Full Paper: We prepared several series of poly(isobutylene) (PIB) gels starting from butyl rubber in dilute toluene solutions using sulfur monochloride as a crosslinking agent. Solution and suspension-crosslinking techniques were used for the preparation of PIB gels in the form of rods, membranes, and beads in the size range of 1 to 3 mm. The gels were subjected to dynamic and equilibrium swelling measurements in toluene and cyclohexane as well as to the elasticity tests. Depending on the amounts of sulfur monochloride and butyl rubber in the crosslinking solution, PIB gels with different swelling capacities and elastic moduli were synthesized. The swelling ratio of the gels first increased rapidly with increasing swelling time but then decreased until an equilibrium was obtained. This unusual swelling behavior was accompanied with an increase of the elastic moduli of the gels during the swelling process. The results were explained with the postcrosslinking reactions taking place during the swelling process of PIB gels. By using the theory of equilibrium swelling, the number of segments in the network chains and the polymer-solvent interaction parameters were calculated for PIB gels prepared under various reaction conditions.



PIB beads of sizes 1-2 mm in swollen state prepared by suspension polymerization technique. c = 10% (w/v). S<sub>2</sub>Cl<sub>2</sub> = 20%.

# Swelling and Mechanical Properties of Solution-Crosslinked Poly(isobutylene) Gels

Selda Durmaz,<sup>1</sup> Sinan Fank,<sup>2</sup> Oguz Okay\*<sup>3</sup>

<sup>1</sup> TUBITAK Marmara Research Center, Department of Chemistry, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey

<sup>2</sup> TUBITAK National Metrology Institute, Force Laboratory, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey

<sup>3</sup> Istanbul Technical University, Department of Chemistry, 80626 Maslak, Istanbul, Turkey

Fax: 0212-2856386; E-mail: okayo@itu.edu.tr

Keywords: elastic modulus; poly(isobutylene) gels; post-crosslinking; solution crosslinking; sulfur monochloride; swelling

## Introduction

Butyl rubber, which is commercially available since 1943, consists of poly(isobutylene) (PIB) chains containing small amounts of isoprene units. The structure of butyl rubber may be represented as follows, where n is a number between 20 to 35:



butyl rubber

Because of the low degree of unsaturation in butyl rubber, its vulcanization requires much more powerful accelerators than the natural rubber.<sup>[1,2]</sup> Due to extensive chain scission reactions occurring in the presence of peroxide initiators such as dibenzoyl peroxide, vulcanization of butyl rubber by free radicals cannot be carried out. For the preparation of heat resistant compounds, e.g., in cable insulation stocks, its vulcanization is carried out using dioximes. For exceptional heat resistant applications such as in tires, phenolic resins are used as the vulcanization agent.

Recently, we have shown that butyl rubber can easily be crosslinked in an organic solution using sulfur monochloride as a crosslinking agent.<sup>[3]</sup> Sulfur monochloride, S<sub>2</sub>Cl<sub>2</sub>, is a liquid at room temperature and soluble in organic solvents. It was shown that sulfur monochloride is an effective crosslinking agent for butyl rubber in organic solutions. We have also demonstrated that the solution-crosslinked PIB gels immersed in toluenemethanol mixtures exhibit an abrupt deswelling, if the toluene content of the external solution is decreased from 97 to 90%.<sup>[3]</sup> By using the theory of equilibrium swelling, it was shown that the gel passes through the critical condition as the quality of the solvent becomes poorer. Besides the fundamental interest of solution-crosslinked PIB gels due to their critical behavior in solvent-nonsolvent mixtures, they are also suitable materials in a variety of applications such as oil separation from aqueous solutions.

In the present study, swelling and mechanical behavior of solution-crosslinked PIB gels were investigated in detail. For this purpose, several series of PIB gels in the form of rods, membranes, as well as beads of sizes 1 to 3 mm were prepared at various crosslinker ( $S_2Cl_2$ ) and butyl rubber concentrations. Solution and suspensioncrosslinking techniques were used for the gel preparation. The swelling ratios of the gels in toluene and in cyclohexane as well as their elastic moduli were measured at various swelling times. As will be seen below, several characteristic features of PIB gels were observed.

# **Experimental Part**

## 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 to 1.8 mol-% isoprene units. This polymer sample was purified by reprecipitation from toluene solution in acetone. Its weightaverage molecular weight  $\overline{M}_{w}$  was determined to be  $3.9 \times 10^5$  g/mol on a gel permeation chromatograph with polystyrene standards (Waters, Model M-6000A). The polydispersity index  $\overline{M}_{w}/\overline{M}_{n}$  was 2.5. The crosslinking agent sulfur monochloride, S2Cl2, 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.<sup>[4]</sup> The purities of both Aldrich and home-made sulfur monochlorides were higher than 98%. Toluene (Merck) was used as the solvent for the solution-crosslinking process. In the swelling experiments, reagent-grade solvents, toluene, and cyclohexane were used without further purification.

#### Synthesis of the Gels

The PIB gels were prepared by solution and suspensioncrosslinking techniques. By the solution-crosslinking process, the gels were prepared according to the following scheme: Five to ten grams of butyl rubber were first dissolved in 100 mL of toluene at room temperature  $(22 \pm 1 \,^{\circ}\text{C})$  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 5 mm internal diameters and about 100 mm length. For the preparation of PIB membranes, the solutions were transferred via syringes into moulds (two 25 cm  $\times$  25 cm glass slides separated by a PTFE gasket of thickness 0.7 mm). The crosslinking reactions proceed at room temperature and result in the formation of solution-crosslinked PIB gels.

After predetermined reaction times at room temperature, the gels were taken out from the glass tubes or from the moulds 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 four weeks. The amount of soluble polymer in toluene solution was checked gravimetrically after evaporation and precipitation in methanol. For reaction times  $\geq 24$  h, the weight fraction of gel was found to be always larger than 0.98 indicating the high crosslinking efficiency of sulfur monochloride.

For the synthesis of PIB gels in the form of beads, suspension-crosslinking technique was employed with water containing additives as the continuous phase. 200 mL of water containing bentonite (0.5 g), gelatin (0.2 g), and sodium chloride (0.8 g) were first introduced into a 500 mL roundbottom reactor and stirred at 450 rpm under nitrogen atmosphere for 10 min. Separately, butyl rubber dissolved in toluene (50 mL) was mixed with the crosslinker 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 under nitrogen atmosphere. After polymerization, the beads were separated from the water phase and they were sieved using ASTM sieves, washed several times first with water, then with acetone, and finally with toluene. The beads were left in toluene for four weeks during which toluene was refreshed every day.

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

1) Butyl rubber concentration *c*:

$$c = \frac{\text{mass of butyl rubber in g}}{\text{volume of toluene in mL}} \times 10^2$$
(1)

2) Crosslinker  $S_2Cl_2$  concentration (v/wt) X:

$$X = \frac{\text{volume of } S_2 Cl_2 \text{ in mL}}{\text{mass of butyl rubber in g}} \times 10^2$$
(2)

#### Swelling Measurements

The swelling capacity of the gels was measured at room temperature  $(22 \pm 1 \,^{\circ}\text{C})$  in toluene or in cyclohexane by using gravimetric and volumetric techniques. By the gravimetric technique, the masses of the gel samples after preparation,  $m_0$ , and after swelling, m, were measured on an electronic

Macromolecular Chemistry and Physics 6

balance (Sartorius BA 310 S). The relative mass of the gel with respect to after preparation state,  $m_r$ , was calculated as:

$$m_{\rm r} = \frac{m}{m_0} \tag{3}$$

By the volumetric technique, the diameters of the gel rods after preparation,  $D_0$ , and after swelling, D, were measured by a calibrated digital compass. The relative volume of the gel samples with respect to after preparation state,  $V_r$ , was calculated as:

$$V_{\rm r} = \left(\frac{D}{D_0}\right)^3 \tag{4}$$

Swelling ratio of the gel samples in the form of beads was also measured by the volumetric technique, in which the diameters of the beads after equilibrium swelling in solvents and after drying 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 interpretation of swelling measurements was made on the basis of volume fraction of polymer during crosslinking and at swelling, designated by  $v_2^0$  and  $v_2$ , respectively, where the volume fraction is defined as the volume of polymer divided by total volume. These variables are related to the relative gel masses by the relations:

$$v_2^0 = \left[1 + \frac{(q_{\rm F} - 1)\rho}{d_1}\right]^{-1} \tag{5}$$

$$v_2 = \left[1 + \frac{(m_r q_F - 1)\rho}{d_1}\right]^{-1}$$
(6)

where  $\rho$  and  $d_1$  are the densities of polymer and solvent, respectively, and  $q_F$  is the degree of swelling of the gel after preparation, i.e.,

$$q_{\rm F} = \left(\frac{\text{mass of the gel after synthesis}}{\text{mass of the dry gel}}\right) \tag{7}$$

 $q_{\rm F}$  of the gels was determined experimentally from the masses of the gel samples after synthesis and after extraction in toluene and drying. Eighteen separate experiments carried out at 10% polymer concentration but at various levels of crosslinker above 0.5% S<sub>2</sub>Cl<sub>2</sub> lead to  $q_{\rm F} = 7.5 \pm 0.3$ , which corresponds to  $v_2^0 = 0.127 \pm 0.005$ .  $q_{\rm F}$  was found to be 15.7 and 12.7 for 0.25 and 0.15% crosslinker, respectively. For calculations, we assumed that  $\rho = 0.92$  g/cm<sup>3</sup>,  $d_1 = 0.867$  g/cm<sup>3</sup>, and 0.779 g/cm<sup>3</sup> for toluene and cyclohexane, respectively.

#### Mechanical Measurements

Uniaxial compression measurements were performed on PIB gel samples in form of rods. All the mechanical measurements were conducted in a thermostated room of  $21 \pm 0.1$  °C. Briefly, cylindrical gel sample immersed in toluene or cyclo-



Figure 1. Typical stress-strain data for PIB gel samples after their preparation. c = 10%. X = 3%. (•) uncorrected data; (o) corrected data.

hexane was placed on a digital balance. A load was transmitted vertically to the gel through a road fitted with a PTFE end-plate. The force acting on the gel was calculated from the reading of the balance m as  $F = m \cdot g$ , where g is the gravitational acceleration, which is 9.803002 m  $\cdot$  s<sup>-2</sup> in the place of the measurement (National Metrology Institute of Turkey, UME, TUBITAK, Turkey). The resulting deformation  $\Delta l = l_0 - l$ , where  $l_0$  and l are the initial undeformed and deformed lengths, respectively, was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10<sup>-3</sup> mm. The force and the resulting deformation were recorded after 20 s of relaxation. The measurements were conducted up to about 20% compression. The deformation ratio a (deformed length/initial length) was calculated as  $\alpha = 1 - \Delta l/l_0$ . The corresponding stress f was calculated as f = F/A, where A is the cross-sectional area of the specimen,  $A = \pi r_0^2$ , where  $r_0$  is its initial radius.

For uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form:<sup>[5]</sup>

$$f = G(a - a^{-2}) \tag{8}$$

where *G* is the elastic modulus of the samples. Typical stress-strain data correlated according to Equation (8) are shown in Figure 1 as filled symbols. A discrepancy from the linear relationship is obvious at small compressions, which was observed in all gel samples prepared in this study. This deviation from theory is due to the imperfect geometry of the surface of the sample, which decreases the contact area between the PTFE plate and the sample at low compression, and results in relatively high deformations at low stresses.<sup>[6]</sup> Such deviations were also reported in the literature.<sup>[7-9]</sup> In order to correct this imperfection, the isotherm was re-drawn

by discarding the data at very low strains. The linear portion of the curve was then extrapolated to a value of  $-(a-a^{-2})$  at f = 0 (dashed curves in Figure 1) from which the corrected initial length was computed and the deformation ratios were suitably adjusted. The data corrected in this manner are also shown in Figure 1 as open symbols. The reversibility of the gel deformation was also checked by several samples and found to be reversible.

## **Results and Discussion**

We discuss the results of our experiments in three subsections. In the first subsection, dynamic swelling and elastic features of PIB gels are discussed. In the second subsection, equilibrium swelling properties of PIB gels and the polymer-solvent interaction parameters are discussed. In the last section, swelling features of PIB gels in the form of beads are given.

## Dynamic Swelling and Elastic Behavior of PIB Gels

Dynamic swelling behavior of PIB gels was investigated using gel samples in the form of rods of 5 mm in diameter and about 1 cm in length. The reaction time for the gel preparation was fixed as one day. In Figure 2, the relative mass  $m_{\rm r}$  and the relative volume  $V_{\rm r}$  of the gel samples measured using gravimetric and volumetric techniques, respectively, are plotted against the swelling time t. Toluene (filled symbols) and cyclohexane (open symbols) were used as the swelling agent in the experiments. The gels were prepared at a butyl rubber concentration c = 5% and at a crosslinker (S<sub>2</sub>Cl<sub>2</sub>) concentration X =10%. Figure 2 shows that after the initial fast swelling period of one day, the rate of swelling decreases and the gel attains a maximum swelling ratio after about two days. Interestingly, further increase in the swelling time results in the deswelling of the gels until they reach a limiting swelling ratio after about 10 d.

The appearance of a maximum in the swelling curve of polymeric gels has not been reported before. This unusual swelling behavior of solution-crosslinked PIB gels was checked by using PIB gel samples prepared under various conditions. In Figure 3,  $m_r$  versus swelling time plots are shown for PIB gels prepared at c = 10% and at various levels of crosslinker  $S_2Cl_2(X)$ , as indicated in the figure. The relative volume  $V_r$  versus swelling time plots of the same gels are shown in Figure 4. In this figure, only gel samples with crosslinker content  $X \ge 3\%$  are shown because those prepared below 3% S<sub>2</sub>Cl<sub>2</sub> were too weak for volumetric determination of their swelling ratios. It is seen that, at low crosslinker contents (X < 3%, Figure 3), the gel swells up to a critical time and then attains a constant mass. The lower the crosslinker content X, the higher both the equilibrium degree of swelling and the initial rate of swelling. This is expected from the usual swelling kinetics of gels. However, for gels prepared at a



Figure 2. The relative mass  $m_r$  and the relative volume  $V_r$  of PIB gels shown as a function of the swelling time. Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 5%. X = 10%. The curves only show the trend of data.

crosslinker concentration *X* higher than 3%, the swelling curves exhibit maxima. Another point shown in Figure 3 and 4 is, that both the maximum swelling ratio and the equilibrium degree of swelling of the gel sample with X = 20% are much higher than those of other samples prepared at X = 5 and 10%.

In order to explain the unusual swelling feature of PIB gels, the elastic modulus measurements were conducted on gel samples at different swelling times. Elastic modulus *G* relates to the crosslink density of a Gaussian network in the rubbery state through the equation:<sup>[5,10]</sup>

$$G = A \frac{\rho}{\overline{M}_{c}} RT(v_{2}^{0})^{2/3} (v_{2})^{1/3}$$
(9)

where  $\rho$  is the polymer density,  $\overline{M}_c$  is the molecular weight of the network chains, *R* and *T* are in their usual



Figure 3. The relative mass  $m_r$  of PIB gels shown as a function of the swelling time. Toluene and cyclohexane were the swelling agents. c = 10%. The amounts of crosslinker X are indicated in the Figure.



Figure 4. The relative volume  $V_r$  of PIB gels shown as a function of the swelling time. Toluene (left) and cyclohexane (right) were the swelling agents. c = 10%. The amounts of crosslinker *X* are indicated in the Figure.

meaning. The front factor A equals to 1 for affine network and  $1-2/\phi$  for phantom networks, where  $\phi$  is the functionality of the crosslinks. The average number of segments between two successive crosslinks N relates to  $\overline{M}_c$ through the equation:

$$N = \left(\frac{\rho}{\overline{M}_{\rm c}} V_{\rm l}\right)^{-1} \tag{10}$$

where  $V_1$  is the molar volume of segment.

The crosslinked polymer concentrations after the gel preparation  $v_2^0$  and after swelling  $v_2$  were calculated from the swelling ratios as explained in the experimental section. In Figure 5A and 5B, the crosslinked polymer concentration in the gel  $v_2$  and the elastic modulus *G* in kPa are shown as a function of the swelling time. The data



Figure 5. Variations of the polymer concentration,  $v_2$ , elastic modulus, *G*, and the number of segments between two successive crosslinks, *N*, with the swelling time of PIB gels. Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 10%. X = 10 (left) and 20% (right).

points are for gels prepared at c = 10% and at two different levels of the crosslinker S<sub>2</sub>Cl<sub>2</sub>, namely at X = 10 (left) and 20% (right). Filled and open symbols represent the results of measurements conducted in toluene and cyclohexane, respectively. As the gel swells in toluene or in cyclohexane, the gel phase becomes dilute so that  $v_2$ decreases. The maxima shown in Figure 4 thus correspond to the minima in  $v_2$  versus time plots. After crossing the minimum,  $v_2$  increases again due to the deswelling of the gels.

Elastic modulus of gels is known to decrease during the swelling process due to the simultaneous decrease of the concentration of the network chains (Equation (9)). However, Figure 5B shows opposite behavior; the modulus *G* rapidly increases in the first day of swelling. Assuming affine network behavior (A = 1), the crosslink densities of the gel samples in terms of *N* were calculated from their polymer concentration  $v_2$  and elastic moduli *G* using Equation (9) and (10). The results are collected in Figure 5C as a function of the swelling time in toluene and cyclohexane. A rapid decrease in *N* is seen in the Figure during the fast swelling period indicating that the crosslink den-



Figure 6. Variations of the polymer volume fraction,  $v_2$ , elastic modulus, *G*, and the number of segments between two successive crosslinks, *N*, with the swelling time of PIB gels. Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 5%. X = 10%.

sity of the gel rapidly increases during the swelling process. At longer swelling times, *N* remains almost constant. Figure 5C also shows that the decrease in *N* during swelling is much more rapid at a high crosslinker content.

In Figure 6, the variations of  $v_2$ , *G*, and *N* with the swelling time are shown for gel samples prepared in a more dilute butyl rubber solution, namely at c = 5%.



Scheme 1.

Comparison of Figure 5 and 6 indicates that the decrease in N becomes more abrupt as c decreases. Thus, the increase of the crosslink density of PIB gels during swelling becomes drastic if the polymer concentration is low or the crosslinker content is high. For example, the gel prepared at c = 5% and X = 10% has an elastic modulus after preparation G = 570 Pa which corresponds to N =2000. After one day of immersion time in cyclohexane, the gel swells and the polymer concentration in the gel  $v_2$ decreases from 0.047 to 0.019. If one assumes that the crosslink density remains constant during swelling, G should decrease from 570 to 420 Pa due to the decrease in the polymer concentration. Opposing this, G increases to 2570 Pa which corresponds to N = 300. Thus, during the initial swelling period of this gel sample, the average number of segments between two successive crosslinks decreases from 2000 to 300 units. This indicates that, as the gel becomes dilute by absorbing solvent, crosslinking reactions occur within the gel volume. It is to be noted that the gel formation reactions in glass tubes were carried out for one day. Increasing the reaction time up to one week resulted no change in the moduli of the gel samples after their preparation. This indicates that the crosslinking reactions taking place during swelling do not occur under the condition of the gel preparation, at which the polymer concentration equals to 5 to 10%. It seems that the increasing degree of dilution during gel swelling promotes the occurrence of the crosslinking reactions.

Our experimental results are consisted with the following scenario: The crosslinking reactions between the PIB chains via sulfur monochloride  $S_2Cl_2$  are believed to proceed in steps as in the reaction between ethylene and  $S_2Cl_2$  (Scheme 1).<sup>[3, 11, 12]</sup>

Attack of sulfur dichloride to the internal vinyl group of the polymer leads to the formation pendant sulfur chloride groups on the PIB chains. These pendant sulfur chloride groups act as potential crosslink points due to

$\frac{\mathbf{S}_{2}\mathbf{Cl}_{2}}{\%}$	$\frac{G \text{ after preparation}}{\text{kPa}}$	N after preparation	N after swelling	mol S <sub>2</sub> Cl <sub>2</sub> /mol vinyl group
3	1.95 (0.05)	1 520 (80)	628 (109)	1.3
5	2.94 (0.6)	1060 (240)	619 (190)	2.2
10	3.34 (0)	890 (5)	415 (35)	4.3
20	1.77 (0.13)	1 690 (140)	526 (8)	8.6
20 <sup>a)</sup>	0.57 (0.08)	1917 (290)	297 (19)	8.6

Table 1. Elastic moduli and the crosslink densities of PIB gels prepared at various crosslinker ( $S_2Cl_2$ ) concentrations. Initial butyl rubber concentration c = 10%. The numbers given in parentheses are the standard deviations.

<sup>a)</sup> Initial butyl rubber concentration c = 5%.

the fact that the reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective crosslinks. For the occurrence of a cross-linking reaction, two PIB chains must first diffuse toward each other through the solvent and then, two segments on different chains bearing vinyl and pendant sulfur chloride groups must re-orient to a position in which they are able to react each other. Thus, the crosslinking reactions between PIB chains via  $S_2Cl_2$  are expected to be diffusion controlled and, under the condition of the gel preparation, the rate of these reactions should decrease rapidly beyond the gel point due to the translational and segmental diffusion limitations.

During the swelling process, as the solvent moves inside the gel phase, the network chains become increasingly mobile. As a result, the probability that one network chain meets another chain increases as the gel swells, so that the rate of crosslinking reactions increases.

In Table 1, the amount of the crosslinker  $S_2Cl_2(X)$  used in the gel preparation, the modulus G after the gel preparation, the number of segments between successive crosslinks N after the gel preparation and after equilibrium swelling are collected. Assuming that the butyl rubber contains 1.5-1.8 mol-% isoprene units, the molar masses of isobutylene, isoprene units, and S<sub>2</sub>Cl<sub>2</sub> are 56, 68, and 135 g/mol, respectively, and the density of S<sub>2</sub>Cl<sub>2</sub> is 1.68 g/mL, a multiplication factor of 0.43 ± 0.04 converts the crosslinker content X into the moles of crosslinker added per mol of vinyl group in the polymer. These values are also given in the last column of Table 1. It is seen, that increasing crosslinker content from 1 to 4 mol of  $S_2Cl_2$  per mol vinyl group decreases the N value after the gel preparation, i.e., increases the crosslink density of the gel after preparation. This is due to the increasing number of potential crosslink points on the chains with increasing S<sub>2</sub>Cl<sub>2</sub> content (Scheme 1), which increases the probability of crosslinking. Further increase in the amount of crosslinker decreases again the crosslink density, indicating that a large excess of crosslinker inhibits the crosslinking reactions. Table 1 also shows that the values of N found in equilibrium swollen gels are almost constant and equal to 547 ± 100. Thus, the post-crosslinking reactions during swelling seem to stop after reaching a critical crosslink density so that all the gel samples prepared at various crosslinker content exhibit almost the same effective crosslink density after swelling. This critical value of N decreased further to 297 (last row in Table 1), if the polymer concentration during the gel preparation is decreased from 10 to 5% due to the simultaneous increase of the mobility of the PIB chains.

By using the Flory's swelling equation for equilibrium swollen gels, i.e.,<sup>[10]</sup>

$$\ln(1-v_2) + v_2 + \chi v_2^2 + N^{-1} (v_2^{1/3} (v_2^0)^{2/3} - v_2/2) = 0$$
(11)

together with the experimentally determined equilibrium  $v_2$  and N values of PIB gels prepared at crosslinker contents X between 3 and 20%, we calculated the polymersolvent interaction parameter  $\chi$  for cyclohexane as 0.44 ± 0.02. This value of  $\chi$  is in good agreement with the previous reported data.<sup>[13]</sup> This indicates that the introduction of sulfur and chlorine atoms in the gel did not change their thermodynamic properties.

## Equilibrium Swelling Behavior

Equilibrium swelling behavior of PIB gels was investigated using gel samples in the form of membranes of various crosslinker contents X between 0.15 and 10%. The initial butyl rubber concentration c was fixed at 10%. The reaction time was also fixed as one week. Swelling experiments were performed both in toluene and cyclohexane. Due to the importance of the post-crosslinking reactions in the present gelling system, all the gel samples were left in solvents for at least four weeks prior to the swelling measurements. The results of equilibrium swelling measurements in toluene and cyclohexane are collected in Figure 7 as the dependencies of  $m_r$  and  $v_2$  on the crosslinker concentration X. The data points shown in the Figure are averages of at least six separate measurements. Loosely crosslinked PIB membranes with swelling capacities up to 25 g of cyclohexane per g of gel could be prepared at crosslinker contents as low as 0.2%. Increasing crosslinker content up to X = 3% decreased the swelling capacity of the gels but then it increased again at higher crosslinker concentrations (Figure 7).



Figure 7. The relative mass,  $m_r$ , and the polymer volume fraction,  $v_2$ , of PIB membranes shown as a function of their crosslinker contents X. Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 10%.

Using the  $\chi$  parameter value of 0.44 found for cyclohexane in the previous section together with the equilibrium polymer concentrations  $v_2$  in cyclohexane (Figure 7), the crosslink density of the gel samples was calculated using Equation (11). The results are shown in Figure 8 as the dependence of N on the crosslinker content X. It is seen that N first decreases with increasing crosslinker content but then it increases again. Thus, in accord with the results of the previous section, presence of a large excess of the crosslinker S<sub>2</sub>Cl<sub>2</sub> decreases the crosslinking efficiency. After finding the crosslink densities of the gels, their swelling ratios in toluene were used to evaluate the interaction parameter  $\chi$  between PIB and toluene by use of Equation (11). The results of calculations are collected in Figure 9 as the dependence of  $\chi$  on the polymer concentration  $v_2$ . It is seen that the  $\chi$  parameter for PIB-



Figure 8. Variation of the number of segments between two successive crosslinks N with the crosslinker content X of PIB gels.



Figure 9. The dependence of  $\chi$  parameter for the PIB-toluene system on the polymer concentration  $v_2$ . The curve is a linear best fit to the data points.

toluene system is dependent on the polymer concentration in the range of  $v_2 = 0.01-0.10$ . A linear best fit to the data points gives the  $\chi$  relation:

$$\chi = 0.49 + 0.25v_2 \tag{12}$$

Using the phantom network model, a similar  $\chi$  equation  $(\chi = 0.49 + 0.21v_2)$  was obtained. It must be pointed out that, for non-ionic gels, the requirement for the polymer collapse, i.e., for the coexistence of two gel phases in



Figure 10. PIB beads of sizes 1-2 mm in swollen state prepared by suspension polymerization technique. c = 10% (w/v). S<sub>2</sub>Cl<sub>2</sub> = 20%.

equilibrium with pure solvent is that the coefficients of Equation (12) should be close to 1/2 and 1/3, respectively.<sup>[14]</sup> Although such a requirement for the polymer collapse is rare for real polymer-solvent systems, Equation (12) suggests that PIB-toluene binary system is a suitable candidate for the observation of the polymer collapse.

## PIB Beads

PIB gels were also prepared in the form of beads using the suspension-crosslinking technique as described in the experimental section. Figure 10 shows PIB beads of sizes 1.0-2.0 mm in the swollen state, prepared at 10% butyl rubber concentration and using 20% S<sub>2</sub>Cl<sub>2</sub> as the crosslinker. The swelling capacities of PIB beads were determined by measuring the diameter of at least 20 beads under a microscope, both after equilibrium swelling and after drying. The equilibrium volume swelling ratio  $q_v$ was calculated as

$$q_{\rm v} = \frac{\text{volume of swollen bead}}{\text{volume of dry bead}} = \left(\frac{D}{D_{\rm dry}}\right)^3 \qquad (13)$$

where *D* and  $D_{dry}$  are the diameter of equilibrium swollen and dry bead, respectively. The dependence of  $q_v$  in toluene and cyclohexane on the crosslinker content shown in Figure 11 indicates that the volume swelling ratio first decreases with increasing amount of crosslinker up to 10% and then increases again. This type of dependence is in accord with the results of previous sections (Figure 3–7). The large error bars in the figure is due to the bead-to-bead variation of the swelling ratios. The particle size dependence of the volume swelling ratio in toluene and cyclohexane is illustrated in Figure 12. The beads were prepared at 10% crosslinker content. It is seen



Figure 11. Variation of the volume swelling ratio of PIB beads,  $q_{\nu}$ , with their crosslinker contents. Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 10%.



Figure 12. Variation of the volume swelling ratio of PIB beads,  $q_{\nu}$ , with the particle diameter in dry state,  $D_{dry}$ . Toluene (filled symbols) and cyclohexane (open symbols) were the swelling agents. c = 10%. X = 10%.

that the beads of smaller diameter swell much more than those of larger diameter. This is probably due to the increase of the total surface area of beads with decreasing diameter, which increases the contact area between the organic and continuous (aqueous) phases during the gel formation process and results in an increasing extent of hydrolysis of the crosslinker  $S_2Cl_2$  during the suspensioncrosslinking.

# Conclusions

Depending on the amounts of sulfur monochloride and butyl rubber in the crosslinking solution, PIB gels with different swelling capacities and elastic moduli were synthesized. The swelling ratio of the gels first increased rapidly with increasing swelling time but then decreased until an equilibrium was obtained. This unusual swelling behavior was accompanied with an increase of the elastic moduli of the gels during the swelling process. The results were explained with the post-crosslinking reactions taking place during the swelling process of PIB gels. By using the theory of equilibrium swelling, the number of segments in the network chains and the polymer-solvent interaction parameters were calculated for PIB gels prepared under various reaction conditions.

Acknowledgement: We thank Mr. Ayhan Mesci from Marmara Research Center for technical assistance during the course of this work.

- Received: July 3, 2001
- Revised: September 27, 2001
- Accepted: September 28, 2001

- H. F. Mark, N. G. Gaylord, N. M. Bikales, "Encyclopedia of Polymer Science and Technology", Vol. 2, 1st ed., Interscience Publ., New York 1965, p. 777.
- [2] L. W. Codd, K. Dijkhoff, J. H. Fearon, C. I. van Oss, H. G. Roebersen, E. G. Stanford, "*Materials and Technology*", Vol. 5, 1<sup>st</sup> ed., Longman Group Ltd., London 1972, p. 485.
- [3] O. Okay, S. Durmaz, B. Erman, *Macromolecules* **2000**, *33*, 4822.
- [4] F. Feher, "Sulfur, selenium, tellurium", in: *Handbook of Preparative Inorganic Chemistry*, G. Brauer, Ed., Vol. 1, 2<sup>nd</sup> ed., Academic Press, New York 1963, p. 341.
- [5] L. R. G. Treloar, "*The Physics of Rubber Elasticity*", University Press, Oxford 1975.
- [6] C. Sayil, O. Okay, *Polymer* **2001**, *42*, 7639.
- [7] F. Rietsch, D. Froelich, Polymer 1975, 16, 873.
- [8] D. Froelich, D. Crawford, T. Rozek, W. Prins, *Macromolecules* 1972, 5, 100.
- [9] R. W. Richards, N. S. Davidson, *Macromolecules* 1986, 19, 1381.
- [10] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY 1953.
- [11] H. F. Mark, J. J. McKetta, D. F. Othmer, "Encyclopedia of Chemical Technology", Vol. 19, 1<sup>st</sup> ed., Interscience Publ., New York 1969, p. 392.
- [12] M. Akiba, A. S. Hashim, Prog. Polym. Sci. 1997, 22, 475.
- [13] "Polymer Data Handbook", J. E. Mark, Ed., Oxford University Press, 1999.
- [14] B. Erman, P. J. Flory, Macromolecules 1986, 19, 2342.