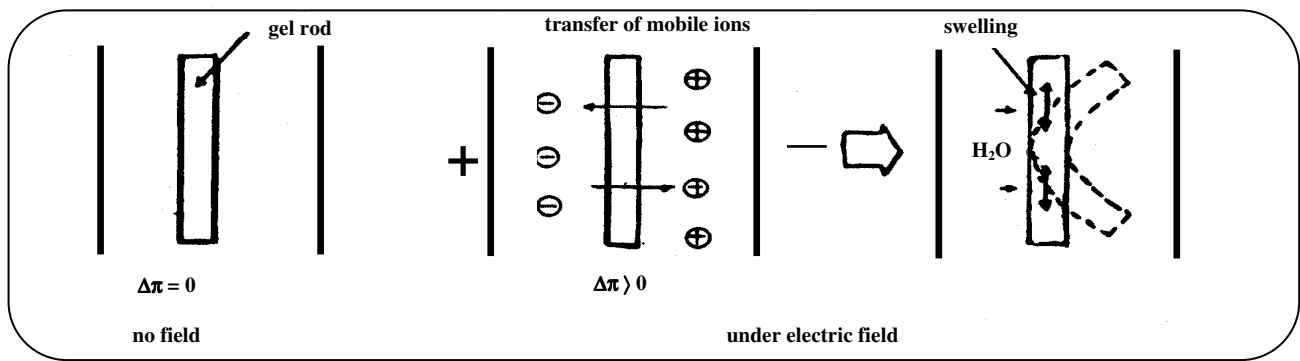


Fig. 11: Schematic representation of deflection mechanism.

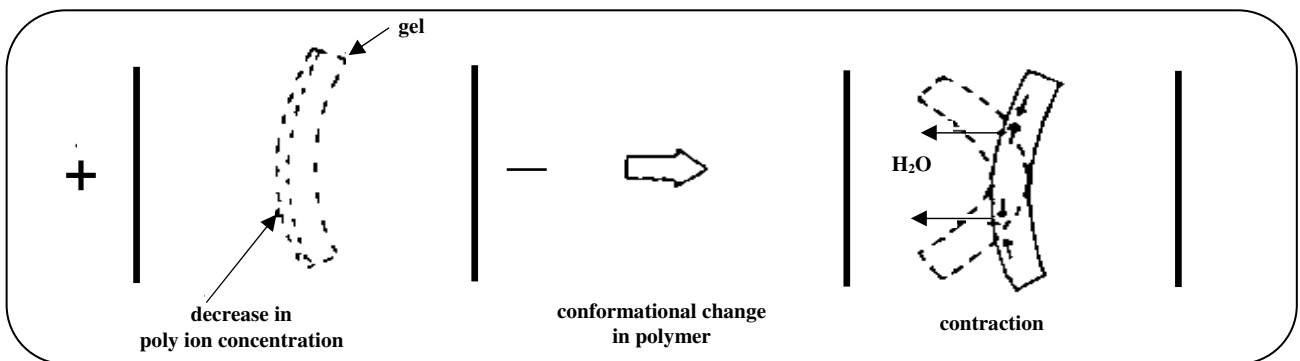


Fig. 12: Mechanism of bending towards anode.

mixing of solvent with the polymer network and $(\Delta\mu)_{el}$ is the change in chemical potential arising from the elastic expansion of the polymer network. At equilibrium the swelling pressure reduces to zero, [58] i.e.

$$(\Delta\mu_1/\bar{V}_1) = 0 \quad (6)$$

where $(\Delta\mu)_1$ and V_1 respectively represent the change in chemical potential and the partial molar volume of the solvent within the gel. In the case of networks with fixed charges, the concentrations of mobile ions inside the gel are different from the external bathing solution, and as is well known it leads to an additional contribution to the osmotic pressure difference [52,59]. Thus, at equilibrium:

$$(\Delta\mu)_t = (\Delta\mu)_{mix} + (\Delta\mu)_D = 0 \quad (7)$$

$$\pi_{net} v + RT \sum_i (C_{ig} - C_{is}) = 0 \quad (8)$$

where R is the gas constant, T the temperature, $(\Delta\mu)_D$ the chemical potential difference due to Donnan (unequality of mobile ion concentrations), C_{ig} and C_{is} respectively are the mobile ion concentration inside and outside the gel, and v is the gel volume. The equilibrium

volume of the gel can be calculated from Eq. (8). However, since deformation of the gel is a consequence of its anisotropic change in volume, only the second term in this equation needs to be taken into consideration. Under the Donnan equilibrium condition, the tendency of ions to leave the gel in response to their concentration gradient is balanced by the force exerted on them by the generated potential field at the gel/solution boundary, $\Delta\tilde{\Psi} = \tilde{\Psi}_g - \tilde{\Psi}_s$ [37, 60, 61]. Hence the Donnan ratio p is defined as:

$$p = C_{ig}/C_{is} = \exp(-z_i \Delta\Psi) \quad (9)$$

where z_i represents the valance of the mobile ion, $\Delta\Psi = F(\Delta\tilde{\Psi}/RT)$, F is the Faraday's number and R is the gas constant. To determine $\Delta\pi$ in the absence of an applied field, it is necessary to find the concentration of the ionic species and the difference in the electrical potential. This will set the initial conditions for the submerged gel exposed to an applied electric field [62]. In view of charge neutrality:

$$C_{as} + C_{Hs} = C_{bs} = C_{OHs} \quad (10)$$

$$C_g + C_{Hg} = C_{bg} + C_{OHg} + C_{cg} \quad (11)$$

Where C is the concentration and subscripts a, b, c, H and OH respectively represent the mobile anions cations, fixed carboxyl ions, proton and hydroxyl ions in the gel, g, and in the bathing solution, s.

$$C_{Hs} \cdot C_{OHs} = C_{Hg} \cdot C_{OHg} = K_w \quad (12)$$

$$(C_{Hg} - C_{cg}) / (C_m - C_{cg}) = K_g \quad (13)$$

where C_m is the total concentration of carboxyl groups in the gel and K_g is the relevant dissociation constant.

Equations (5)-(13) represent 8 equations with 10 unknowns. Thus, a prior knowledge of two of them will aid determining the rest. To this end the dependence of $\Delta\pi$ on C_{as} and C_{bs} is attempted. From equations (11) and (12) the concentration of H^+ or OH^- in solution is found as:

$$C_{Hs} = 1/2 \left[C_{bs} - C_{as} + ((C_{as} - C_{bs})^2 + 4K)_1^{1/2} \right] \quad (14)$$

If $C_{as} > C_{bs}$; solution is alkaline, and if $C_{as} < C_{bs}$, it is acidic. Considering equations (9)-(13), one can write:

$$(p - \frac{1}{p})(C_{as} + C_{Hs}) = \frac{C_m K_g}{p C_{Hs} + K_g} \quad (15)$$

Thus a knowledge of C_{as} and C_{bs} allows the determination of C_{Hs} from Eq. (14), p from Eq. (15), and the osmotic pressure difference, $\Delta\pi$ from Eq. (8):

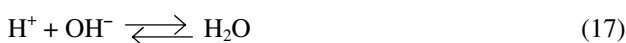
$$\Delta\pi/Rt = (p + 1/p - 2)(C_{as} + C_{Hs}) \quad (16)$$

Dynamics of Ions

Up to this point the equilibrium conditions in the absence of an external electric field, i.e. the initial conditions were considered. Now we attempt to determine the profile of ionic distribution under an applied electric field in one dimension. The results can then easily be extended to three dimensions.

Kinetic Equations

These equations express the spatio-temporal distribution of the five ions involved, (C_a , C_b , C_H , C_{OH} and C_c). Concomitant with the migration of ions within the gel the following equilibria are operative at every point:



Assuming a and b are univalent, their flux under the influence of the electric field may be expressed as:

$$J_i = J_d + J_e \quad (19)$$

where J_i is the flux of ion i, J_d is the diffusive flux, and J_e represents the flux due to the applied electric field. Hence according to Fick's second law in one dimension:

$$\frac{\partial C_i}{\partial t} = \left(\frac{\partial J_i}{\partial x} \right)_t \quad (20)$$

$$\frac{\partial C_a}{\partial t} = D_a \frac{\partial}{\partial x} \left(\frac{\partial C_a}{\partial x} + C_a \frac{\partial \Psi}{\partial x} \right) \quad (21)$$

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial}{\partial x} \left(\frac{\partial C_b}{\partial x} + C_b \frac{\partial \Psi}{\partial x} \right) \quad (22)$$

Here D_a and D_b represent the diffusion coefficients of a and b in the gel.

In the case of H^+ , OH^- and COO^- the kinetic equations must as well include the influence of their respective equilibria, Eqs. (13) and (14). Hence:

$$\frac{\partial C_H}{\partial t} = D_H \frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial x} \right) + C_H \left(\frac{\partial \Psi}{\partial x} \right) + r_1 + r_2 \quad (23)$$

$$\frac{\partial C_{OH}}{\partial t} = D_{OH} \frac{\partial}{\partial x} \left(\frac{\partial C_{OH}}{\partial x} \right) + C_{OH} \left(\frac{\partial \Psi}{\partial x} \right) + r_1; \frac{\partial C_c}{\partial t} = r_2 \quad (24)$$

where r_1 and r_2 respectively represent the amount of ions formed (or disappeared) as a consequence of Eqs. (17) and (14), per unit time. The electric potential ψ is determined by the poisson equation. However, it is practically easier to numerically solve the problem by using the electroneutrality condition, Eqs. (10) and (11) and inserting in Eqs. (21)-(23):

$$\sum_1 z_i D_i \frac{\partial}{\partial x} \left(\frac{\partial C_i}{\partial x} + z_i C_i \frac{\partial \Psi}{\partial x} \right) = 0 \quad (24)$$

the current density will be:

$$I = F \sum_i z_i J_i \quad (25)$$

$$I = F \sum_1 z_i D_i \left(\frac{\partial C_i}{\partial x} + z_i C_i \frac{\partial \Psi}{\partial x} \right) \quad (26)$$

The latter equation guarantees the constancy of the electric current (its derivative is zero). Assuming that dissociation-association reactions occur much faster than diffusion, use can be made of Eqs. (21) and (22) to

determine C_a and C_b . Replacing these in Eqs. (11-14) allows the determination of C_H , C_{OH} and C_c .

Gel-Solution Boundaries

According to Donnan equilibrium there is a discontinuity in the electrical potential and concentration of ions at the gel/solution boundaries. When the submerged gel is placed in an electric field, it is expected the distribution of ions at the boundaries to differ from that of the equilibrium state. However, if the field strength is not sufficiently high and the migration rate of ions are not very high, one can safely ignore the resultant distortion and write:

$$p = C_{ig}/C_{is} = \exp[-Z_i(\Psi_g - \Psi_s)] = \exp(-Z_i\Delta\Psi) \quad (27)$$

The last point to consider is the continuity equations for the ionic species a and b:

$$D_i \left(\frac{\partial C_{is}}{\partial x} + Z_i C_i \frac{\partial \Psi_s}{\partial x} \right) = D_i \left(\frac{\partial C_{ig}}{\partial x} + Z_i C_{ig} \frac{\partial \Psi_g}{\partial x} \right) \quad (28)$$

Numerical Solution

Initially, an equilibrium in the absence of the electric current is considered, i.e. when $t=0$, $C_a = C_a^0$ and $C_b = C_b^0$. The variation of concentration of ions as a function of time is found as follow:

1. Starting with given values of C_a at time t , the values of C_H , C_{OH} and C_c are obtained from the electroneutrality principle and equilibrium dissociation.

2. From a knowledge of C_i at time t , the value for $\partial\Psi/\partial x$ is derived from Eq. (26).

3. With the use of diffusion equations (21) and (22) and the boundary conditions (27) and (28), C_a and C_b for time $(t + \Delta t)$ are found and the process is reiterated.

Analytical Solution

When the bathing solution is alkaline the gel is in the fully ionized form, i.e. $C_c = C_m$. Thus in view of electroneutrality:

$$C_{as} = C_{bs} + C_{OHs} \text{ in solution}$$

$$C_{ag} = C_{bg} + C_{OHg} \quad C_m \text{ in gel}$$

Assuming the diffusion coefficients are equal, Eq. (26) can be simplified as:

$$D \frac{\partial}{\partial x} (\sum_i Z_i C_i) + D \frac{\partial \Psi}{\partial x} \sum_i C_i = I/F \quad (29)$$

In view of electroneutrality, the first term vanishes. If one defines the specific velocity as $U = I/FC_m$; it can be deduced from Eq. (29) that:

$$\frac{\partial \Psi}{\partial x} = \frac{I}{DF(C_a + C_b + C_{OH})}$$

$$\frac{\partial \Psi}{\partial x} = \frac{C_m}{2DC_a} U \quad \text{in solution} \quad (30)$$

$$\frac{\partial \Psi}{\partial x} = \frac{C_m}{D(2C_a - C_m)} U \quad \text{in gel} \quad (31)$$

Thus Eq. (21) can be written as:

$$\frac{\partial \Psi}{\partial t} = D \frac{\partial^2 C_a}{\partial x^2} \quad \text{in solution} \quad (32)$$

$$\frac{\partial \Psi}{\partial t} = D \frac{\partial^2 C_a}{\partial x^2} - \frac{\partial}{\partial x} \left(V \frac{C_m C_a}{2DC_a - C_m} \right) \quad \text{in gel} \quad (33)$$

The second term in (33) is small compared to the first and may be ignored. The boundary conditions are:

$$C_a|_g = p C_a|_s$$

$$C_a|_g = \frac{1}{2} \left[\frac{C_m}{C_a} + \left(\frac{C_m}{C_a} \right)^2 + 4 \right]^{1/2} \text{ Donnan equilibrium} \quad (34)$$

and for the continuity of ionic fluxes

$$-D \frac{\partial C_a}{\partial x} + \frac{VC_a C_m}{2C_a C_m} |_g = D \frac{\partial C_a}{\partial x} + \frac{V}{2} C_m |_g \quad (35)$$

From Eqs. (32)-(34), $C_a(x,t)$ can be determined, via Laplace transform:

$$p = \frac{1}{2} \left[\frac{C_m}{C_{as}} + \left(\frac{C_m}{C_{as}} \right)^2 + 4 \right]^{1/2} \quad (36)$$

$$\frac{\partial C_a}{\partial x} |_g - \frac{\partial C_a}{\partial x} |_s = \frac{V \bar{C}_a}{D} \quad (37)$$

wherein:

$$\bar{C}_a = \left(\frac{C_{ag}}{2C_{ag} - C_m} - \frac{1}{2} \right) C_m \quad (38)$$

Diffusion equations were solved using the Laplace transform and integrations were carried out with the aid of a basic computer program. Representative results for a gel located between electrodes are plotted in Fig. 13. As can be seen the cation concentration in the anodic region of the gel decreases as a function of time whereas in

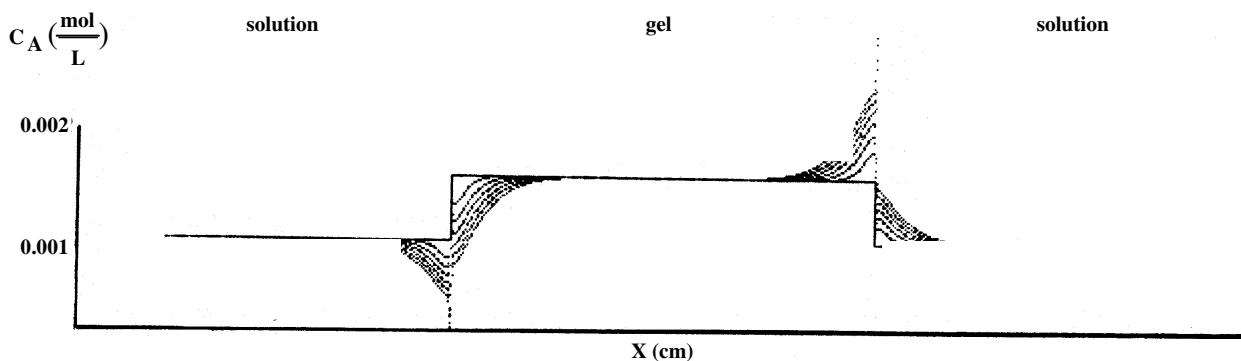


Fig. 13: Theoretical concentration profile of ions at the gel/solution boundaries, as function of time

the cathodic region it increases. $\Delta\pi$ is an increasing function of the decrease in concentration, thus causing the welling of the anodic side (and gel bends towards cathode). After reaching a maximum $\Delta\pi$ decreases with time and a gradual deformation in reverse direction begins. Numerical solution of the Eq. (16) also yields the same results.

CONCLUSIONS

The bending behavior of partially hydrolyzed polyacrylamide gel rods, submerged in water, in response to D.C. electric field is explained as follows:

1. The electric field establishes an osmotic gradient within the gel, the anodic side being higher, causing it to bend towards cathode.

2. With progressive hydrolysis of water, proton migration from the anode into the gel side facing it, converts the charged $-\text{COO}^-$ groups to neutral $-\text{COOH}$ groups, reducing their repulsion and contraction of the gel in the anodic region and gradual reverse deformation and bending towards anode.

3. The extent and rate of deformation is dependent on: charge density on the gel, length and thickness, electric field intensity, temperature, and the pH of the bathing solution.

4. In all cases, bending of the gel rods obeys the equation for the three-point mechanical deformation of solid rods.

5. A theoretical formulation for quantitative description of electrically induced deformation of submerged polyanionic gels is developed, which is capable of making satisfactory predictions, namely:

- a) When the gel rod is placed parallel to electrodes the concentration of cation decreases in its anodic side, leading to an increase in $\Delta\pi$ (swelling) in that region and bending of the gel ends towards cathode.

- b) After reaching a maximum $\Delta\pi$ begins a diminishing trend which together with the decrease in network Coulombic repulsions cause a gradual deformation in the reverse direction.

Acknowledgement

The authors wish to express their appreciation to the Research Council of Tehran University for their support of this project.

Received : 10th, January, 2000 ; Accepted : 27th, July, 2003

REFERENCES

- [1] Shibayama, M., Tanaka, T., *Adv. Polym. Sci.*, **109**, 54 (1993).
- [2] Ratner, B. D., Hoffman, A. S., in: "Hydrogels for Medical and Related Applications". Andrade, J.D.(Ed.), CRC Press, Florida, 1 (1976).
- [3] Sperling, L. H., "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, 121 (1981).
- [4] Peppas, N. A., Nikosi, A. C., in "Hydrogels in Medicine and Pharmacy" Peppas, N. A. (Ed.), CRC Press, Boca Raton, Florida, 1 (1987).
- [5] Peppas, N. A., Barr-Howell, B.D., in: "Hydrogels in Medicine and Pharmacy". Peppas N. A. (Ed.), CRC Press, Boca Raton, Florida, 27 (1987).
- [6] Iman, F., Tanaka, T., Kokufuta, E. *Nature*, 349, 400 (1991).

- [7] DeRessi, D., (Eds.), "Polymer Gels", Plenum Press (1991); Tanaka, T., *Sci. Amer.*, **244**, 110 (1981); Tanaka, T., in: "Encycl. Polym. Sci. Technol.", H.F. Mark, Ed., Wiley, N. Y., Vol. 7, pp. 713 (1987).
- [8] Otake, K., H., Komo, M., *Macromol.*, **23**, 283 (1990).
- [9] Katayana, S., *J. Phys. Chem.*, **96**, 5209 (1992).
- [10] Tanaka, T., *Phys. Rev. Lett.*, **40**, 820 (1978).
- [11] Tanaka, T., *Phys. Rev. Lett.*, **45**, 1636 (1980).
- [12] Tanaka, T., Amiya, T., *Macromol.*, **20**, 1162 (1978).
- [13] Katayana, T., Ohta, A., *Macromol.*, **18**, 2781 (1985).
- [14] Katchalsky, A., Kunzle, O., Kuhn, W., *J. Polym. Sci.*, **5**, 283 (1950).
- [15] Hirokawa, Y., Tanaka, T., Katayana, S., *Life. Sci. Res. Rep.* **31**, 177 (1984).
- [16] Hirokawa, Y., Tanaka, T., *J. Chem. Phys.*, **81**, 6379 (1985).
- [17] Ohmin, I., Tanaka, T., *J. Chem. Phys.*, **77**, 5725 (1982).
- [18] Shiga, T., Hirose, Okada, A., *J. Appl. Polym. Sci.*, **46** (41), 635 (1992).
- [19] Shiga, T., Hirose, Y., Okata, A., Korauchi, I., *J. Appl. Polym. Sci.*, **47** (1), 113 (1993).
- [20] Onoki, A., *Phys. Rev. A.*, **36**, 2192 (1988).
- [21] Irie, M., *Macromol.*, **19**, 2890 (1986).
- [22] Suzuki, A., Tanaka, T., *Nature*, **346**, 245 (1990).
- [23] Mamada, A., Tanaka, T., Ine, M., *Macromol.*, **23**, 1517 (1990).
- [24] Kokufuta, E., Tanaka, T., *Macromol.*, **24** (7), 1605 (1991).
- [25] Kishi, R., Hara, M., Sawahata, K., Osada, Y., in: "Polymer Gels", DeRessi, D., et al. (Eds), Plenum Press, New York, 205 (1991).
- [26] Katchalsky, A., Elsenberg, H., *Nature*, **166**, 207 (1950).
- [27] Park, T. G., Hoffman, A. S. *Biotechnol. Prog.*, **10**, 82 (1994).
- [28] DeRessi, D. Chiarelli, P., *Progr. Colloid. Polym. Sci.*, **78**, 4 (1988).
- [29] Chicreli, P., Basser, P. J., Derossi, D., Goldstein, S., *Biorheology*, **29**, 381 (1992).
- [30] Kabara, B. G., Gchike, S. H., *Polym. Mater. Sci. Eng.*, **69**, 533 (1993).
- [31] Frank, S., Lauterbur, P.G., *Nature*, **363**, 334 (1993).
- [32] Ross Murphy, S. B., Kajiwarak, K., *Nature*, **355**, 208 (1992).
- [33] Hoffman, A. S., Antonsen, K. P., *Polymer Preprints.*, **34** (1), 828 (1993).
- [34] Kwon, I. C., Bae, Y. H., Kim, S. W., *Nature*, **354**, 291 (1991).
- [35] Osada, Y., Okuza ki, H., Hori, H., *Nature*, **355**, 242 (1992).
- [36] DeRossi, D. E. et al., *Trans. Am. Soc. Artif. Intern. Organs.*, **32**, 157 (1986).
- [37] Grimshaw, P. E., Nussbum, J. H., *J. Chem. Phys.*, **93**, 4462 (1990).
- [38] Shiga, T., Kurauchi, T., *Polym. Progr. Jp.*, **34** (3), 508 (1985).
- [39] Shiga, T., Kurauchi, T., Hirose, Y., Okada. A. *J. Appl. Polym. Sci.*, **44**, 249 (1992).
- [40] Shiga, T., Kurauchi, T., Hirose, Y., Okada, A., *J. Appl. Polym. Sci.*, **39**, 2305 (1990).
- [41] Shiga, t., Kurauchi, T., Hirose, Y., Okada, A., *Intell. Mater. Sys. Structures.*, **4**, 553 (1993).
- [42] Westermeier, R. "Electrophoresis in Practice", 3d Ed, Wiley-VCH, Weinheim (2001).
- [43] Tanaka, T., Nishio, I., Sun, S., Ueno-Nishio, S., *Science*, **218**, 467 (1982).
- [44] Fang, L., Brown, W., *Macromol.*, **25**, 3137 (1992).
- [45] Sandler, S. R., Karow, W., "Polymer Synthesis" Academic Press, New York, Vol. II, 27 (1977).
- [46] Ilavsky, M., Hrouz, J., Stejskai, J., Bouchal, K., *Macromol.*, **17**, 2868 (1984).
- [47] Gordan, A. H.(Ed.) in "Electrophoresis of Proteins in Polyacrylamide and Starch Gels", *Elsevier Sci. Pub.* Amesterdam, (1983).
- [48] Baughnam, R. H., Shackette, L. W., in: "Structure and Dynamics of Biopolymers" Nicoline, C. (Ed); *Martinus Nihoff. Pub.*, London, 559 (1987).
- [49] Flory, P. J. "Principles of Polymer Chemistry", Cornell University Press. Ithaca, Chapter 13 (1953).
- [50] Flory, P. J., *J. Chem. Phys.*, **18**, 108 (1950).
- [51] Janas, V. F., Rodriguez, F., *Macromol.*, **13**, 977 (1980).
- [52] Iiavsky, M., *Macromol.*, **15**, 782 (1982).
- [53] Haper, H., Baker, J. P., Blanch, H. W., *Macromol.*, **23**, 1096 (1990).
- [54] Khokhlow, A. R., *Polymer*, **21**, 4 (1980).
- [55] Doi, M., Matsumoto, M., Hiros, Y., *Macromol.*, **24**, 4504 (1992).
- [56] McCrum, N. G., Buckley, C. P., Bucknall, C. B., "Principles of Polymer Engineering", Oxford University Press, 344 (1994).
- [57] Redriguez, F., "Principles of Polymer Systems", McGrow Hill, New York, Chapter 8, (1983).

- [58] Tanaka, T., *Polymer*, **20**, 969 (1979).
- [59] Hooper, H., Baker, J., Blanch, H. W., *Macromol.*, **23**, 1096 (1990).
- [60] Dorfner, K., "Ion Exchangers, Properties and Applications", Ann Arbor Science, Ann Arbor MI, (1972).
- [61] Helfferich, F., "Ion exchange", McGraw-Hill, New York 1962).
- [62] Shiga, T., Kurauch, T., *J. Appl. Polym. Sci.*, **39**, 2305 (1990).
- [63] Kreyszig, E. in: "Advanced Engineering Mathematics", Fifth Edition, John Wiley and Sons, N. Y. (1989).
- [64] Myint, U. T., "Partial Differential Equations of Mathematical Physics", 2nd. Ed., North-Holland, Publishers; Amsterdam (1989).