## Macroporous Polyisobutylene Gels: A Novel Tough Organogel with Superfast Responsivity

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ABSTRACT: Macroporous gels were prepared by solution crosslinking of butyl rubber (PIB) in frozen benzene solutions using sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>) as a crosslinking agent. The effect of different preparation conditions, including the crosslinker concentration and the gel preparation temperature, on the gel properties was investigated. S<sub>2</sub>Cl<sub>2</sub> was found to be an efficient crosslinking agent even at very low reaction temperatures up to -22 °C and at crosslinker ratios down to about 0.9 mol S<sub>2</sub>Cl<sub>2</sub>/mol internal vinyl group on PIB. The gels prepared from frozen solutions of PIB contain about 97% organic liquid, and they are very tough; they can be compressed up to about 100% strain without any crack development, during which the total liquid inside the gel is removed. Further, the compressed gel immediately swells in contact with good solvents to recover its original shape. The low-temperature gels have a porous structure with irregular large pores of  $10^{1}-10^{2} \mu m$  in diameter, separated by pore walls of about 10  $\mu$ m in width with a high polymer concentration, which provide structural support to the material. The gels also exhibit completely reversible swelling–deswelling cycles in toluene and methanol, respectively, i.e., they return to their original shape and original mass after a short reswelling period. The results suggest that both phase separation of PIB chains at low temperatures and the presence of frozen benzene templates are responsible for the porosity formation in PIB gels.

#### Introduction

Design of gels with a good mechanical performance together with a fast response rate is crucially important in many existing and potential application areas of soft materials. However, polymeric gels that are highly swollen in a liquid are normally very brittle. This feature of gels originates from their very low resistance to crack propagation due to the lack of an efficient energy dissipation mechanism in the gel network.<sup>1,2</sup> A number of techniques for toughening of gels have recently been proposed including the double network gels,<sup>3,4</sup> topological gels,<sup>5</sup> gels formed by hydrophobic associations,<sup>6</sup> gels made by mobile crosslinkers such as clay nanoparticles (nanocomposite hydrogels),<sup>7</sup> and microsphere composite hydrogels.<sup>8</sup> Although these techniques create energy dissipation mechanisms to slow crack propagation, and thus improve the mechanical properties of gels, their response rate against the external stimuli is not as fast as required in many gel applications. In order to increase the response rate, one may create an interconnected pore structure inside the gel network.<sup>9</sup> In porous gels, the absorption or desorption of solvent occurs through the pores by convection, which is much faster than the diffusion process that dominates the nonporous gels. However, porous gels have a complex microstructure and show poor mechanical performance due to the loose pore structure, consisting of rather weakly joined microgel particles.<sup>10</sup> On the basis of the gel properties required by the application areas, an ideal gel can be defined as a soft material exhibiting both a high degree of toughness and a fast response rate against the external stimuli.

Here, we describe the preparation of a novel tough organogel with superfast responsive properties. The main characteristic of the present gel is its macroporous structure consisting of micrometer-sized interconnected pores separated by thick and dense pore walls with a high polymer concentration, which provide structural support to the material. The starting material of the organogel is a linear polyisobutylene containing small amounts of internal unsaturated groups (isoprene units), known as butyl rubber. The structure of butyl rubber may be represented as follows:



butyl rubber

where *n* is 60 for the polymer samples used in the present work. Because of the low degree of unsaturation in butyl rubber, its vulcanization requires much more powerful accelerators than natural rubber.<sup>11,12</sup> Further, solution crosslinking of butyl rubber by free-radicals cannot be carried out due to the extensive chain scission reactions.<sup>13,14</sup> Previous work within this department has shown that the dilute solutions of butyl rubber can easily be crosslinked using sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>) as a crosslinking agent.13 Sulfur monochloride, a liquid at room temperature and soluble in organic solvents, was found to be an effective crosslinker for the crosslinking processes of butyl rubber in toluene solutions. However, the gels thus obtained were very brittle and show a slow rate of response against the external stimuli. For example, collapsed gels in methanol attained their equilibrium swollen states in toluene within a few days.<sup>13</sup> The lack of mechanical stability as well as the slow rate of response of gels based on butyl rubber limited their applications, i.e., as oil sorbent materials in the oil spill cleanup from surface waters.

Herein, we introduce a general method that allows the preparation of superfast responsive butyl rubber gels with excellent mechanical properties. The gels containing about 97% organic liquid can be compressed up to about 100% strain without any crack development. Further, the compressed gel immediately swells in contact with good solvents. Our strategy to prepare such gels is to conduct the solution crosslinking reactions of butyl rubber under frozen state conditions. It should be noted that the freezing method has been used before for the preparation of porous hydrogels.<sup>15</sup> In the present work, benzene

was selected as the solvent due to the relatively high freezing point (5.5 °C) compared to toluene (-95 °C) so that the reactions in the frozen state can be conducted at much higher temperatures. In the preliminary experiments, it was found that when a 5 w/v % butyl rubber solution is frozen at -18 °C, 14% of benzene remains unfrozen in the apparently frozen system. Thus, as benzene freezes, the polymer chains are excluded from the frozen benzene structure and they accumulate in the unfrozen microregions, making the butyl rubber concentration in these regions about 36 w/v %, high enough to conduct the crosslinking reactions even at -18 °C. Further, since benzene is a poor solvent for polyisobutylene at low temperatures, a phase separation also occurs during the freezing process, contributing to the accumulation of polymer chains in the unfrozen regions. The solution crosslinking of butyl rubber at temperatures below the freezing point of the reaction system followed removal of benzene crystals produced macroporous organogels containing pores with the approximate shape and dimensions of the benzene crystals.

#### **Experimental Part**

**Materials.** Butyl rubber (Butyl 165, Exxon Chem. Co) used in this work contained 1.5-1.8 mol % isoprene units. 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, S<sub>2</sub>Cl<sub>2</sub>, was purchased from Aldrich Co. Benzene, toluene, and methanol (all Merck grades) were used as the solvent for the solution crosslinking reactions, swelling, and deswelling agents, respectively.

Synthesis of the Gels. The gels were prepared by the solution crosslinking technique according to the following scheme: Butyl rubber (0.01-5 g) was first dissolved in 100 mL of benzene at room temperature (20  $\pm$  1 °C) overnight. Then, portions of this solution, each about 10 mL, were transferred to volumetric flasks, and different amounts of sulfur monochloride were added under vigorous stirring at 20 °C. The homogeneous reaction solutions were transferred with a syringe into several glass tubes of 8 mm internal diameter and about 100 mm length. For mechanical tests, the gel samples were prepared in plastic syringes of about 16 mm internal diameter. The crosslinking reactions were carried out in a freezer at predetermined temperatures for 24 h. The cooling profiles of the reaction solutions to attain the final temperature  $T_{\text{prep}}$  were measured by immersing a thermocouple into the reaction solutions. The following variables were used for defining the composition of the gel forming systems: (a) gel preparation temperature,  $T_{\text{prep}}$ , the temperature of the reaction solution at thermal equilibrium, (b) butyl rubber concentration,  $c_{\rm P}$ ,

$$c_{\rm P} = \frac{\text{mass of butyl rubber in g}}{\text{volume of solution in mL}} \times 10^2$$
(1)

(c) crosslinker concentration, S<sub>2</sub>Cl<sub>2</sub> %,

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

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  $0.43 \pm 0.04$  converts S<sub>2</sub>Cl<sub>2</sub> % into the molar ratio of the crosslinker S<sub>2</sub>Cl<sub>2</sub> to the vinyl group in the polymer. Three sets of gelation experiments were carried out (Table 1). In the first set, the butyl rubber concentration  $c_P$ was varied between 0.01 and 5% while  $T_{\text{prep}}$  and S<sub>2</sub>Cl<sub>2</sub> % were set to  $-18 \,^{\circ}$ C and 6%, respectively. In the second set, the temperature  $T_{\text{prep}}$  was varied between  $-22 \,^{\circ}$ C and 21  $^{\circ}$ C. In the third set, the crosslinker concentration was varied between 2 and 10% at  $T_{\text{prep}}$  $= -22 \,^{\circ}$ C and  $c_P = 5\%$ .

Table 1. The Three Sets of Gelation Experiments Conducted at Various Reaction Conditions

code	$c_{\rm P}  (w/v \%)$	$T_{\text{prep}}$ (°C)	$S_2Cl_2$ (v/w%)
1	$0.01 \rightarrow 5$	-18	6
2	5	$-22 \rightarrow +21$	6
3	5	-22	$2 \rightarrow 10$

**Characterization of Gels.** PIB gels were taken out of 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 at 20 °C, and toluene was replaced every other day over a period of at least for 1 month to wash out the soluble polymer and the unreacted crosslinker. The swelling equilibrium was tested by measuring the diameter of the gel samples by using an image analyzing system consisting of a microscope (XSZ single zoom microscope), a CDD digital camera (TK 1381 EG), and a PC with the data analyzing system Image-Pro Plus. The swelling equilibrium was also tested by weighing the gel samples. In order to dry the equilibrium swollen gel samples, they were first immersed in methanol over night and then dried under vacuum. The gel fraction  $W_g$  defined as the amount of crosslinked (insoluble) polymer obtained from one gram of butyl rubber was calculated as

$$W_{\rm g} = \frac{m_{\rm dry}}{m_{\rm o}c_{\rm P}/100} \tag{3}$$

where  $m_{\rm dry}$  and  $m_{\rm o}$  are the weights of the gel samples after drying and just after preparation, respectively. The equilibrium volume and the equilibrium weight swelling ratios of the gels,  $q_{\rm v}$  and  $q_{\rm w}$ , respectively, were calculated as

$$q_{\rm v} = \left(D/D_{\rm drv}\right)^3 \tag{4a}$$

$$q_{\rm w} = (m/m_{\rm dry}) \tag{4b}$$

where D and  $D_{dry}$  are the diameters of the equilibrium swollen and dry gels, respectively, m and  $m_{dry}$  are the weight of gels after equilibrium swelling in toluene and after drying, respectively.

For the deswelling kinetics measurements, the equilibrium swollen gel samples in toluene were immersed in methanol at 20 °C. The weight changes of gels were measured gravimetrically after blotting the excess surface solvent at regular time intervals. For the measurement of the swelling kinetics of gels, the collapsed gel samples in methanol were transferred into toluene at 20 °C. The weight changes of gels were also determined gravimetrically as described above. The results were interpreted in terms of the normalized gel mass with respect to its swollen state  $m_{rel} = m_t/m$ , where  $m_t$  is the mass of the gel sample at time t. The swelling kinetics measurements were also conducted in situ by following the diameter of the gel samples under the microscope using the image analyzing system mentioned above. The results were given as the relative volume swelling ratio  $V_{rel} = (D_t/D)^3$  where  $D_t$  is the gel diameter at time t.

Uniaxial compression measurements were performed on equilibrium swollen gels in toluene. All the mechanical measurements were conducted in a thermostated room of  $20 \pm 0.5$  °C. The stressstrain isotherms were measured by using an apparatus previously described.<sup>16</sup> The elastic modulus *G* was determined from the initial slope of linear dependence,  $f = G (\alpha - \alpha^{-2})$ , where *f* is the force acting per unit cross-sectional area of the undeformed gel specimen, and  $\alpha$  is the deformation ratio (deformed length/initial length).

To estimate the nonfreezable benzene content of the gels, DSC measurements were carried out on a Perkin-Elmer Diamond DSC. Solutions of 5% butyl rubber in benzene were first frozen at -18 °C for 48 h, and then a portion of this solution (about 0.01 g) was placed in the aluminum sample pan of the instrument. The pan with frozen solution was sealed and weighed. Then, it was held within the instrument at -18 °C for 2 h and then heated to 20 °C with a scanning rate of 1 °C/min. In this way, the transition enthalpy  $\Delta H$  for the melting of frozen benzene was determined.



**Figure 1.** Gel fraction  $W_g$  shown as functions of the gel preparation temperature  $T_{\text{prep}}$  and initial PIB concentration  $c_P$ . (A)  $c_P = 5\%$ ,  $S_2Cl_2 = 6\%$ . (B)  $S_2Cl_2 = 6\%$ ,  $T_{\text{prep}} = -18$  °C. The inset to Figure 1B shows the gel fraction data obtained at  $c_P \le 0.05\%$ .

After the scans, the pans were punctured and dried at 80 °C to constant weight. The total benzene content of the gel sample  $m_{\text{benzene}}$  was calculated as  $m_{\text{benzene}} = m_1 - m_2$ , where  $m_1$  is the weight of pan with solution and  $m_2$  is the same weight but after drying. The mass fraction of nonfreezable benzene in the solution,  $f_{\text{benzene}}$  was estimated as

$$f_{\text{benzene}} = 1 - (\Delta H / \Delta H_{\text{m}}) / m_{\text{benzene}}$$
(5)

where  $\Delta H_{\rm m}$  is the heat of melting of benzene in J/g.

The pore volume  $V_p$  of the networks was estimated through uptake of methanol of dry gels. Since methanol is a nonsolvent for PIB, it only enters into the pores of the polymer networks. Thus,  $V_p$  (milliliter pores in one gram of dry polymer network) was calculated as

$$V_{\rm p} = (m_{\rm M} - m_{\rm dry})/(d_{\rm M}m_{\rm dry}) \tag{6}$$

where  $m_{\rm M}$  is the weight of the network immersed in methanol after 2 h and  $d_{\rm M}$  is the density of methanol.

For the texture determination of dry gels, scanning electron microscopy studies were carried out at various magnifications between 50 and 300 times (Jeol JSM 6335F field emission SEM). Prior to the measurements, network samples were sputter-coated with gold for 3 min using a sputter-coater S150 B Edwards instrument. The texture of dry gels was also investigated under XSZ single zoom microscope using the image analyzing system Image-Pro Plus.

#### **Results and Discussion**

The solution crosslinking of butyl rubber (hereafter abbreviated as PIB) in benzene using sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>) as a crosslinker was carried out at various temperatures  $T_{\text{prep}}$  between -22 and 21 °C. We first monitored the variation of the crosslinking efficiency of S2Cl2 depending on the gel preparation temperature  $T_{\text{prep}}$  by the gel fraction measurements. Figure 1A shows the gel fraction  $W_g$  plotted as a function of  $T_{prep}$ . For this set of experiments, the concentrations of PIB and S<sub>2</sub>Cl<sub>2</sub> were set to 5 and 6%, respectively.  $W_g$  is higher than 0.85 for all the gel samples prepared at or above -22 °C. Thus, reducing  $T_{\rm prep}$  below the bulk freezing temperature of the reaction system does not decrease the amount of the crosslinked polymer in the crude gels. At  $T_{\text{prep}} = -22$  °C and, in the range of the crosslinker concentration between 2 and 10%, the gel fraction was also found to be always larger than 0.85. This indicates high crosslinking efficiency of sulfur monochloride even at very low reaction temperatures and at crosslinker ratios down to about 0.9 mol S<sub>2</sub>Cl<sub>2</sub>/mol internal vinyl group of PIB.



**Figure 2.** (A, B) The equilibrium weight  $(q_w, \bullet)$  and the equilibrium volume swelling ratios  $(q_v, \bigcirc)$  of PIB gels in toluene shown as a function of S<sub>2</sub>Cl<sub>2</sub> concentration and the gel preparation temperature  $T_{\text{prep.}}$  (C, D) Swollen state porosities  $P_s$  of PIB gels shown as a function of S<sub>2</sub>Cl<sub>2</sub> concentration and  $T_{\text{prep.}}$  (A, C)  $T_{\text{prep}} = -22 \text{ °C}$ ,  $c_P = 5\%$ ; (B, D)  $c_P = 5\%$ , S<sub>2</sub>Cl<sub>2</sub> = 6%.

To determine the critical polymer concentration for the onset of gelation, a series of experiments were carried out at PIB concentrations  $c_{\rm P}$  between 0.01 and 5%. The temperature  $T_{\rm prep}$ and the crosslinker content were set to -18 °C and 6% S<sub>2</sub>Cl<sub>2</sub>, respectively. In Figure 1B,  $W_g$ , is plotted against the polymer concentration  $c_{\rm P}$ . In the range of  $c_{\rm P}$  between 2 and 5%, the gel fraction is around 0.90 while it starts to decrease as  $c_{\rm P}$  is decreased below 2%, indicating an increasing number of PIB chains remains unattached to the gel after the reaction. At  $c_{\rm P} =$ 0.1%, formation of a macroscopic gel was observed; however, after extraction with toluene, the gel was too weak for the gravimetric tests. At or below  $c_{\rm P} = 0.05\%$ , the reaction system dissolved completely in toluene. Thus, the critical polymer concentration for gelation is 0.08  $\pm$  0.02%, compared to the reported value of 4% at  $T_{\rm prep} = 20$  °C.<sup>13</sup> It is seen that, decreasing the reaction temperature from 20 to -18 °C leads to a 50-fold decrease in the critical polymer concentration for the onset of gelation. The result demonstrates that  $S_2Cl_2$  acts as an effective crosslinker at low temperatures due to the high local concentration of polymer and the crosslinker in the apparently frozen reaction system. As mentioned above, 14% of benzene in the reaction solution does not freeze at -18 °C. This means that, although the initial concentration of polymer is 5%, its concentration in the unfrozen liquid phase is about 36%. Thus, the reduced rate constant of the crosslinking reaction between sulfur chloride and vinyl groups at low temperatures seems to be compensated by the increased polymer concentration in the reaction zones. The reason why benzene does not freeze completely at below the bulk freezing temperature is due to the freezing point depression caused by the polymer.<sup>15,17,18</sup> Although the usual polymer concentrations can lower the freezing point by only a few degrees, once benzene crystals are present, the effect is enhanced. This is because polymer chains are excluded from the solid benzene structure and become more concentrated in the remaining unfrozen regions. Thus, as benzene freezes, the polymer concentration in the liquid-phase rises continuously so that successively greater osmotic pressure



**Figure 3.** (A, B) SEM and (C, D) optical microscopy images of PIB networks. (A, C, and D)  $T_{\text{prep}} = -22 \text{ °C}$  and (B) 17 °C.  $S_2Cl_2 = 6\%$ ,  $c_P = 5\%$ . The scaling bars and magnifications of SEM are 100  $\mu$ m and  $\times 200 \mu$ m, respectively. The dark area corresponds to the pores, while the light area corresponds to the walls.

is required to keep the liquid phase in equilibrium with the pure frozen benzene phase. It was shown that, in frozen poly(ethyl acrylate) gels swollen in benzene, up to about 30% benzene remains unfrozen at low temperatures.<sup>19</sup>

The swelling capacities of PIB gels are shown in Figure 2A,B, where the equilibrium weight  $(q_w)$  and volume swelling ratios  $(q_v)$  of gels in toluene are plotted against the crosslinker (S<sub>2</sub>-Cl<sub>2</sub>) concentration and the gel preparation temperature  $T_{\text{prep}}$ , respectively. The gels were prepared starting from a 5% PIB solution at  $T_{\text{prep}} = -22$  °C (in Figure 2A) and at 6% S<sub>2</sub>Cl<sub>2</sub> (in Figure 2B). The weight swelling ratio  $q_w$  of PIB gels does not change much with the experimental parameters and remains



**Figure 4.** SEM of PIB networks formed at various crosslinker (S<sub>2</sub>-Cl<sub>2</sub>) concentration, as indicated in the images.  $T_{\text{prep}} = -22$  °C,  $c_{\text{P}} = 5\%$ . The scaling bars are 100  $\mu$ m. Magnification =  $\times 200$ 

around 30. In contrast, the volume swelling ratio  $q_v$  increases and approaches  $q_w$  as the crosslinker concentration or the temperature  $T_{\text{prep}}$  is increased. The relative values of  $q_w$  and  $q_v$ of gels provide information about their internal structure in the swollen state.<sup>9</sup> This is due to the fact that the weight swelling ratio includes the solvent located in both pores and in the polymer region of the gel, while, assuming isotropic swelling, the volume swelling only includes the solvent in the polymer region. Thus, the larger the difference between  $q_w$  and  $q_v$ , the larger the amount of solvent in the pores, i.e., the larger the volume of pores. From the weight and volume swelling ratios of PIB gels, their swollen state porosities  $P_s$  can be estimated using the equation<sup>9</sup>

$$P_{\rm s} \% = \left(1 - \frac{q_{\rm v}}{1 + (q_{\rm w} - 1)d_2/d_1}\right) \times 10^2 \tag{7}$$

where  $d_1$  and  $d_2$  are the densities of the swelling agent (toluene) and the polymer, respectively.

Assuming that  $d_1 = 0.876$  g/mL and  $d_2 = 0.920$  g/mL, the calculated swollen state porosities  $P_s$  are shown in parts C and C of Figure 2 plotted against the crosslinker concentration and the temperature  $T_{\text{prep}}$ . The gels formed at subzero temperatures exhibit significant porosities.  $P_s$  is close to 80% at low S<sub>2</sub>Cl<sub>2</sub> contents while it slightly decreases to about 50% as the crosslinker content is increased. Further, the swollen state porosity rapidly decreases as  $T_{\text{prep}}$  is increased and becomes zero above the freezing point of benzene.

To visualize the pores in PIB gels, the network samples were investigated by both scanning electron microscopy (SEM) and optical microscopy. Figures 3A,B shows SEM images of the network samples prepared at  $T_{\text{prep}} = -22$  and 17 °C, respectively. In accord with Figure 2C, the gels prepared at 17 °C



**Figure 5.** Images taken from the optical microscope of the network samples prepared at  $T_{\text{prep}} = (A) 17$ , (B) -2, (C) -10, and (D) -18 °C.  $c_P = 5\%$ ,  $S_2Cl_2 = 6\%$ . The scaling bars are 50  $\mu$ m. The dark area corresponds to the pores, while the light area corresponds to the walls.



**Figure 6.** The normalized mass  $m_{\rm rel}$  of PIB gels shown as a function of the time of deswelling in methanol and reswelling in toluene.  $T_{\rm prep} = 17 \,^{\circ}\text{C}$  ( $\bullet$ ) and  $-22 \,^{\circ}\text{C}$  ( $\bigcirc$ ).  $S_2\text{Cl}_2 = 6\%$ .  $c_{\rm P} = 5\%$ .

exhibit glasslike fracture surfaces but without pronounced microstructure. The low-temperature gels have a porous structure with irregular large pores of  $10^1 - 10^2 \,\mu\text{m}$  in diameter. The total volume of the pores  $V_p$  was estimated from the uptake of methanol as 7.5 mL/g for gels prepared at  $T_{\text{prep}} = -22$  °C, while those formed at 17 °C exhibited negligible pore volumes. The images shown in Figure 3C,D were taken from the -22 °C gel network using the optical microscope at two different magnifications. Both SEM and optical microscopy images of lowtemperature PIB networks exhibit clearly different morphologies when compared with macroporous networks formed by reaction induced phase separation, where the structure looks like cauliflower and consists of aggregates of various sizes.<sup>9</sup> The morphology of the present networks also significantly differs from the honeycomb morphology of cryogels obtained from hydrophilic monomers.<sup>15,17,18</sup> The characteristic of the texture of PIB networks is thick pore walls of about 10  $\mu$ m in width which provide structural support to the material. The different morphology of the present gels is likely due to the formation of the porous structure by both the thermally induced phase separation mechanism and by the presence of solid benzene templates. The crosslinking solvent benzene is a poor solvent



**Figure 7.** Swelling–deswelling cycles of PIB gels in toluene and in methanol, respectively, shown as the variation of the relative gel mass  $m_{\rm rel}$  with the time of swelling or deswelling.  $c_{\rm P} = 5\%$ . Gel preparation temperature  $T_{\rm prep} = (A) -22$  °C and (B) +17 °C. Crosslinker (S<sub>2</sub>Cl<sub>2</sub>) concentration = 4 ( $\bigcirc$ ), 6 ( $\blacktriangle$ ), 8 ( $\blacksquare$ ), and 10% ( $\diamondsuit$ ).

for PIB with an upper critical solution temperature of 24.5 °C.<sup>20–22</sup> Thus, as the reaction system is cooled down to  $T_{\text{prep}}$ , liquid—liquid-phase separation occurs together with the separation of benzene crystals; crosslinking reactions in the polymer-rich phase leads to the formation of dense polymer domains surrounding the macroscopic benzene crystals.

The influence of the crosslinker concentration on the network microstructure of gels formed at  $T_{\text{prep}} = -22$  °C is shown in Figure 4 where the SEM images of dried PIB gels prepared at various S<sub>2</sub>Cl<sub>2</sub> concentrations between 2 and 10% are given. It



**Figure 8.** Typical stress-strain data of PIB gels as the dependence of f on (A) ( $\alpha - \alpha^{-2}$ ) and (B)  $1 - \alpha$ . Gel preparation temperatures are indicated.  $c_{\rm P} = 5\%$ . S<sub>2</sub>Cl<sub>2</sub> = 6%. The gel samples subjected to the mechanical tests were 16 mm in diameter and about 10 mm in length.

is seen that the architecture or morphology of the networks essentially does not depend on the crosslinker concentration, whereas the size of the structure changes: As the crosslinker concentration is decreased, both the polydispersity and the average diameter of the pores increase. The morphologies of dried gel samples formed at various  $T_{\text{prep}}$  were also systematically investigated. In Figure 5, the images taken from the optical microscope are shown for PIB networks formed at  $c_{\text{P}} = 5 \text{ w/v}$ % and 6% S<sub>2</sub>Cl<sub>2</sub>. All the PIB networks formed below the freezing point of benzene have a porous structure. To characterize the pore structure, a large number of images (at least 50) taken from each network somple were analyzed using the image analyzing system. The average width and the average length of the pores in PIB networks formed below the freezing point of benzene were calculated as  $40 \pm 12 \ \mu\text{m}$  and  $58 \pm 17 \ \mu\text{m}$ ,

respectively, independent of  $T_{\rm prep}$ . The average diameter of the pore walls was calculated as 17 ± 16  $\mu$ m. It is seen that, although the swollen state porosity  $P_{\rm s}$  decreases with increasing  $T_{\rm prep}$  (Figure 2D), the size of the pores remains unchanged. This indicates that the number of pores decreases but their size remains constant as  $T_{\rm prep}$  is increased below the freezing point of benzene.

The semilogaritmic plots in Figure 6 compares the response rate of two PIB gel samples prepared at -22 °C (O) and 17 °C (•). Here, the normalized gel mass  $m_{\rm rel}$  (mass of gel at time t/equilibrium swollen mass in toluene) is plotted against the time t of deswelling in methanol and reswelling in toluene. Both the swelling and deswelling rates of the gel prepared at -22 °C are much faster than those prepared at 17 °C. The lowtemperature gel attains its equilibrium collapsed and equilibrium swollen states within 2 min while the conventional gel requires 80 and 200 min to attain the equilibrium states in acetone and in water, respectively. Figure 7 shows swelling-deswelling cycles of low-temperature gels (-22 °C, part A) and conventional gels (17 °C, part B) prepared at various crosslinker contents. Independent of the crosslinker content, all the PIB gels prepared at -22 °C attain their equilibrium collapsed and equilibrium swollen states in less than 2 min. They also exhibit completely reversible swelling-deswelling cycles, i.e., the gels return to their original shape and original mass after a short reswelling period. It seems that the differences in the microstructure of the gels depending on the crosslinker concentrations do not affect their response rate against the solvent changes. The gels formed at 17 °C exhibit, however, irreversible cycles; after the first deswelling process in methanol, the initial swollen mass of the gel cannot be recovered in the following cycles.



**Figure 9.** Photographs of PIB gels formed at 17 °C and at -2 °C during the compression test. After compression of the -2 °C gel, addition of toluene converts the gel back to its initial state.  $c_P = 5\%$ . S<sub>2</sub>Cl<sub>2</sub> = 6%.



**Figure 10.** (A and B) The temperature of the gelation solutions immersed in a cryostat ( $\bigcirc$ ) and placed in a freezer ( $\bigcirc$ ) shown as a function of the reaction time. (C and D) The relative volume swelling ratio  $V_{\rm rel}$  of gels prepared in a cryostat ( $\bigcirc$ ) and in a freezer ( $\bigcirc$ ) shown as a function of the swelling time in toluene.  $c_{\rm P} = 5\%$ . S<sub>2</sub>Cl<sub>2</sub> = 5%. The final temperatures are indicated.

The effect of the gel preparation temperature  $T_{\text{prep}}$  on the response rate of gels was also investigated by swelling and deswelling tests in toluene and in methanol, respectively. No substantial differences were observed for all the gel samples prepared at or below -2 °C.

The mechanical properties of PIB gels were investigated by the compression tests. Typical stress-strain data of gels in the form of f versus ( $\alpha - \alpha^{-2}$ ) plots are shown in Figure 8A. An interpretation of the stress-strain dependence of heterogeneous gels is complicated due to the complex character of their deformation process. In such irregular porous material of sponge morphology, bending-type deformations become also operative with increasing porosity due to the buckling of the pore walls. The general trend shown in Figure 8A is that all the gels prepared below the freezing point exhibited moduli of elasticity (initial slope of f versus  $-(\alpha - \alpha^{-2})$  dependence) of about 2 ×  $10^2$  Pa, 1 order of magnitude lower than the modulus of gels obtained at room temperature, which was 2400 Pa. Although the gels prepared at a low temperature exhibit a low elastic modulus, they were very tough and can be compressed up to about 100% strain without any crack development. This behavior is shown in Figure 8B where the stress f is plotted against the fractional deformation (length change/initial length,  $1 - \alpha$ ) for gels formed at various  $T_{\text{prep}}$ . The gels prepared at room temperature broke at a stress of 8 kPa and a strain of about 40%. However, all the low-temperature gels did not break even at a strain of about 100%.23 Photographs in Figure 9 also demonstrate how the low-temperature PIB gel sustains a high compression. As shown in the upper panel of Figure 9, the swollen gels prepared at room-temperature fractured under low deformation suggesting that cracks develop easily in the gel. However, those obtained at a low temperature remain mechanically stable up to complete compression (bottom panel of Figure 9). An important point is that as the low-temperature gel is squeezed under the piston, the gel releases all its toluene so



**Figure 11.** SEM of PIB networks prepared at  $T_{\text{prep}} = -22$  °C at initial cooling rates of (A) 50 °C/min and (B) 6 °C/min.  $c_{\text{P}} = 5\%$ . S<sub>2</sub>Cl<sub>2</sub> = 5%. The scaling bars are 10  $\mu$ m. Magnification =  $\times 500$ .

that it can completely be compressed. After the release of the load, and after addition of toluene, the sample immediately recovers its original shape, as shown in Figure 9 and in the movie attached as the Supporting Information.

It should be mentioned that all the macroporous PIB gels reported above were prepared by incubating the reaction solutions in a freezer, so that the freezing of the solution occurs in an air bath at slow rates. Indeed, the initial rates of cooling of the reaction solutions were measured as between 1 and 7 °C/min, depending on the final temperature  $T_{\text{prep}}$ . The lower the final temperature  $T_{\text{prep}}$ , the faster the initial rate of cooling of the reaction solution, and thus, the shorter is the time period until the freezing temperature of the reaction solution is reached. From the experimental data of gels formed at various  $T_{\text{prep}}$ , we may conclude that both the final freezing temperature  $T_{\text{prep}}$  and the rate of cooling between 1 and 7 °C/min or combination of both do not affect the properties of PIB gels. To highlight the effect of the cooling rate on the gel properties, a series of experiments were carried out by a rapid temperature quench to  $T_{\rm prep}$  with initial cooling rates in the range 10–50 °C/min. This was achieved by immersion of the reaction system in a cryostat filled with an antifreeze solution. Figure 10A,B shows the cooling profiles of the gelation systems in the cryostat (O) and in the freezer ( $\bullet$ ), adjusted to  $T_{\text{prep}} = -18$  and -22 °C, respectively. For a fixed final temperature, the cooling profile significantly differs depending on the type of cooling; the cryostat provides an 8-fold faster initial cooling rate compared to the freezer. The gels thus obtained from rapidly and slowly cooled reaction solutions were subjected to swelling-deswelling tests. Although no differences in the deswelling rates of gels were detected, the reswelling of the collapsed gels in toluene showed great differences. Figure 10C,D illustrates the swelling behavior of the gels prepared in the cryostat (O) and in the freezer ( $\bullet$ ), where their relative volume swelling ratios  $V_{\rm rel}$  in toluene are plotted against the swelling time. The measurements were carried out by on-line monitoring of the diameter of the gel samples immersed in toluene under an optical microscope coupled with an automatic image analyzing system. It is seen that the gels obtained from the rapidly cooled solution swell in toluene much slower than those obtained from slowly cooled solutions. In Figure 11, typical SEM images of the gels prepared at  $T_{\text{prep}} = -22 \text{ °C}$  with fast (50 °C/min, part A) and slow initial cooling rates (6 °C/min, part B) are given. If the gelation solution is rapidly cooled, the gel network consists of agglomerates of large polymer domains; the interstices between these domains constitute the porous structures. Further, the gels obtained from rapidly cooled solutions were mechanically fragile with very low fracture toughness as the porous gels obtained by the

reaction induced phase separation technique. One may expect that, at fast cooling rates, a macro phase separation occurs before freezing of the reaction system so that the porous structure forms due to the  $\chi$ -induced syneresis.<sup>9,24,25</sup> The phase separated polymer particles agglomerate into larger clusters and in continuing the reactions increase the number of clusters in the reaction system so that the polymer phase becomes continuous. Moreover, fast cooling may also induce formation of a large number of nuclei of freezing benzene, and this leads to a small size of benzene ice and therefore small pores. Thus, the cooling rate of the gelation solution is an important parameter determining the gel properties. Tough PIB gels with a fast response rate were obtained at cooling rates ranging between 1 and 7 °C/min.

#### Conclusion

We described the preparation of a novel tough organogel with superfast responsive properties. The gels were prepared from frozen solutions of butyl rubber in benzene using sulfur monochloride  $(S_2Cl_2)$  as a crosslinking agent. Effects of the crosslinker concentration and gel preparation temperature  $T_{prep}$ on the properties of PIB gels were investigated. S2Cl2 was found to be an efficient crosslinking agent even at very low reaction temperatures up to -22 °C and at crosslinker ratios down to about 0.9 mol S<sub>2</sub>Cl<sub>2</sub>/mol internal vinyl group on PIB. The gels prepared from frozen solutions of PIB contained about 97% organic liquid and they were very tough; they can be compressed up to about 100% strain without any crack development. The compressed gel immediately swells in contact with good solvents to recover its original shape. The low-temperature gels have a porous structure with irregular large pores of  $10^{1}-10^{2} \mu m$  in diameter, separated by pore walls of about 10  $\mu$ m in width with a high polymer concentration, which provide structural support to the material. All the gels prepared at or below -2 °C exhibit completely reversible swelling-deswelling cycles in toluene and methanol, respectively, i.e., the gels return to their original shape and original mass after a short reswelling period. It was also found that the cooling rate of the gelation system to the gel preparation temperature  $T_{\text{prep}}$  is an important parameter determining the gel properties. Tough gels with fast responsivity were obtained at low cooling rates ranging between 1 and 7 °C/min.

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#### **References and Notes**

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- (23) The weight swelling ratio of low temperature gels in toluene is around 30 (Figure 2). This means that 97% of their volume or mass consist of toluene. Thus, assuming that the diameter of the cylindrical gel samples remains constant, the fractional deformation becomes 0.97 at complete removal of the solvent under force. However, due to the barrellike deformation at large stresses, a fractional deformation of up to above 0.995 was realized, which was called as complete compression.
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