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SWELLING KINETICS AND MECHANISTIC ASPECTS OF THERMOSENSITIVE INTERPENETRATING POLYMER NETWORKS

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SWELLING KINETICS AND MECHANISTIC ASPECTS OF THERMOSENSITIVE INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

Full interpenetrating polymer networks (FIPNs) of cross-linked gelatin with polyacrylamide [Gelx-PAamx] and *N*-isopropylacrylamide [Gelx-PNIPAx] of several compositions were prepared, respectively. Their dynamic swelling studies as a function of temperature were monitored. The rate of swelling increased with the rise in ambient temperature for [Gelx-PAamx]. For [Gelx-NIPAx] with the increase in temperature above its LCST (lower critical solution temperature) (i.e., 32°C) decreased the swelling and below its LCST increased in swelling. From the Fickian equation, the transport mechanism for [Gelx-PAamx] was determined to be anomalous, and for [Gelx-PNIPAx] below its LCST is anomalous and above, is Fickian type of diffusion. The activation energies were determined from the initial rate of swelling, which were found to be positive for [Gelx-PAamx] ranging from 36 to 55 kcal/mol, whereas for [Gelx-PNIPAx], the values were negative ranging from −331 to −55 kcal/mol. The enthalpies for these FIPNS were also estimated.

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Key Words: Activation energies; Diffusion; Hydrogels; Swelling behavior; Thermosensitive

INTRODUCTION

A dry glassy hydrogel, when brought in contact with water, it swells and reaches equilibrium. The extent of swelling for the hydrogel depends on the external conditions such as temperature, pH, ionic strength, and solvent composition (1–6). The process by which a dry glassy hydrogel specimen imbibes water and swells to an equilibrium state is phenomenological and quantitatively akin to the sorption of penetrate molecule in a polymer matrix. Consequently, the thermodynamic and kinetic laws governing sorption are also applicable to the swelling processes. It has also been recognized that in situations, where sorption of a penetrate leads to significant swelling and dimensional changes of the polymer matrix, conventional Fick's law of diffusion does not apply as such, but requires modification.

The first step during the transport of penetrate through the homogenous matrix is the mixing of the penetrate molecule in the surface layer of the matrix. From here, through a process of diffusion driven by chemical potential gradient, the penetrate molecules migrate and pervade the entire matrix until the gel reaches an equilibrium. To accommodate these penetrate molecules, a finite number of Van der Waals' type and other interactions between chain segments have be broken. For a given polymer, the amount of energy required for this rearrangement will increase as the size and shape of the penetrate molecule increases. This picture immediately suggests that the swelling rate will depend on the relative rates of penetrate diffusion and segmental rearrangement, or in other words the segmental relaxation time.

Polymers exhibit a wide range of relaxation times related to a variety of relaxation modes. The overall swelling process will depend on these relaxation motions which occur on a time scale comparable to, or greater than, the diffusion rate of the penetrate. Indeed, a Deborah number can be defined as the ratio of the relaxation time to the diffusion time. When that number is very much less than unity, relaxation is the fast process, diffusion the slowest and hence, rate determining step. This is the typical Fickian behavior. When the segmental relaxation rate becomes slower than diffusion the Deborah number will have much greater than unity. If the number is close to unity, both processes occur on a comparable time scale (7–10).

Hence, it becomes explicit that deviations from Fickian behavior are a consequence of the finite rates at where, therefore, changes in the polymer structure occur in response to the stresses imposed upon the matrix during the swelling process. The swelling stresses and resultant creep effects to establish equilibrium are very important, because non-Fickian behavior can be related to either or both the changes in the structure or the stress per se.

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Thus, is general, the diffusion behavior and transport of small molecules in glassy polymers have been classified into 3 clear types, which can be distinguished by the shape of the swelling curve, represented by Equation (1) (11–14).

$$Q_t/Q_\infty = kt^n \tag{1}$$

where Q_t is the relative weight gain at time t and Q_∞ is the equilibrium weight gain at ∞ and k and n are constants (15–16).

Type 1: the Fickian system, where penetrate diffusion rate is the slowest and hence rate determining step ($n = 0.5$).

Type 2: the other extreme, called case 2, where the segmental relaxation processes are the slowest and hence, the rate determining step ($n = 1$).

Type 3: an intermediate situation called the anomalous type, when the penetrate mobility and segmental relaxation are on a comparable time scale ($0.5 < n < 1$).

Types 1 and 2 can be visualized as two limiting cases of transport processes with type 3 being an intermediate case, where both processes are operative in a coupled manner. The anomalous type is presumed to be operative in hard glassy polymers, which are below their T_g. Above the T_g, the behavior is confined to the Fickian type (17–18).

What kind of mechanism is operative in the hydrogels? Does the mechanism change with the temperature? What will be the values for activation energies for the swelling process? With these objectives in mind, we carried out the temperature-dependent swelling studies.

EXPERIMENTAL

Materials

Gelatin, 25% aqueous solution of gulateraldehyde (GLA), and acrylamide (Aam) were purchased from Loba Chemicals (Bombay, India). *N*-isopropylacrylamide (NIPA) was obtained from Eastman Kodak Company (Rochester, NY). The crosslinker bisacrylamide (bisAam) was obtained from Sisco (Bombay, India). The accelerator *N*,*N*,*N*,*N*-tetramethylethylenediamine (Temed) and initiator ammonium persulfate (APS) were from Spectrochemi (Bombay, India) and Sarabhai M. Chemicals (Baroda, India), respectively. Double distilled water was used for all the experiments.

Preparation of IPNs

The various compositions of [Gelx-PAamx] that are listed in Table 1 were prepared as reported (19). Required amounts of gelatin were dissolved in water at 100°C. To this aqueous solution, a calculated amount of Aam was added, stirred well, followed by bisAam (<4%), APS, and Temed. The solution was stirred

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Table 1. Compositions of [Gelx-PAamx] FIPNs

	Percentage of		
Sample Code	Gelatin	Acrylamide	Total Polymer
P1	5	5	10
P3	5	15	20
P4	5	25	30
G3	15	5	20
G5	25	5	30

thoroughly and poured between the rectangular glass plates separated by Teflon gaskets of 0.5-cm thickness. The system was left undisturbed overnight; a gelled slab was dislodged carefully, cut into circular discs of 1.6 cm in diameter, and immersed in 1% GLA solution for 6 hours. The crosslinked gels were washed thoroughly and dried at room temperature at constant weight. [Gelx-PNIPAx] hydrogels of various compositions, as indicated in Table 2, were prepared exactly by the same procedure used for [Gelx-PAamx] hydrogels.

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Swelling Kinetics

Swelling studies were monitored as a function of temperature (from 30°C to 60°C with intervals of 5°C). In a typical case the dried gel disk was weighed (w_i) and transferred into the water. At regular intervals the disk was removed from the water, its surface was pressed gently with tissue paper to remove excess water on the surface, weighted (w_t), and then transferred to the medium. This process of swelling and weighing was continued until the disk attained a constant final weight (w_t). The calculations were performed as follows:

$$\text{Degree of swelling at time } t \text{ DS} = wt - w_i/w_i \quad (2)$$

$$\text{Maximum degree of swelling DS}_{MAX} = w_f - w_i/w_i \quad (3)$$

Table 2. Compositions of [Gelx-PNIPAx]

	Percentage of		
Sample Code	Gelatin	NIPA	Total Polymer
Gelx	10	10	10
N1	8	2	10
N2	6	4	10
N3	5	5	10
N4	4	6	10
N5	2	8	10
PNIPax	0	10	10

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RESULTS AND DISCUSSION

Mechanistic Aspects of Swelling

The solvent diffusion into the hydrogel network is not passive diffusion into the void spaces of the network but includes a concomitant stretching of the network segments by advancing solvent front, which results in the plasticization of the material with a large change in the volume of the sample. Therefore, when treated from the sorption point of view, the time versus penetrate uptake curve more often than not deviate from the classical Fickian mode. What are the comparative rates for the solvent diffusion and the chain relaxation?

Our discussions are confined to the initial phase of swelling. During this phase, the dry and collapsed network is struggling to expand under the influence of the penetrating water molecules. The slope n of the double logarithmic plot of Equation (1) was computed using a simple computer program. The value of n indicates the type of transport mechanism.

The [Gelx-PAamx] is a full IPN, where the percentages of both components are on a comparable scale. The dynamic swelling curves and as well as maximum degree of swelling are shown in Figures 1 and 2, respectively. The swelling for

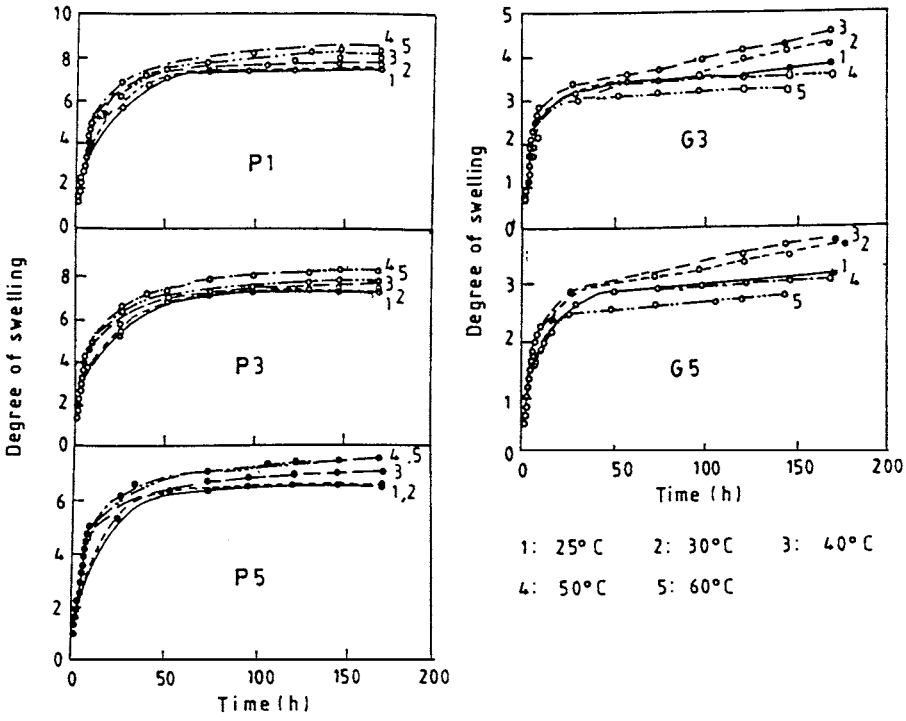

Figure 1. Dynamic swelling curves for [Gelx-PAamx] FIPNs at different temperatures. P_1..... and G_1..... as in Table 1.

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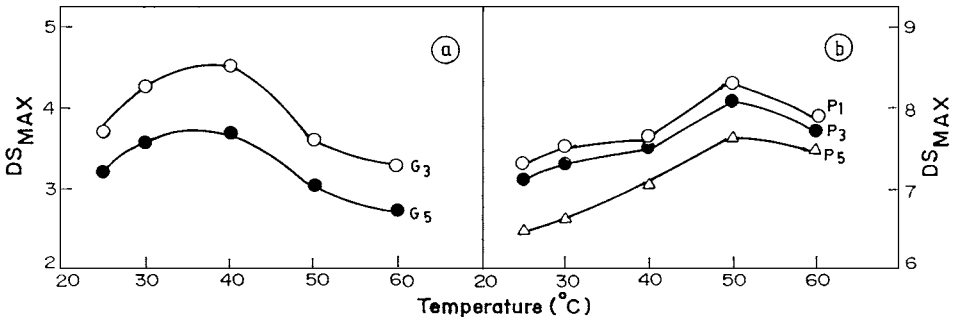

Figure 2. The maximum degrees of swelling for [Gelx-Paamx] FIPN gels as a function of (a) G_1..... and (b) P_1..... as in Table 1.

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these hydrogels exhibit a positive response with the rise in temperature. The general trend is an increase in the initial rate of swelling and as well as maximum degree of swelling, with the rise in temperature. However, there is a note of precaution, at temperatures above 40°C, the maximum degree of swelling declines. It is possible that these gels may not be thermostable. Because uncrosslinked gelatin gels melt into solution above 40°C, due to the rupture of innumerable hydrogen bonds that hold them together. With the breakage of the hydrogen bonds, the gels are held together only by GLA crosslinks. The weight gain registered on swelling, for the first 6 h, for the [Gelx-PAamx] samples, is substituted in Equation (4) (15,20).

$$\log(Q_t/Q_\infty) = n \log(t) \tag{4}$$

The values of n for the different gel compositions studied as a function of temperature are given in Table 3. The deviations are too small to be of any significance. Hence, it can be logically concluded that n is invariant with the temperature and composition. Both numerical calculations and graphical estimation yield a value of 0.6 for n.

This means a change from anomalous to the Fickian mode with an increase in temperature is not happening in this system, as has been suggested by several investigators (21,22). Although we were intrigued at first, subsequent differential

Table 3. n Values for [Gelx-PAamx] FIPNs at Various Temperatures

	n Values for					
Temperature (°C)	P1	P3	P5	G3	G5	PAamx
25	0.61	0.62	0.61	0.59	0.57	—
30	0.60	0.60	0.59	0.61	0.59	0.58
40	0.56	0.59	0.60	0.59	0.56	0.57
50	0.57	0.57	0.57	0.56	0.55	0.58
60	0.52	0.54	0.59	0.52	0.52	0.59

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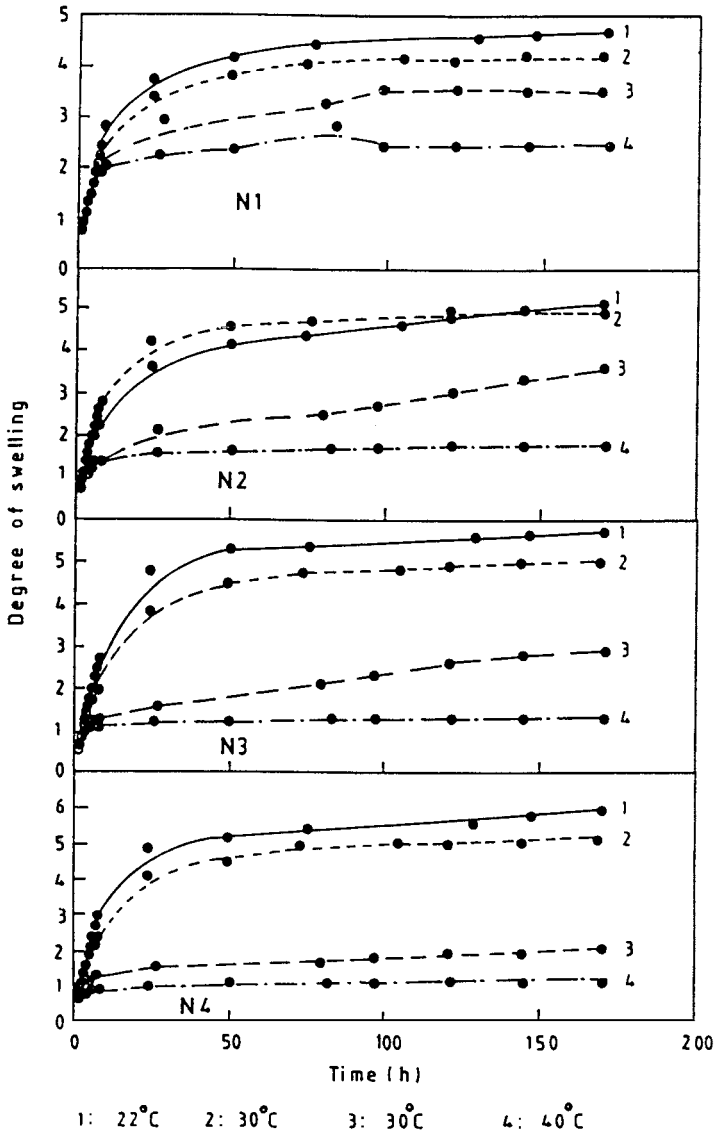

Figure 3. Dynamic swelling curves for [Gelx-PINPAx] FIPNs at different temperatures. N1.... N4 as in Table 2.

scanning calorimetric experiments provided a satisfactory explanation. Glutaraldehyde crosslinked gels did not register a T_g in their thermograms. This is perfectly understandable, because gelatin being a protein decomposes on heating before it can soften or melt (23). Indeed, we observed that above 40°C, the gels lose mechanical strength, become soft, and a general degradation process in the protein sets in at higher temperature (5). This presumably could be the reason why temperature induced anomalous to Fickian mode is not seen at all.

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The uniqueness of [Gelx-PNIPAx] system shows up in the n values and reflects on the mechanism of swelling. The dynamic swelling curves of this system are shown in Figure 3. The n values computed as in the case of the previous systems are complied in Table 4. At temperatures below the LCST (22°C and 30°C), the gels have an average value of 0.6 (20). Above the LCST (i.e., at 35°C and 40°C) the gels rich in PNIPA register a conspicuous decrease in n value. For example, at 40°C pure PNIPAx gel has an n value as low as 0.34. What does this imply? We believe that this reflects the increased propensity of the PNIPA segments to resist the advancing solvent molecules. At 40°C, the gel is above it LCST and in a collapsed state with the predominantly hydrophobic character (Fig. 4).

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The Activation Energies for Swelling

Important information regarding the activation energies of swelling can be obtained by the analysis of the initial rates of swelling. The Flory-Rehner model treats the volume change that accompanies the swelling of crosslinked polymer network in terms of two interrelated processes in operation (24).

$$\Delta F_{\text{swelling}} = \Delta F_{\text{mix}} + \Delta F_{\text{el}} \tag{5}$$

Several theoretical models have been proposed that calculate the mixing contribution from the lattice theory and the elastic contribution from the affine or phantom network theory (25–27). Conceptually, the term on the right-hand side of the equation collectively stands for the solvent-induced plasticization of the network, which is essentially the kinetically envisaged penetrant diffusion and consequent chain-stretching process.

The rate of swelling during the first 15 minutes at different temperatures is calculated from the dynamic swelling curves. This phase essentially includes the entry of water molecules into the glassy network and the resultant unfolding and stretching of the crumbled segments. We have not attempted to itemize the individual contributions of the process involved because this would necessitate a large number of disputable assumptions. Moreover, swelling is a physical phenomenon and the rate depends on both the polymer weight fraction and the size and shape

Table 4. n Values for [Gelx-PNIPAx] FIPNs at Various Temperatures

	n Values for					
Temperature (°C)	N1	N2	N3	N4	N5	N6
22	0.57	0.60	0.61	0.63	0.64	0.56
30	0.57	0.61	0.58	0.59	0.57	0.46
35	0.57	0.49	0.51	0.52	0.48	0.29
40	0.5	0.50	0.47	0.38	0.46	0.34

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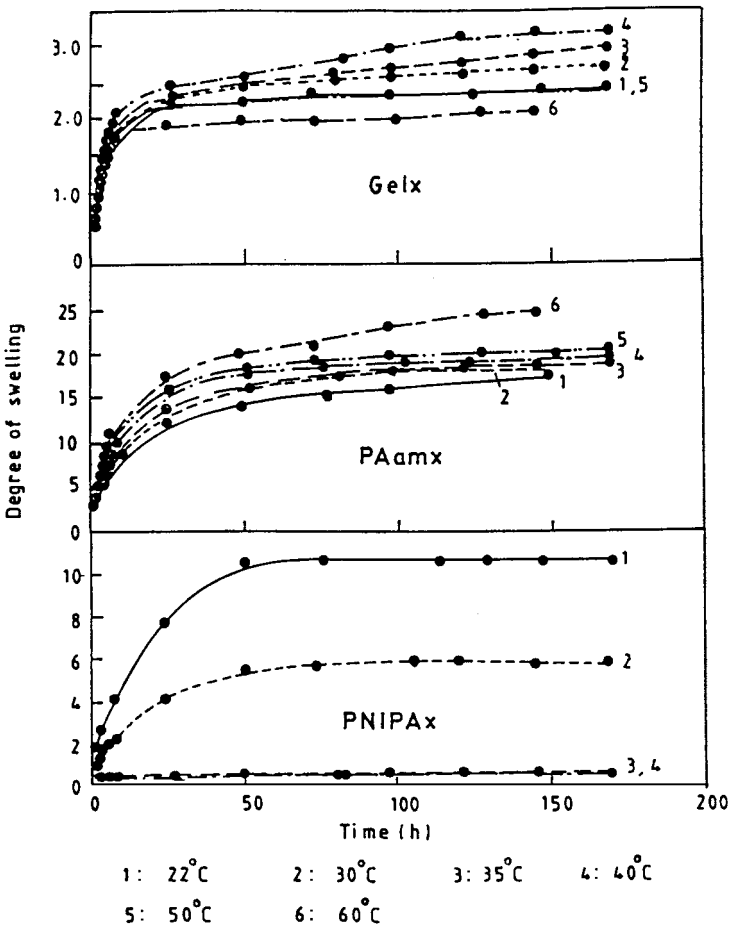

Figure 4. Dynamic swelling curves for 10 Gelx, PAamx, and PNIPAx gels.

of the samples. How to calculate the corresponding rate constants? Analyzing the permeation of organic solvents in polymer membranes,Hargoppad and Aminabhavi (11), have used a first order rate equation of the type:

$$dC/dt(k(C_\infty - C_t) \tag{6}$$

where C_∞ and C_t are the concentration of the penetrate in the polymer film at saturation and at time t. However, we believe that this equation is inadequate in the present situation because this equation treats the polymer characteristics as inconsequential. This assumption is perfectly valid for the kind of systems where the polymer matrix does not undergo enormous dimensional changes in response to the permeating species. In contrast, the hydrogel samples are not passive percolation beds but respond to the permeating species by swelling or shrinking as the case may be.

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Table 5. Activation Energies for [Gelx-PAamx] FIPNs

Sample Code	Activation Energies (kcal/mol)
P1	53.8
P2	54.2
P3	55.27
G3	49.7
G5	55.4
PAamx	36.8

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As we have seen in earlier sections, the rate of swelling has a very complex relationship with the polymer content, because the total phenomenon of swelling is the consequence of the solvent mixing with the polymer segments and extensive stretching of the segments. The rate constant for swelling is not a simple molecular quantity; instead, it is an average of the individual rate constants over the population of all different probe states of the system. Hence, we devised the following strategy: if the size and shape of the samples can be standardized, then the only variable will be the polymer content. Hence, it is safer to write an equation of the type:

$$\text{Rate of swelling } R_s = k \cdot [\text{P}]^x \tag{7}$$

where [p] is the polymer weight fraction. In the dry gel [p] = 1, then k is numerically equal to R_s. To avoid further computational complications, we normalized the values to the rate of swelling for 1 g of the dry gel.

The activation energies for [Gelx-PAamx] are tabulated in Table 5. The activation energy for the swelling of PAamx hydrogels comes out to be ∼37 kcal/mol and for 10% Gelx it is ∼76 kcal/mol (Fig. 5a). Because of this, perhaps the inclusion of PAamx in the gelatin network brings down the activation energy of the IPN hydrogel by almost 20 kcal/mol on an average.

There are several reports in the literature regarding the activation energies for the diffusion and the permeation of the solvent molecules into the polymer films (28–32). These are in the range of 15–29 kcal/mol. In contrast, the values in Table 5 are on the higher side.

It should be noted that there is a qualitative and quantitative difference between these solution crosslinked hydrogel networks and those networks reported in the literature (33,34). The reported values stand for the passive diffusion and permeation of the solvent molecules through polymer matrices, which do not undergo any dimensional change. In contrast, the energies listed in Table 5 are for the solvent entry, stretching of the network segments, and consequent large-scale macroscopic dimensional changes in the sample.

The [Gelx-PNIPAx] is an exceptional system, because it is a two-component interpenetrating hydrogel system, one component is thermoswelling and the other thermoshrinking. The 10% PNIPA hydrogels, which are different from the conventional trend, because the rate of swelling decreases with increase in temperature.

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Table 6. Activation Energies for [Gelx-PNIPAx] FIPNs

Sample Code	Activation Energies (kcal/mol)
N1	−55.27
N2	−66.33
N3	−93.27
N4	−97.73
N5	−138.87
PAamx	−331.63

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In the literature, these are referred to as negative Arrhenius plots and the activation energy as negative. This is indeed consistent with the thermoshrinking behavior of PNIPAx.

We observed a general decline in swelling for the [Gelx-PNIPax] IPNs (Fig. 3), because the thermoshrinking characteristics of PNIPAx override the thermoswelling property of gelatin at the temperatures studied. The activation energies are calculated from the Arrhenius plots and are tabulated in Table 6. For these hydrogels, the total polymer content is constant at 10% with one component varying from 0 to 10%. All the gels, regardless of the gelatin content, show thermoshrinkage. As PNIPA content increases, the activation energy too becomes increasingly negative, reflecting the resistance of the gels to swell. For pure PNIPAx hydrogels, the value is as negative as −330 kcal/mol.

Enthalpies of Swelling

What exactly could be the significance of the negative activation energy? The general form of the Arrhenius equation is:

$$k = A \cdot e^{-E_a/RT} \tag{8}$$

By definition, E_a is the increase in the internal energy of the reacting species required to bring about the physical or chemical process under consideration. Any type of energy exchange between a system and its surroundings involves either heat or work. When a system absorbs heat (q), this energy is not lost; it is stored and can be recovered. Absorption of heat increases the internal energy or the energy content (E) of the system. When a system performs work (w), this is done at the expense of the total energy of the system. This indeed is the first law of the thermodynamics and has the form:

$$E_2 - E_1 = \Delta E = q - w \tag{9}$$

E_2 and E_1 represent the value of internal energy when the process is carried out at constant pressure, q becomes the enthalpy or the heat content, H and Equation (9)

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Table 7. Ethalpies for 10% Gelx, PAamx, PNIPAx, and [Gelx-NIPAx] as in Table 2

Temperature (°C)	Gelx	PAamx	PNIPAX	N1	N2	N3	N4	N5
22	80.68	57.18	−316.08	−45.92	−57.39	−85.13	−89.29	−132.97
30	82.13	62.21	−319.27	−46.06	−58.82	−85.2	−89.25	−134.46
35	82.42	66.85	−327.5	−46.74	−59.49	−87.8	−92.47	−135.72
40	43.56	69.02	−329.3	−47.51	−60.36	−88.2	−92.69	−136.16
50	82.42	71.9						
60	83.75	74.4						

can be rewritten as:

$$\Delta E = \Delta H - P\Delta V \tag{10}$$

When applied to the swelling process, ΔH will be the enthalpy of swelling and $P\Delta V$ the actual pressure volume work performed due to the expansion of the polymer network. For the [Gelx-PAamx] system the Arrhenius plots are the conventional types, yielding positive activation energies. Because the rate of swelling increases with the temperature, this is an endothermic process, with H also positive. The pressure volume work performed is also positive because there is a large increase in volume.

This situation is different for the PNIPAx and IPN hydrogels. The Arrhenius plot itself is negative, yielding negative activation energies. The swelling decreases with the temperature, implying the exothermic in process, the pressure volume work performed is negative because the system undergoes shrinkage. These explanations fit in very well with the observed values. We start with the Glex that has activation energy of 76 kcal/mol. Looking at the values in Table 6 we find that increasing amounts of PNIPA pushes the E_a value to more and more negative side, till we reach pure PNIPAx, which has a E_a of −330 kcal/mol at 40°C.

We have calculated the enthalpy of swelling (18) of the gels Gelx, PAamx, PNIPAx, and IPNs [Gelx-PNIPAx], the values for Gelx and PAamx are positive, but the values are negative for PNIPAx and IPNs of [Gelx-PNIPAx]. The recorded values are listed in Table 7.

CONCLUSION

From the results, we conclude that with a rise in temperature the [GelxPAamx] IPNs experience an anomalous type of diffusion, whereas, for [GelxPNIPAx], above its LCST; the diffusion deviates from anomalous to Fickian, due to the predominance of the hydrophobic character of NIPA, resisting the advancing of solvent molecules.

The solution crosslinked [Gelx-PAamx]; IPNs have undergone the large macroscopic dimensional changes due to solvent entry with the increase in temperature. Hence, they resulted in higher and positive activation energies, which are in contrast to the lower activation energies reported in the literature. But the

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[Gelx-PNIPAx] IPNs attained increasingly negative activation energies regardless of the gelatin content, because the thermoshrinking property of PNIPA overrides the thermoswelling property of Gelx.

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