Solution Cross-Linked Poly(isobutylene) Gels: Synthesis and Swelling Behavior

Oguz Okay,[†,‡] Selda Durmaz,[†] and Burak Erman*,[§]

TUBITAK Marmara Research Center, Department of Chemistry, P.O. Box 21, 41420 Gebze, Kocaeli, Turkey, Istanbul Technical University, Department of Chemistry, 80626 Maslak, Istanbul, Turkey, and Sabanci University, Faculty of Engineering and Natural Sciences, Orhanli, 81474 Tuzla, Istanbul, Turkey

ABSTRACT: We prepared several series of PIB gels starting from butyl rubber in dilute toluene solutions using sulfur monochloride as a cross-linking agent. By using solution and suspension cross-linking techniques, PIB gels in the form of rods or beads in the size range of 0.1−2 mm were prepared and subjected to swelling in solvent−nonsolvent mixtures. The swelling capacity of the gels in toluene increased with decreasing concentration of sulfur monochloride or butyl rubber in the organic phase. The solubility parameter of the solution cross-linked PIB gels was found to be 16.8 ± 0.8 MPa$^{0.5}$, in accord with the reported value for bulk cross-linked gels. In toluene−methanol mixtures, PIB gels with 4% cross-linker content exhibited an abrupt deswelling when the toluene content of the external solution was decreased from 97 to 90%. By using the theory of equilibrium swelling, it was shown that the gel passes through critical conditions as the quality of the solvent becomes poorer.

Introduction

Polymer gels are important materials of both fundamental and technological interest. Investigations of the swelling behavior of hydrophilic gels called hydrogels have been reported repeatedly in the past four decades. In recent years attention has turned to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of a first-order phase transition in polymer networks has been predicted theoretically[1] and verified experimentally on ionic acrylamide-based hydrogels swollen in solvents.[2] In such a transition, a change in a variable like pH, solvent composition, or temperature can induce a discontinuous change in the volume of the swollen gel.[3] As Tanaka and others have shown, a small proportion of ionizable units on the polymer chains seems to be essential for a discontinuous shrinkage of the gel.[3]

However, more detailed calculations indicate that a strong concentration dependence of the solvent−polymer interaction parameter χ may also induce a discontinuous shrinkage of the swollen network, irrespective of its ionic group content.[4,5] The solvent−polymer interaction parameter χ is usually represented as a function of composition by the empirical equation

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \dots \qquad (1)$$

where v_2 is the volume fraction of the polymer. In ref 4 it was shown that, for nonionic gels, the requirement for the polymer collapse, i.e., for the coexistence of two gel phases in equilibrium with pure solvent, is $\chi_1 \leq \frac{1}{2}$ and $\chi_2 > \frac{1}{3}$. Although the indicated requirement for the polymer collapse is rare for real polymer−solvent systems, the χ parameter reported for the poly(isobutylene)

(PIB)−benzene system exhibits a strong concentration dependence.[6] Results of experimental measurements of osmotic pressures and vapor pressures give the following χ equation for PIB in benzene at 24.5 °C:[4,6]

$$\chi = 0.500 + 0.30 v_2 + 0.30 v_2^2 \qquad (1a)$$

where the coefficients χ_1 and χ_2 are subject to uncertainties of ± 0.05 and ± 0.1, respectively.[4] Equation 1a suggests that the PIB gels are suitable candidates for the investigation of their swelling behavior in solvent−nonsolvent mixtures. Observation of a phase transition in gels is facilitated in the presence of a large amount of a good solvent as an inert diluent during the network formation process. Moreover, solution cross-linking process is known to produce gels having a high swelling capacity suitable in a variety of applications such as oil separation from aqueous solutions. These considerations point to the advantages of preparing the PIB gels in a dilute homogeneous solution.

The present paper is the first report on the preparation of PIB gels in a homogeneous dilute solution. To the best of our knowledge, the synthesis of solution cross-linked PIB gels has not been described before. As the starting material of these gels, we selected a linear PIB containing small amounts of internal unsaturated groups (isoprene units), which is known as butyl rubber and commercially available since 1943. The structure of butyl rubber may be represented as follows:
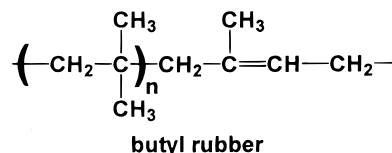
butyl rubber

where *n* is 30−200. Because of the low degree of unsaturation in butyl rubber, its vulcanization requires much powerful accelerators than natural rubber.[7,8] Although a large number of patents and publications

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[†] TUBITAK Marmara Research Center.
[‡] Istanbul Technical University.
[§] Sabanci University.
* Corresponding author.

have been reported on the vulcanization of butyl rubber in bulk, no work has been found in the literature on its cross-linking in solution. Our preliminary experiments showed that, due to the extensive chain scission reactions occurring in the presence of peroxide initiators such as dibenzoyl peroxide or cumene hydroperoxide, solution cross-linking of butyl rubber by free radicals cannot be carried out.

Here, we show that butyl rubber can easily be cross-linked in an organic solution using sulfur monochloride (S_2Cl_2) as a cross-linking agent. Sulfur monochloride is known as a cold vulcanization agent for natural rubber, and it vulcanizes natural rubber so fast that the rubber cannot be mixed into rubber compounds.[8] Therefore, its use as a vulcanization agent is less common. However, because sulfur monochloride is a liquid at room temperature and soluble in organic solvents, we selected it as the cross-linking agent for butyl rubber in dilute solutions. Our preliminary experiments indeed showed that sulfur monochloride is an efficient cross-linking agent for solution cross-linking process of butyl rubber in toluene solutions, even at very low polymer concentrations.

By using solution and suspension cross-linking techniques, a series of PIB gels in the form of rods as well as beads in the size range of $0.1-2$ mm were prepared. Depending on the amounts of sulfur monochloride and butyl rubber in the initial reaction solution, PIB gels with different swelling capacities were synthesized and subjected to swelling experiments in solvent–nonsolvent mixtures.

Experimental Section

Materials. The main component in the gel synthesis is butyl rubber, which was purchased from Exxon Chem. Co. The butyl rubber sample Butyl 268 used in this work contained $1.5-1.8$ mol % isoprene units. This polymer sample was purified by reprecipitation from toluene solution in acetone. Its weight-average molecular weight $\bar{M}_w$ was determined to be 3.9×10^5 g/mol on a gel permeation chromatograph with polystyrene standards (Waters, model M-6000A). The polydispersity index $\bar{M}_w/\bar{M}_n$ was 2.5. The cross-linking agent sulfur monochloride, S_2Cl_2, was partially purchased from Aldrich Co. Some of the gels were prepared with sulfur monochloride synthesized from sulfur and dry chlorine gas at $50-80$ °C according to a method described by Feher.[9] The purities of both Aldrich and homemade sulfur monochlorides were higher than 98%. Toluene (Merck) was used as the solvent for the solution cross-linking process. In the swelling experiments, reagent-grade solvents, toluene, benzene, cyclohexane, methylcyclohexane, carbon tetrachloride, xylene, *n*-heptane, *n*-hexane, *n*-pentane, acetone, methanol, ethanol, and methyl ethyl ketone were used without further purification.

Synthesis of the Gels. The PIB gels were prepared by solution and suspension cross-linking techniques. By the solution cross-linking process, the gels were prepared according to the following scheme: $1-10$ g of butyl rubber was first dissolved in 100 mL of toluene at room temperature (20 ± 1 °C) overnight. After bubbling nitrogen for 20 min, different amounts of sulfur monochloride were added under rigorous stirring, and the homogeneous solutions were transferred with a syringe into several glass tubes of 8 mm internal diameters and about 100 mm length. The cross-linking reactions proceed at room temperature and result in the formation of preswollen gels.

After predetermined reaction times at room temperature, the gels were taken out from the glass tubes, and they were cut into specimens of approximately 10 mm in length. Each gel sample was placed in an excess of toluene, and toluene was replaced every other day over a period of at least 3 weeks. The amount of soluble polymer in toluene solution was checked

gravimetrically after evaporation and precipitation in methanol. For initial butyl rubber concentrations $c \geq 5$ w/v % and for the reaction times of about 24 h, the weight fraction of gel was found to be always larger than 0.98, indicating the high cross-linking efficiency of sulfur monochloride.

For the synthesis of PIB gels in the form of beads, the suspension cross-linking technique was employed with water containing additives as the continuous phase. A 200 mL aliquot of water containing bentonite (0.5 g), gelatin (0.2 g), and sodium chloride (0.8 g) was first introduced into a 500 mL round-bottom reactor and stirred at 450 rpm under nitrogen atmosphere for 10 min. Separately, butyl rubber dissolved in toluene (50 mL) was mixed with the cross-linker sulfur monochloride in an Erlenmeyer flask, and nitrogen was bubbled through the organic solution for 10 min. The toluene solution was then transferred into the reactor, and the reaction was allowed to proceed for 8 h at room temperature (20 ± 1 °C) under nitrogen atmosphere. After polymerization, the beads were separated from the water phase, and they were sieved using ASTM sieves and washed several times first with water, then with acetone, and finally with toluene. The beads were left in toluene for 4 weeks during which toluene was refreshed every other day.

The following variables were used for defining the composition of the gel-forming systems:

(1) butyl rubber concentration c:

$$c = \frac{\text{mass of butyl rubber in g}}{\text{volume of toluene in mL}} \times 10^2 \tag{2}$$

(2) cross-linker concentration S_2Cl_2 (v/w %):

$$S_2Cl_2\ (\%) = \frac{\text{volume of } S_2Cl_2 \text{ in mL}}{\text{mass of butyl rubber in g}} \times 10^2 \tag{3}$$

Methods. The swelling capacity of the gels in the form of rods was measured by the gravimetric technique. The equilibrium swollen gel samples were weighed on an electronic balance (Sartorius BA 310 S). The weight swelling ratio q_w (mass of swollen gel/mass of dry gel) was calculated as

$$q_w = \left(\frac{\text{mass of the swollen gel}}{\text{mass of the gel after synthesis}}\right) \times$$
$$\left(\frac{\text{mass of the gel after synthesis}}{\text{mass of the dry gel}}\right) \tag{4a}$$

$$q_w = \left(\frac{m}{m_0}\right) q_F \tag{4b}$$

where m and m_0 are the masses of the swollen gel and the gel after synthesis, respectively, and q_F is the degree of swelling of the gel after preparation. q_F of the gels can be determined experimentally from the masses of the gel samples after synthesis and after drying. Assuming additivity of the volumes of polymer and solvent, q_F can also be calculated as

$$q_F = \left(\frac{1}{W_g}\right)\left(\frac{100 d_1}{c} + 1\right) \tag{4c}$$

where W_g is the gel fraction and d_1 is the density of the polymerization solvent (toluene, 0.867 g/mL). By using 15 separate measurements, it was found that, for an butyl rubber concentration of $c = 5\%$, the experimental value of q_F equals 18 ± 4.8 compared to its theoretical value of 18.34 calculated using eq 4c for $W_g = 1$.

The interpretation of swelling measurements was made on the basis of volume fraction of polymer during cross-linking and at equilibrium swelling, designated by v_{2c} and v_2, respectively, where the volume fraction is defined as the volume of polymer divided by total volume. These variables are related to weight fractions by the relations

$$v_{2c} = \frac{1}{1 + \dfrac{d_p}{d_1}(q_F - 1)} \tag{5a}$$

$$v_2 = \frac{1}{1 + \dfrac{d_p}{d_s}(q_w - 1)} \tag{5b}$$

where d_p and d_s are the densities of polymer and solvent, respectively.

The swelling capacity of the gel samples in the form of beads was measured in various solvents and solvent mixtures by the volumetric technique, in which the diameters of the beads after equilibrium swelling in solvent (D) and after drying (D_{dry}) were measured using an image analyzing system consisting of a stereo microscope (Olympus Stereomicroscope SZ), a video camera (TK 1381 EG), and Pentium 2 PC with a data analyzing software (BS-200 BAB). The equilibrium volume swelling ratio of the beads, q_v, was calculated using the following equation:

$$q_v = \left(\frac{D}{D_{dry}}\right)^3 \tag{6}$$

For the determination of the composition of the networks, IR spectra of the samples in KBr pellets were recorded on a Perkin-Elmer 983 spectrophotometer. The sulfur content of dried PIB gels was determined by the Leco SC 32 sulfur analyzer (ASTM 4239-93).

Results and Discussion

We discuss the results of our experiments in two subsections. In the first subsection, characteristic features of the cross-linking reactions and the swelling features of the networks are discussed. In the second subsection, the possibility of obtaining critical conditions for PIB gels in mixed solvents is discussed, and experimental observations are interpreted.

(1) Cross-Linking and Swelling. Addition of a small quantity of sulfur monochloride into the toluene solution of butyl rubber at room temperature (20 ± 1 °C) results in the formation of a polymeric gel within a few hours up to a few days. The cross-linking reactions between the PIB chains via sulfur monochloride is believed to proceed in steps as in the reaction between ethylene and sulfur monochloride[10,11] (Scheme 1). According to this scheme, attack of sulfur dichloride to the internal vinyl group of the polymer leads to the formation of pendant sulfur chloride groups on the PIB chains acting as potential cross-link points. Reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective cross-links. We tried to follow the development of the cross-linking process by using IR spectroscopy. However, the concentration of cross-linked units in the network was too low for IR detection. The dried PIB gels after synthesis were also subjected to sulfur analysis. The analysis results gave 0.9 and 2.4% sulfur (based on the dry mass of the network) for the gels prepared in the presence of 2 and 20% S_2Cl_2 as the cross-linker, respectively. Thus, increasing cross-linker concentration in the feed also increases the sulfur content of the networks. From the sulfur contents, the number of sulfur atoms in the cross-link points (x in Scheme 1) was calculated as 2 and 5 for 2 and 20% S_2Cl_2, respectively. Thus, if an excess of the cross-linker S_2Cl_2 (about 10 mol per mole of vinyl group) is used in the cross-linking process, S_5 bridges form between the PIB chains, whereas at less or equal
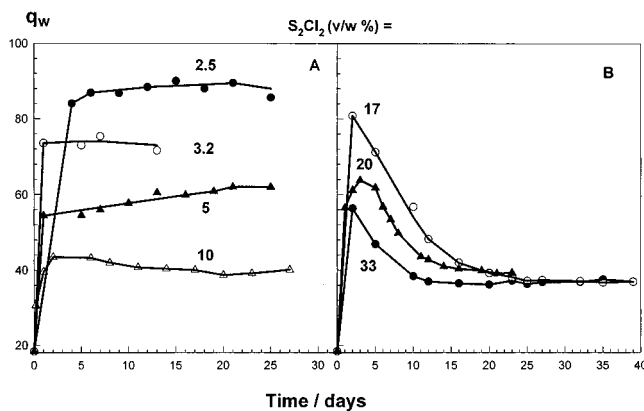
Figure 1. Variation of the weight swelling ratio of PIB gels q_w with their immersion time in toluene at room temperature. $c = 5$ w/v %. Cross-linker (S_2Cl_2) concentrations are indicated in the figure.
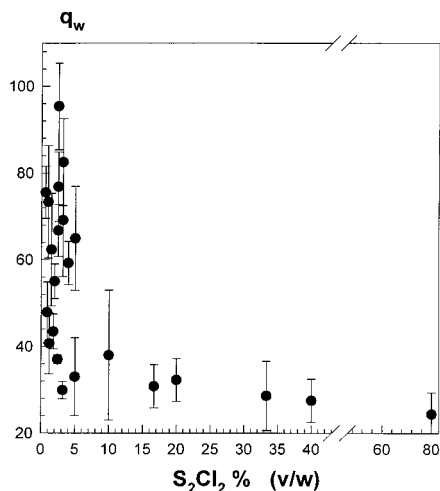
Scheme 1
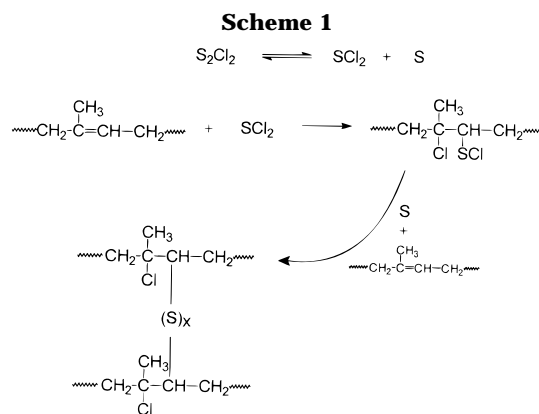
amounts of the cross-linker, the number of sulfur atoms in the bridges reduces to two.

The development of cross-linking in the gels was also monitored from the variation of the swelling degrees of the gels with time. For this purpose, we prepared a series of gels at 5% butyl rubber concentration but at different levels of S_2Cl_2. The gel preparation time was set to 1 day. Thereafter, the gels were cut into samples and immersed in an excess of toluene, during which the swelling capacity of the gels was measured as a function of time. Figure 1 shows how the equilibrium weight swelling ratio q_w of the gels varies with the immersion time in toluene. The curves in the figure were drawn for the eye. If the cross-linker concentration is less than 17% (with respect to butyl rubber), the gels swell up to about 3 days and then attain an almost constant mass (Figure 1A). This is expected from the usual swelling kinetics of gels. However, for gels prepared at higher cross-linker concentrations (Figure 1B), after the initial swelling period of about 3 days the gels start to deswell in toluene until they reach a limiting value after about 15 days. This behavior, which was observed on about 40 gel samples prepared separately, is probably a result of the post-cross-linking reactions occurring within the gel volume between the pendant sulfur chloride and internal vinyl groups of the network chains. The cross-linking reactions seem to continue after the network formation process in the reaction tubes. Assuming that the butyl rubber contains 1.5–1.8 mol % isoprene units, the molar masses of isobutylene, isoprene units, and S_2Cl_2 are 56, 68, and 135 g/mol, respectively, and the density of S_2Cl_2 is 1.68 g/mL; a multiplication factor of 0.43 ± 0.04 converts percent S_2Cl_2 into the moles of

Table 1. Synthesis Conditions and Toluene Absorption Capacities of Butyl Rubber Gels at Room Temperature

butyl rubber concn (w/v) %	S_2Cl_2 concn (v/w %)	reaction time	equilib weight swelling ratio (q_w)
≤3	5	6 days	*a*
4	5	48 h	49 ± 8
5	5	44 h	29 ± 2
10	5	22 h	20.3 ± 0.5

a No gel formation.

Figure 2. Equilibrium weight swelling ratio of the PIB gels q_w shown as a function of the cross-linker (S_2Cl_2) concentration used in the gel preparation. c = 5 w/v %.

Figure 3. PIB beads of sizes 1−2 mm in dry state prepared by the suspension polymerization technique. c = 10 w/v %; S_2Cl_2 = 20%.

cross-linker added per mole of vinyl group in the polymer. According to Figure 1, a large excess of cross-linker (7−14 mol per mole of vinyl group) leads to the deswelling of the gels after their preparation. This behavior is not seen if the cross-linker concentration is below this value. Because of the importance of the post-cross-linking reactions in the present gelling system, all the gel samples prepared in this study were left in toluene for at least 3 weeks prior to swelling measurements.

Table 1 shows the results of experiments carried out at a fixed amount of the cross-linker S_2Cl_2 (5%) but at different polymer concentrations. If the butyl rubber concentration is less than 4%, no continuous gel forms in the reaction system after 6 days. Increasing concentration of butyl rubber in toluene decreases the swelling capacity of the gels. Another set of experiments was carried out at 5% butyl rubber concentration but at different levels of the cross-linker S_2Cl_2. From the molar mass of butyl rubber (3.9 × 10⁵ g/mol), one may calculate that 0.01% of S_2Cl_2 is sufficient to connect all the polymer chains into an infinite network. However, no gel formation was observed at S_2Cl_2 concentrations less than 0.6%. This means that a 60-fold excess of the cross-linker was necessary in order to produce a macroscopic network. This is probably due to the cycliztion reactions occurring between sulfur chloride and vinyl groups attached on the same polymer chains (Scheme 1).

Figure 2 shows the equilibrium weight swelling ratio q_w of the gels prepared at 5% polymer concentration plotted as a function of the cross-linker content used in the experiments. The reaction time was set to 3 days for cross-linker concentrations less than 2.5%. For higher concentrations, the reactions were carried out for 1 day. Each data point in Figure 2 is an average of
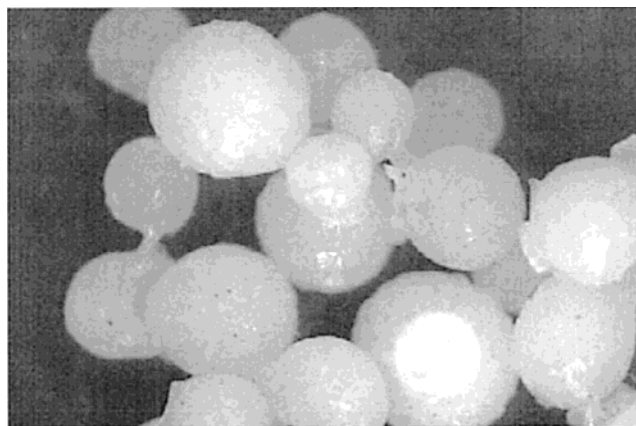
at least six separate experiments. The large error bars showing the standard deviations mainly arise from the inhomogeneity of the gel samples. We always observed that, during the cross-linking process, the macroscopic gel starts to form from the bottom part of the reaction tube. The gel samples which were cut from the same gel were found to swell at different extents; i.e., the upper part of the gel swells more than the lower part. Figure 2 indicates that the equilibrium swelling degree q_w of the gels increases first slightly with decreasing S_2Cl_2 concentration up to about 5%, but then q_w rapidly increases below this value and approaches 100 at S_2Cl_2 concentrations of 0.6−1.0%.

PIB gels in the form of beads were prepared using the suspension polymerization technique as described in the Experimental Section. Figure 3 shows PIB beads of sizes 1.0−2.0 mm in the dry state, prepared at 10% butyl rubber concentration in toluene and using 20% S_2Cl_2 as the cross-linker. By measuring the diameter of about 20 beads under microscope, their volume swelling ratio q_v in toluene was found to be 41 ± 8. The swelling behavior of the PIB beads in various solvents is shown in Figure 4. Here, the diameter of the beads in various solvents normalized with respect to that in cyclohexane (D/D_{CH}) is plotted as a function of the solubility parameter δ of the solvents. The largest bead diameter was recorded in cyclohexane with δ = 16.8 (MPa)⁰·⁵ whereas the diameter decreased by changing cyclohexane with methyl cyclohexane (δ = 16.0 (MPa)⁰·⁵) or with carbon tetrachloride (δ = 17.6 (MPa)⁰·⁵). Thus, the solubility parameter of solution cross-linked butyl rubber gels is 16.8 ± 0.8 (MPa)⁰·⁵, in accord with the reported value[12] of 16.5 (MPa)⁰·⁵ for bulk cross-linked butyl rubber. As in the PIB gels obtained by solution cross-linking process, the swelling capacity of the PIB beads in toluene increased with decreasing concentration of S_2Cl_2 or butyl rubber in the organic phase.

(2) Swelling in Mixed Solvents and Critical Conditions. Figure 5 shows swelling behavior of the PIB beads in cyclohexane/acetone (CH/Ace) and cyclohexane/methyl ethyl ketone (CH/MEK) mixtures. The swelling ratios are given in terms of the volume of the bead, normalized with respect to that in cyclohexane (V/V_{CH}). Addition of Ace or MEK into cyclohexane as a poor solvent decreases the volume of the bead in the solvent mixture. The beads deswell continuously between 40 and 70% MEK or between 30 and 60% Ace.
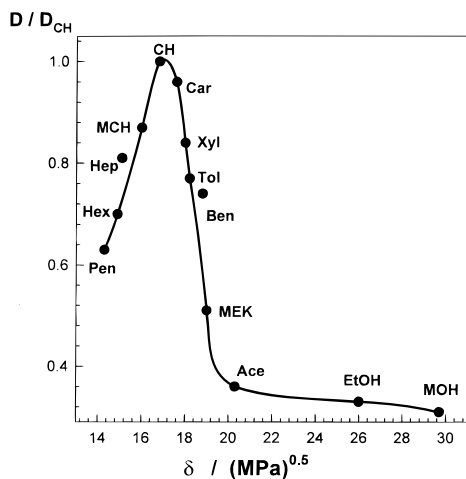
Figure 4. Normalized diameter of the PIB beads in various solvents shown as a function of the solubility parameter of the solvents. $c = 10$ w/v %; $S_2Cl_2 = 20\%$. Pen = n-pentane, Hex = n-hexane, Hep = n-heptane, MCH = methylcyclohexane, CH = cyclohexane, Car = carbon tetrachloride, Xyl = xylene, Tol = toluene, Ben = benzene, MEK = methyl ethyl ketone, Ace = acetone, EtOH = ethanol, MOH = methanol.
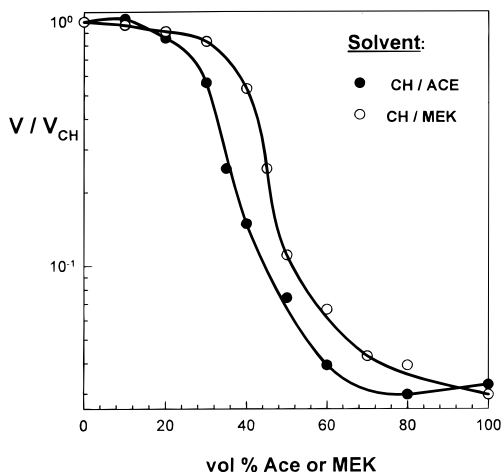

Figure 5. Normalized volume of the PIB beads in cyclohexane−acetone and cyclohexane−methyl ethyl ketone mixtures shown as a function of the solvent composition. $c = 10$ w/v %; $S_2Cl_2 = 20\%$.

In Figure 6, the equilibrium swelling degrees of the PIB gels in toluene/methanol mixtures are shown in terms of the polymer volume fraction v_2 plotted as a function of the toluene content of the external solution. For these swelling experiments, the gels were prepared by solution cross-linking process at four different cross-linker contents (4, 8, 17, and 24% S_2Cl_2) but at a fixed butyl rubber concentration corresponding to $v_{2c} = 0.047$. In all cases, the PIB gels in toluene/methanol mixtures with less than 3% methanol are in a swollen state. They exhibit a large degree of deswelling when the toluene content of the external solution is decreased from 97 to 90%. For instance, the loosely cross-linked gel with 4% S_2Cl_2 swells in toluene 61 times its dry mass. Addition of methanol in toluene as a poor solvent decreases its swelling capacity significantly, and a 7-fold decrease in gel volume was observed with a further increase in the methanol content of the solution, as may be seen from Figure 6. This swelling behavior is similar to that of acrylamide-based hydrogels in solvent/nonsolvent mixtures.[1,13] The shape of the swelling curve for the gel with 4% cross-linker shown in Figure 6 indicates that this
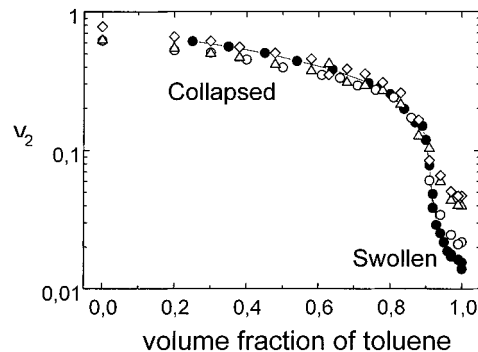
Figure 6. Dependence of the volume fraction of polymer in the swollen gels v_2 on the amount of toluene in toluene/methanol mixture. The filled circles represent results from the sample with lowest cross-link density, and the line through these points is a best fitting line. $c = 5\%$. Cross-linker contents used in the gel synthesis are 4 (●), 8 (○), 17 (△), and 24 v/w % (◇).
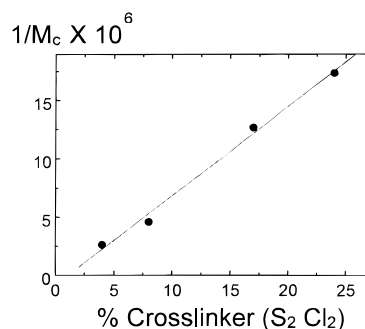
Figure 7. Dependence of degree of cross-linking on the amount of cross-linker. The ordinate values give inverse molecular weight between cross-links (in daltons), and the abscissa shows the v/w % of cross-linker S_2Cl_2.

gel may be in a critical state. In the following paragraphs, we show that this gel indeed passes through critical conditions as the quality of the solvent becomes poorer.

The cross-link density of the gels shown in Figure 6 was calculated from swelling measurements in cyclohexane, which is a good solvent for PIB at room temperature, with a χ parameter of 0.44.[12] The equilibrium swelling volume fraction was measured, and the average molecular weight M_c between cross-links was calculated from the expression[5]

$$M_c = -\frac{d_p\left(1 - \dfrac{2}{\phi}\right)V_1 v_{2c}^{2/3} v_2^{1/3}}{\ln(1 - v_2) + \chi v_2^2 + v_2} \qquad (7)$$

where ϕ is the functionality of junctions and V_1 is the molar volume of solvent. Results of calculations for four different degrees of cross-linking are shown in Figure 7. The straight line through the experimental points is a least-squares line, showing that the degree of cross-linking varies linearly with the amount of cross-linker S_2Cl_2 between 4 and 24%. The values of M_c for the four networks with cross-linker amount of 4, 8, 17, and 24% are 3.8×10^5, 2.2×10^5, 0.79×10^5, and 0.58×10^5, respectively.

After finding the cross-link densities of the gels M_c, the interaction parameter between the mixed solvent (toluene/methanol) and network may be obtained by solving eq 7 for χ as a function of v_2. For the 4% cross-linker sample, the values of χ obtained in this manner
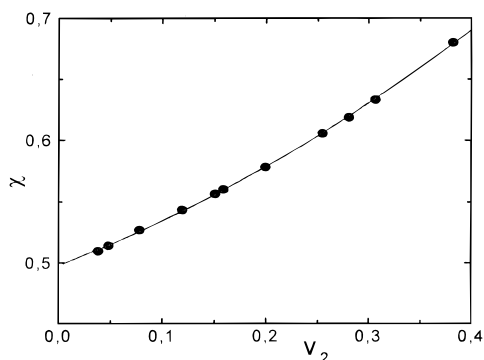
Figure 8. Dependence of the χ parameter on the volume fraction of polymer in the gel for system PIB−toluene/methanol.

are shown in Figure 8. The χ parameter of the mixed solvent toluene/methanol thus appears to be strongly dependent on v_2. In this case, changing the toluene/methanol ratio is analogous to changing the pH or temperature of the previous hydrogel experiments.[3] The curve in Figure 8 is obtained by least squares as

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 \qquad (8)$$

where $\chi_1 = 0.4995$, $\chi_2 = 0.3177$, and $\chi_3 = 0.3839$.

In earlier work, Erman and Flory[4] showed that when the χ parameter is expressed as a linear function of v_2, a necessary condition for the gel to go through critical conditions is to have $\chi_1 < 1/2$ and $\chi_2 > 1/3$. Equation 8 shows that the first of these conditions is satisfied, and the second one is within close proximity of $1/3$. Besides, the third coefficient, χ_3, which was neglected in previous work[4] is significant for the system PIB−toluene−methanol. Substitution of eq 8 in the expression for the chemical potential of solvent, $\Delta\mu_1/RT$, and equating to zero, one obtains

$$\Delta\mu_1/RT = \left(\chi_1 - \frac{1}{2}\right)v_2^2 + \left(\chi_2 - \frac{1}{3}\right)v_2^3 + \left(\chi_3 - \frac{1}{4}\right)v_2^4 +$$
$$\frac{v_{2c}^{2/3}}{M_c/V_1}v_2^{1/3} = 0 \quad (9)$$

At the critical point, eq 9 as well as its first and second derivatives with respect to v_2 equates to zero. For the 4% cross-linker sample, eq 9, as well as its second derivative, both equate to zero at $v_2 = 0.0889$. At this value of v_2, the first derivative of eq 9 does not equate to zero (having a value of -1.3×10^{-4}) but has two zero values in the close vicinity of $v_2 = 0.034$ and 0.129. Considering the uncertainities in the measurement of v_2, one can therefore assume that the first derivative is approximately zero around $v_2 = 0.088$ and that the gel passes very close to critical conditions around this point. In the three samples having higher cross-link densities, application of the above analysis showed that these samples are far from critical conditions at all values of swelling.

It is to be noted, in conclusion, that the system poly-(dimethylsiloxane)−benzene is another suitable candidate with regard to the extension of the present study.

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