Compressive Elastic Modulus of Polyacrylamide Hydrogels and Semi-IPNs with Poly(*N*-isopropylacrylamide)

E. C. Muniz* and G. Geuskens

Université Libre de Bruxelles, Campus Plaine CP 206/1, B1050 Brussels, Belgium

Received July 11, 2000; Revised Manuscript Received March 27, 2001

ABSTRACT: Hydrogels of a semiinterpenetrated polymer network, semi-IPN [based on cross-linked polyacrylamide (PAAm) having poly(*N*-isopropylacrylamide) (PNIPAAm) inside], were synthesized, and their properties, such as swelling ratio and compressing elastic moduli, were studied at several temperatures. Equilibrium swelling ratios of semi-IPN markedly decreased due to the presence of less hydrophilic PNIPAAm chains. The semi-IPN presented a greater elastic modulus when compared to the cross-linked PAAm hydrogel. The values of apparent cross-linking density were determined from the mechanical compression measurements, made at temperatures that ranged from 25 to 40 °C. The presence of PNIPAAm chains on the network increases the polymer volume fraction of the swollen gel. At 25 °C the effect induces the formation of physical entanglements, increasing the apparent cross-linking density and then enlarging the compressing elastic modulus. Above 32 °C, the LCST of PNIPAAm in water, semi-IPN hydrogels presented higher values of the compressive elastic modulus. The effect was explained as being an additional contribution of the PNIPAAm chains, which collapsed around the PAAm networks, to the elastic modulus. By analysis of the swelling ratio, it was concluded that the collapsing of PNIPAAm chains is not accompanied by large shrinking of the gel. It was pointed out that the PAAm networks support the collapsed chains. According to the results presented in this work, semi-IPN hydrogels present better mechanical properties than PAAm hydrogel, mainly when the PNIPAAm chains are in a collapsed state.

Introduction

The collapse of temperature-sensitive hydrogels is a phase transition in which the gel undergoes a discontinuous volume changes in a narrow range of temperature.[1−4] This interesting characteristic may be used in a variety of applications—for instance, in controlled drug delivery,[5] molecular separation processes,[6] tissue culture substrates,[7] etc. Many works have focused on hydrogels made of cross-linked poly(*N*-isopropylacrylamide) (PNIPAAm) that undergo a sharp volume transition, at a temperature close to 32 °C, which is the lower critical solution temperature (LCST) of the linear polymer in water.[1−4,8−11] When PNIPAAm is heated above its LCST, the polymer chains collapse dramatically.[11] However, a serious limitation of PNIPAAm hydrogels, in many applications, is the low mechanical strength of these gels in a highly swollen state.[12−14] Modifications such as copolymerization[15] or semi-IPN formation[16,17] were shown to improve the mechanical properties without affecting the gel collapsing temperature. Takigawa et al.[18] showed that PNIPAAm gels present an elastic modulus around 17 times higher in the collapsed state than in the swollen state. Zaroslov et al.[19] published an interesting paper concerning the changes in the elastic modulus of strongly charged hydrogels near the collapsing transition, where a relation between the swelling ratio and the elastic modulus was described.

In a previous work,[17] we synthesized semi-IPNs of cross-linked polyacrylamide (PAAm) having PNIPAAm inside. The semi-IPNs presented qualitatively good mechanical properties, even in the swollen state. In addition, the absence of large shrinking of the semi-IPN hydrogels at temperatures above the LCST of PNIPAAm was observed. This was used to build a model in order to explain the sharp increase of the permeability of Orange II at temperatures above LCST of PNIPAAm. Thus, it was suggested that the collapsed PNIPAAm chains are mechanically supported by the PAAm network.[17] Measurements of the elastic moduli of these hydrogels as a function of temperature could be used to confirm those achievements. In this work, we have measured, by compressing experiments, the elastic modulus of the cross-linked PAAm gels having different amounts of PNIPAAm inside, at several temperatures, and for the sake of comparison, we have also measured the same properties of pure PAAm hydrogels.

Experimental Section

Synthesis of PNIPAAm. Poly(*N*-isopropylacrylamide)-homopolymer (PNIPAAm) was prepared by redox polymerization.[20] Aqueous solution (100 mL) was prepared by dissolving 44.3 mmol of *N*-isopropylacrylamide and 1.7 mmol of sodium persulfate in distilled water. This solution was previously purged with nitrogen for at least 30 min to completely remove the oxygen. Afterward, 336 μmol of tetramethylenediamine (TEMED) was added, and the flask was closed. The polymerization was carried out at ambient temperature for 24 h. The intrinsic viscosity, $[\eta]$, of the polymer was 247 $cm^3\ g^{-1}$, measured in water at 25 °C. From that value, the average viscosimetric molecular weight, M_V, of PNIPAAm was 1.6×10^3 $kg\ mol^{-1}$, calculated using the Mark−Houwink−Sakurada equation. The values of a and K were 0.97 and 2.26×10^{-4} $cm^3\ g^{-1}$, respectively, according to Chiantore et al.[21]

Synthesis of Hydrogels. Polyacrylamide homopolymer gels were prepared by photoinitiated polymerization. 50 mmol

---

* To whom correspondence should be addressed. Permanent address: Universidade Estadual de Maringá, Departamento de Química, 87020-970 Maringá (Paraná), Brazil. E-mail: ecmuniz@uem.br.

10.1021/ma001192l CCC: $20.00

of acrylamide (AAm) and 500 μmol of N,N'-methylenebis(acrylamide) (MBAAm), as cross-linking agent, were added to 10 mL of distilled water. To obtain semi-IPN, PNIPAAm aqueous solution of desired concentration was added instead of water. After the bubbling of nitrogen for 20 min, the solution was poured in a glass test tube of 1.2 cm diameter and 12 cm height. The tube, filled with the solution, was closed and exposed to γ-radiation from ^{60}Co in a Gammacell 220 (Atomic Energy of Canada Ltd.) at a dose rate of 0.216 kGy h^{-1}. The total absorbed dose was 0.250 kGy. After the exposition, the test tube was carefully broken, and the gel, in its cylindrical form, was recovered. Four kinds of hydrogels were prepared. The notation ($M-X-P$), used to characterize the gels, means M = the molality of AAm in the feed solution before polymerization (in mol of AAm by kg of water), X = the molar ratio of cross-linking agent N,N'-methylenebis(acrylamide) (MBAAm) to AAm (in mol %), and P = the concentration (in wt %) of the PNIPAAm in the aqueous solution used.

In this work, the (5−1−0) hydrogel and the (5−1−1.3), (5−1−2.5), and (5−1−5) semi-IPNs were synthesized.

Stress−Strain Measurements. The cylindrical gels, obtained as described before, were cut in pieces of 1.0 cm height. Before the compressive experiments, the gels were maintained in water for 1 week, at a desired temperature, to remove unreacted monomers and to allow the gel to achieve swelling equilibrium. Using a J. J. Lloy Instruments tensile testing machine, model T5000, uniaxial compression experiments were performed on the cut PAAm and semi-IPN hydrogels, at temperatures of 25, 30, 35, and 40 °C. The experiments were performed using a crosshead speed of 1.0 cm min^{-1} and a load cell of 100 N sensibility. After adjusting the experimental parameters, each compressive experiment was carried out in less than 1 min to avoid loss of water during the measurement. Five samples of each kind of gel were used. The elastic modulus, E, was determined from the slope of linear dependence

$$\sigma = f/S_0 = E(\lambda - \lambda^{-2}) \qquad (1)$$

where σ is the applied stress in Pa m^{-2}, f is the value of measured force, S_0 is the cross section of the undeformed swollen specimen, and λ is the relative deformation of the specimen. The apparent cross-linking density, ν_e, was determined using the equation[12]

$$\sigma = RT(\phi_{p,0}/\phi_p)^{2/3}\phi_p\nu_e(\lambda - \lambda^{-2}) \qquad (2)$$

where $\phi_{p,0}$ and ϕ_p are the polymer volume fractions of the gel in the relaxed state (just after polymerization) and in the swollen state, respectively.

Swelling Experiments. Cylindrical gels, with the same dimensions of those used in the compressive experiments, were swollen to equilibrium in water at temperatures of 25, 30, 35, and 40 °C. The swelling ratios were determined as being the ratio of the swollen gel weight to the dry gel weight.

Results and Discussion

Swelling Ratio. Figure 1 illustrates the dependence of the swelling ratio (Q) on the amount of PNIPAAm at several temperatures, obtained for cylindrical hydrogels samples. Each point represents the average obtained from triplicate. After cross-linking the PNIPAAm chains were trapped in the PAAm networks. Inclusion of the less hydrophilic PNIPAAm in the PAAm network results in a decrease of the swelling ratio of the respective semi-IPN hydrogels, starting from (5−1−0) to (5−1−5) as shown in Figure 1. As the amount of cross-linking agent was maintained constant, it could be pointed out that the swelling ratio of semi-IPNs is very sensitive to the presence of PNIPAAm: 5 wt % of PNIPAAm in the gel is enough to decrease the swelling ratio in about 18%, relative to the swelling ratio of PAAm hydrogel, at 25 °C. The entanglements of the PNIPAAm chains, which may exist inside the semi-IPN hydrogels, could contribute to decrease the swelling ratio due to the higher polymer volume fraction. The swelling ratio seems to be only slightly dependent on the temperature. The temperature increase induces a small raising in the Q value of the PAAm hydrogels, but, on the other hand, it decreases the Q value of the semi-IPN hydrogels. The increase of Q with the temperature, as observed for PAAm hydrogels, is due to the changes in the polymer−solvent interactions that alter the thermodynamic properties, mainly ΔG of the mixture.[22] A small increase of Q in temperatures ranging from 25 to 40 °C was also observed by other researchers in PAAm hydrogels.[16] In this work, it was observed that the temperature influence in swelling ratio of semi-IPN is not important. The greatest relative change in Q due to the temperature, for a respective hydrogel, is only 0.5 or ca. 7%. The absence of large shrinking in the semi-IPN hydrogels based in PAAm and having PNIPAAm inside, at temperatures above the LCST of PNIPAAm, was already observed in our previous work.[17] The results presented in Figure 1 confirm the absence of large shrinking at temperatures above the LCST of PNIPAAm. As will be discussed later, the collapsed PNIPAAm chains inside the semi-IPN hydrogels could be mechanically supported by the PAAm network.

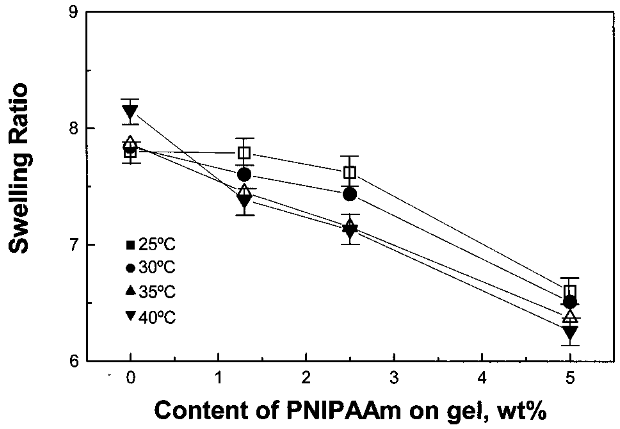

Figure 1. Swelling ratio as a function of PNIPAAm content for PAAm hydrogel and semi-IPNs at several temperatures.

Mechanical Behavior of Gels. Figure 2 shows the measured force for compressing the (5−1−5) hydrogel at 25 °C (curve A). It was observed that the slope of that curve is smaller at low deformation. All the hydrogels presented this behavior, and this was attributed to the fact that the initial surface of the cylindrical sample is not perfectly flat. If the surface is smaller than the nominal surface, the compression strength will be smaller. Then, after 5% of deformation, the contact between them could be the same as the whole nominal surface. It may be observed that above 5% of deformation the slope increases and the curve tends to an almost straight line. The procedure was taken as standard: in all compression experiments the experimental data obtained up to about 5% of deformation were rejected. The dependence of the stress to the deformation ratio of hydrogels is presented in curve B of Figure 2. From the slope of that almost straight line, the elastic modulus was calculated.

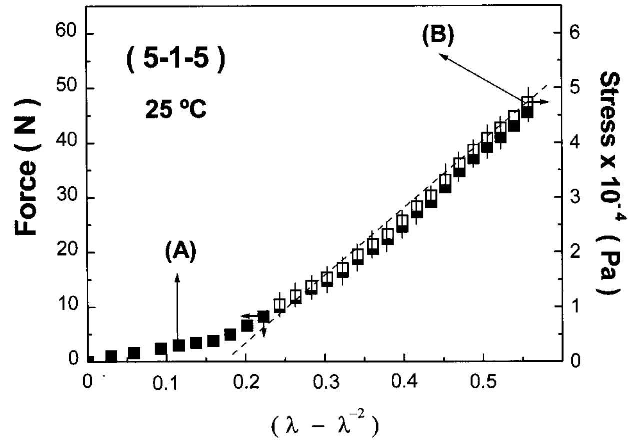

Figure 2. Measured force (curve A) and stress (curve B) as a function of ($\lambda - \lambda^{-2}$) for the (5−1−5) hydrogel at 25 °C.

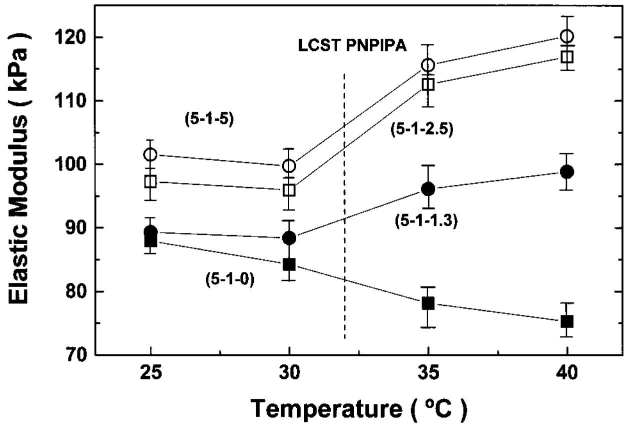

Figure 3. Compressing elastic modulus of hydrogels as a function temperature obtained for PAAm hydrogel and semi-IPNs.

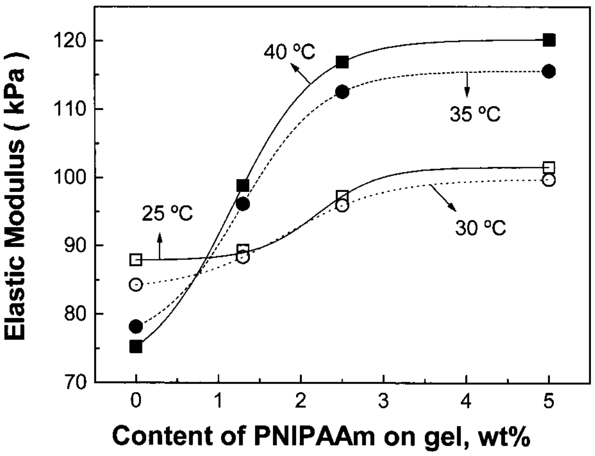

Figure 4. Compressing elastic modulus of hydrogels as a function of PNIPAAm content obtained for PAAm hydrogel and semi-IPNs at several temperatures.

The values of elastic modulus for PAAm hydrogels are in accordance with the values published by Shin et al.[16] for other kind of gels but had around the same cross-linking density. It may be observed that the elastic modulus of the (5−1−0) hydrogel decreases as the temperature is increased, as presented in Figure 3. On the other hand, the semi-IPNs present a different behavior: the value of elastic modulus decreases slightly from 25 to 30 °C. The decrease of the elastic modulus observed for the (5−1−0) hydrogel as the temperature is increased may be better understood by taking into account the dependence of the swelling ratio on the temperature, as presented in Figure 1. As the hydrogel became more swollen, it presented a lower network density and became softer. This caused lowering in the values of the elastic modulus for the (5−1−0) hydrogel as the temperature was increased. For instance, the value of the elastic modulus of the (5−1−0) hydrogel decreases from 87.9 kPa (25 °C) to 75.3 kPa (40 °C). Although the semi-IPNs present negative dependence on the elastic modulus to the temperature in the range 25−30 °C, positive dependence in the range 30−40 °C was observed, as it may be checked in the curves of Figure 3. The negative dependence of the elastic modulus to the temperature in the semi-IPNs hydrogel is not as important as the one verified in the (5−1−0) hydrogel. Some changes in the semi-IPNs structure, which occur at LCST temperature and above, may induce the semi-IPNs hydrogels to a less soft material. The presence of PNIPAAm chains inside of the gel networks make the semi-IPNs material denser, reinforcing the gel and leading to an increase in the elastic modulus, even at temperatures below the LCST. For instance, at 25 °C the value of elastic modulus increases from 87.9 to 101.5 kPa when the amount of the PNIPAAm in the hydrogel was increased from 0 to 5 wt %. This represents an increment of 15.4% in the elastic modulus if the value of the (5−1−0) hydrogel is used as reference. By changing the PNIPAAm content from the (5−1−0) hydrogel to the (5−1−5) hydrogel, at 30 °C, an increase of the value of the elastic modulus in ca. 18% was also observed. The effect of the PNIPAAm content on the elastic modulus of semi-IPNs may be more properly visualized by analyzing the curves in Figure 4. The presence of PNIPAAm chains in the hydrogels minimizes the negative dependence of elastic modulus to the temperature, as can be verified in the (5−1−0) hydrogel. From the curves presented in Figure 4, it could be suggested that 1 wt % is the minimum required concentration of PNIPAAm in aqueous solution, used in the gelation process, to avoid a negative dependence of the elastic modulus of the semi-IPNs to the temperature. At temperatures below the LCST, the increment on elastic modulus of semi-IPNs may be understood as a contribution of the denser hydrogels. But, as can be also visualized in Figure 4, an additional increase was observed in temperatures above the LCST. Then, it could be pointed out that the collapsed chains induce the semi-IPN to be more rigid hydrogels than those observed at temperatures below the LCST. As was pointed out in our previous work[17] and as shown in Figure 1, the collapsing of PNIPAAm chains on (5−1−1.3), (5−1−2.5), and (5−1−5) semi-IPNs is not accompanied by a large amount of shrinking because the PAAm networks mechanically support the hydrogel. In addition, from the dependence of the elastic modulus on the temperature, as presented in Figure 3, it could be suggested that, at temperatures above the LCST, the collapsed PNIPAAm chains improve the mechanical properties of the gel. At temperatures above the LCST, 35 and 40 °C, the semi-IPNs present a higher elastic modulus than below LCST, 25 and 30 °C. In this way, it could also be suggested that the collapsed coils lead to a stronger material.

The apparent cross-linking density, determined from the elastic modulus and from the swelling ratio data,

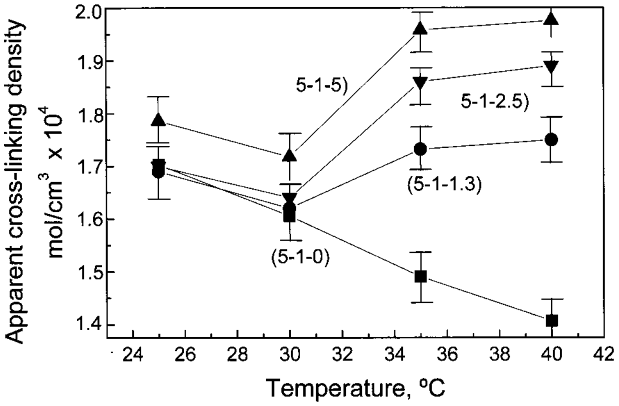

Figure 5. Apparent cross-linking density PAAm hydrogel and semi-IPNs at several temperatures.

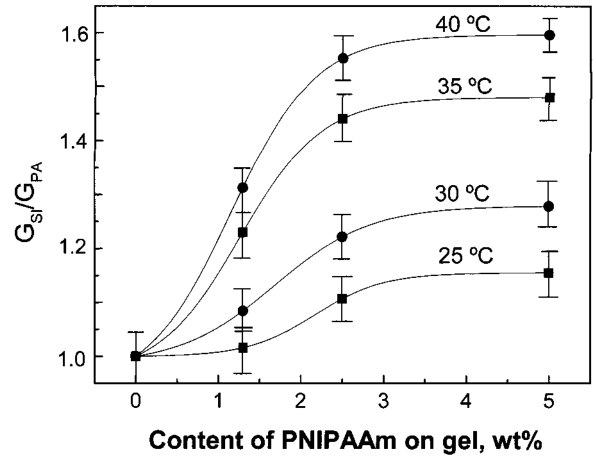

Figure 6. Dependence of G_{SI}/G_{PA} as a function of PNIPAAm content PAAm hydrogel and semi-IPNs at several temperatures.

was calculated using eq 2. It was observed that the apparent cross-linking density increases as the content of PNIPAAm in the gel is raised. The apparent cross-linking density of the (5−1−0) hydrogel ranges from 1.70×10^{-4} to 1.41×10^{-4} mol cm^{-3} when the temperature is increased from 25 to 40 °C. On the other hand, an increment in the cross-linking density was verified on the semi-IPNs at temperatures above the LCST, as presented in Figure 5. The increase of the cross-linking density means that the material became more rigid, and this is reflected in the values of elastic modulus. Two factors could be related to this effect: (i) the collapsed PNIPAAm chains around the PAAm networks and (ii) the shrinking of the gel, even in a small amount. Although the PNIPAAm chains are not chemically linked to the gel, they may exhibit physical interactions: at temperatures below LCST, entanglements of PNIPAAm chains may contribute to the apparent physical cross-linking; at temperatures above LCST, the collapsed chains may have an additional contribution to the apparent cross-linking density. Both contributions tend to increase the value of compressive elastic modulus. By measuring the compressing elastic modulus, Gutowska et al.[12] observed an increment in the cross-linking density by addition of different amount of Biomer, a copoly(ether urethane−urea), on the PNIPAAm cross-linked hydrogels, forming semi-IPNs. In that case, the increment on the apparent cross-linking density was attributed to the strong noncovalent interactions between the Biomers moieties and also between the Biomer and PNIPAAm networks. The authors pointed out that the formation of entanglements among Biomer chains is not probable, due to the relatively low molecular weight of Biomer. In this work, the PNIPAAm chains could be entangled due to their high molecular weight. Shin et al.[16] also observed an increment in the apparent cross-linking in PNIPAAm/poly(acrylic acid) IPNs when the temperature is around 44 °C. The observed effect was accompanied by a decreasing on the swelling ratio. The authors attributed the effect to the formation of strong noncovalent interaction in addition to the chemical network done by a chemical cross-linker.

In this work, the effective cross-linking density was calculated taking the value of 5×10^{-4} mol cm^{-3} as 100% of cross-linking density. Then, a cross-linking efficiency of about 34%, at 25 °C, was obtained. Cross-linking efficiency is dependent on the polymerization conditions.[19] For example, a relatively low cross-linking efficiency of 9% was obtained from the cross-linked PNIPAAm synthesized by UV polymerization. Cross-linked PNIPAAm obtained by temperature-initiated polymerization in dioxane presented cross-linking efficiency of 31% for PNIPAAm networks synthesized with 1 mol % of ethylene glycol dimethylacrylamide or EGDMA.[12,23] In this work, the same amount, i.e., 1 mol % of MBAAm, was used. This means that the cross-linking process using a γ-radiation dose of 0.250 kGy induces on AAm monomers, dissolved in water, an effective cross-linking density similar to the one verified on the temperature-initiated cross-linking of NIPAAm monomers, dissolved in dioxane.

To highlight the effect of PNIPAAm chains on semi-IPN hydrogels at different temperatures, relative change in the elastic modulus was calculated taking the elastic modulus of PAAm hydrogel as reference. In this way, the G_{SI}/G_{PA} ratio was determined at several temperatures, G_{SI} and G_{PA} being the calculated elastic modulus of PAAm and semi-IPN hydrogels, respectively. The dependence of the G_{SI}/G_{PA} ratio on the amount of PNIPAAm is presented in Figure 6. It could be observed that an increment of the amount of PNIPAAm causes an increase in the elastic modulus, despite temperature. The effect is more important at temperatures above the LCST.

The kinetics of shrinking of PNIPAAm gels, near the volume phase transition temperature, was recently studied by Shibayama and Nagai.[2] The authors observed that the kinetic of shrinking is slow at temperatures below 45 °C and fast above this temperature. The formation of bubbles on the gel surface was observed by the optical microscopy technique. The authors pointed out that the minimum time necessary to visualize the bubble formation or to detect any shrink is around 3−5 min, if the temperature is rapidly changed from 25 °C to above the LCST but still below of 40 °C and if the cross-linking agent (MBAAm) is ca. 1 mol % in relation to monomer (NIPAAm). In this study, the ratio of MBAAm to AAm was kept constant at 1 mol %. This means that no considerable water was expelled from the gels during each compression experiment performed in this work, done in ca. 1 min. In fact, it was suggested by Kaneko and co-workers,[11] in another work, that the formation of a skin on the gel surface is due to the hydrophobic characteristics of PNIPAAm above its LCST. According to these authors, the skin would avoid the rapid expelling of water.

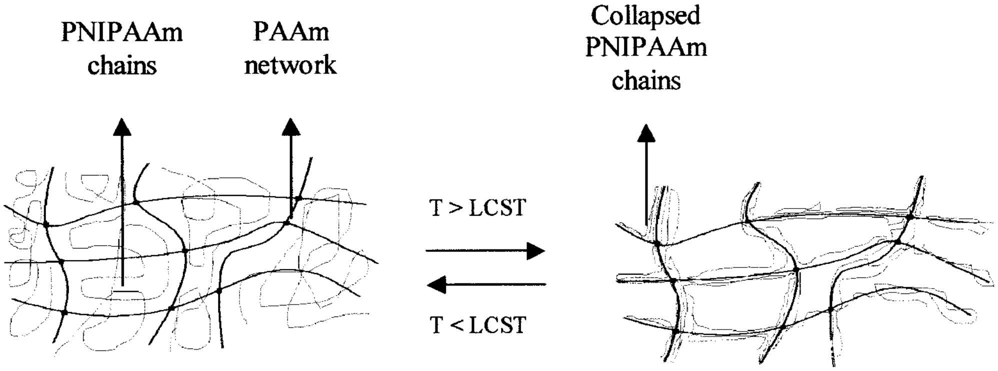

Figure 7. Pictorial representation of the structural support of the collapsed PNIPAAm chains by the PAAm networks swollen in water.

In this work, it is noteworthy that above 32 °C the collapsing of the entangled PNIPAAm chains does not result in a large shrinking of semi-IPN hydrogel, as shown in Figure 1. The PNIPAAm chains are water solvated and randomly distributed at temperatures below LCST but became collapsed near or above the LCST. Thus, the PNIPAAm chains became more hydrophobic, but large shrinking is avoided by the presence of PAAm network. It could be emphasized that the transparent semi-IPNs hydrogels used in this work become opalescent when heated above the LCST. The effect is reversible and takes only a few minutes to occur. A pictorial representation of the structural support of the PNIPAAm chains by the PAAm networks is shown in Figure 7.

According to the results presented in this work, it could be suggested that the semi-IPNs present higher compressive elastic modulus than the PAAm hydrogel, especially when the PNIPAAm chains are in a collapsed state. Experiments on semi-IPN membranes using a DMA oscillatory equipment are under way.

Conclusions

Hydrogels of semi-IPNs based on cross-linked PAAm having PNIPAAm inside were synthesized. The swelling ratio is sensitive to the presence of PNIPAAm: the semi-IPN swelling ratio decreases due to the hydrophobic contribution of the PNIPAAm chains. The semi-IPNs present a higher elastic modulus when compared to the cross-linked PAAm hydrogel. At 25 °C the effect was attributed to the presence of PNIPAAm chains that increase the polymer volume fraction of the swollen gel. Above 32 °C, the LCST of PNIPAAm, the effect is more important and was explained as an additional contribution of the collapsed PNIPAAm chains. By swelling ratio measurements, it was verified that the collapsing of PNIPAAm chains is not accompanied by a large shrinking of the semi-IPN hydrogel. It was suggested that the PAAm networks mechanically support the collapsed chains. According to the results presented in this work, it is possible to conclude that the semi-IPNs present better mechanical properties than the PAAm hydrogel, especially when the PNIPAAm chains are in a collapsed state.

Acknowledgment. E.C.M. is grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil) for a fellowship (Proc. no 200609/98-0).

References and Notes

(1) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214–1218.
(2) Shibayma, M.; Nagai, K. *Macromolecules* **1999**, *32*, 7461–7468.
(3) Wu, C. *Polymer* **1998**, *39*, 4609–4619.
(4) Gao, J.; Wu, C. *Macromolecules* **1997**, *30*, 6872–6876.
(5) Wu, M. H.; Bao, B. R.; Chen, J.; Xy, Y. J.; Zao, S. R.; Ma, Z. J. *Radiat. Phys. Chem.* **1999**, *56*, 341–346.
(6) Freitas, R. F. S.; Cussler, E. L. *Sep. Sci. Technol.* **1987**, *22*, 911–919.
(7) von Recum, H.; Okano, T.; Kim, S. W. *J. Controlled Release* **1998**, *55*, 121–130.
(8) Liu, H. Y.; Zhu, X. X. *Polymer* **1999**, *40*, 6985–6990.
(9) Tanaka, N.; Matsukawa, S.; Kurosu, H.; Ando, I. *Polymer* **1998**, *39*, 4703–4706.
(10) Ito, K.; Ujihira, Y.; Yamashita, T.; Hiroe, K. *Polymer* **1999**, *40*, 4315–4323.
(11) Kaneko, Y.; Nakamura, S.; Sakai, K.; Aoyagi, T.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Macromolecules* **1998**, *31*, 6099–6105.
(12) Gutowska, A.; Bae, Y. H.; Jacobs, H.; Feijen, J.; Kim, S. W. *Macromolecules* **1994**, *27*, 4167–4175.
(13) Shibayama, M.; Morimoto, M.; Nomura, S. *Macromolecules* **1994**, *27*, 5060–5066.
(14) Hirotsu, S. *J. Chem. Phys.* **1991**, *94*, 3949–3957.
(15) Mukae, K.; Bae, H. Y.; Okano, T.; Kim, S. W. *Polym. J.* **1990**, *22*, 250–265.
(16) Shin, B. C.; Jhon, M. S.; Lee, H. B.; Yuk, S. K. *Eur. Polym. J.* **1998**, *34*, 1675–1681.
(17) Muniz, E. C.; Geuskens, G. *J. Membr. Sci.* **2000**, *172*, 287–293.
(18) Takigawa, T.; Yamawaki, T.; Takahashia, K.; Masuda, T. *Polym. Gels Networks* **1997**, *5*, 585–589.
(19) Zaroslov, Y. D.; Philippova, O. E.; Khokhlov, A. *Macromolecules* **1999**, *32*, 1508–1513.
(20) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163–249.
(21) Chiantore, O.; Guaita, M.; Trossarelli, L. *Makromol. Chem.* **1979**, *180*, 969–973.
(22) Kayman, N.; Okay, O.; Baysal, B. M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1313–1320.
(23) Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *J. Membr. Sci.* **1991**, *64*, 283–294.

MA001192L