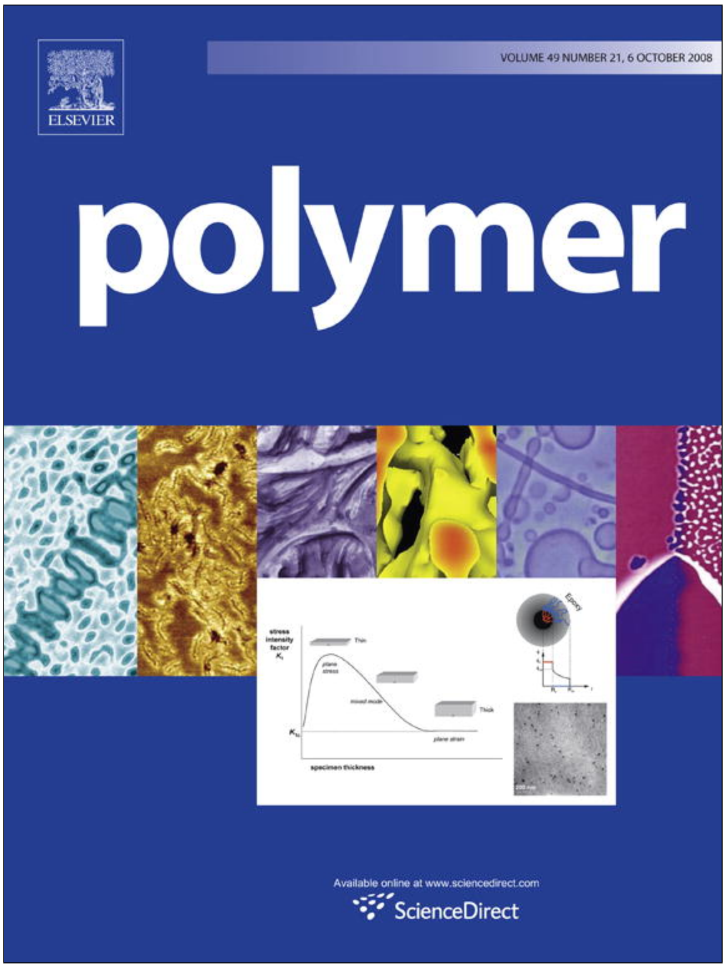
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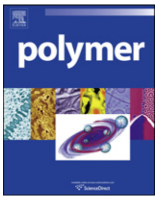

Tough organogels based on polyisobutylene with aligned porous structures

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A R T I C L E I N F O

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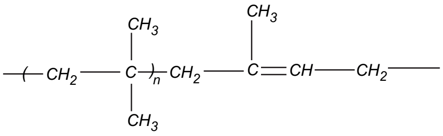
Macroporous gels with aligned porous structures were prepared by solution crosslinking of butyl rubber (PIB) in cyclohexane at subzero temperatures. Sulfur monochloride was used as a crosslinker in the organogel preparation. The reactions were carried out at various temperatures between 20 and −22 °C as well as at various freezing rates. The structure of the gel networks formed at −2 °C consists of pores of about 100 μm in length and 50 μm in width, separated by polymer domains of 10–20 μm in thickness. The aligned porous structure of PIB gels indicates directional freezing of the solvent crystals in the direction of the temperature gradient. The size of the pores in the organogels could be regulated by changing the freezing rate of the reaction solution. The results suggest that frozen cyclohexane templates are responsible for the porosity formation in cyclohexane. In contrast to the regular morphology of the gels formed in cyclohexane, benzene as a crosslinking solvent produces irregular pores with a broad size distribution from micrometer to millimeter sizes due to the phase separation of PIB chains at low temperatures. Macroporous organogels prepared at subzero temperatures are very tough and can be compressed up to about 100% strain without any crack development. The gels also exhibit superfast swelling and deswelling properties as well as reversible swelling–deswelling cycles in toluene and methanol, respectively.

1. 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 and exhibit a slow rate of response against the external stimuli. A number of techniques for toughening of gels have recently been proposed including the double network gels [1,2], topological gels [3], gels formed by mobile crosslinkers [4,5], and microsphere composite hydrogels [6]. Although these techniques slow down the rate of crack propagation in such materials by creating energy dissipation mechanisms 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 achieve rapid changes in the gel volume, a common strategy is to create an interconnected pore structure inside the gel network [7]. However, the formation of pores in gels inevitably causes a significant reduction in their mechanical properties.

Cryogelation is a simple route for the preparation of macroporous gels exhibiting a fast response rate and a high degree of toughness [8]. This technique is based on the natural principle that sea ice is less salty than seawater, i.e., rejection of brine from freezing salt solutions. This principle is a consequence of the insolubility of the salts in ice compared to their excellent solubility in water. In cryogelation reactions, aqueous reaction solution containing the monomers and the initiator is cooled below the freezing point of the system; since the monomers and the initiator will be enriched in the unfrozen microzones surrounded by ice crystals, the polymerization reactions only proceed in these unfrozen regions containing a high concentration of monomer [9–14]. After polymerization and after removing the ice, macropores appear that are templated from the spaces occupied by the ice crystals. The synthesized cryogels do not display the undesirable properties such as brittleness, which is commonly observed for macroporous gels formed by phase separation polymerization.

Recently, we have shown that tough organogels with superfast responsive properties can be prepared by conducting the cryogelation reaction in organic solutions [15]. The starting material of the organogel was butyl rubber (hereafter abbreviated as PIB, Scheme 1), a linear polyisobutylene containing small amounts of



Scheme 1. The structure of butyl rubber.

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internal unsaturated groups (isoprene units). It was shown that the dilute solutions of PIB in benzene can easily be crosslinked using sulfur monochloride (S_2Cl_2) as a crosslinking agent at temperatures down to −20 °C, i.e., about 25 °C below the freezing point of the solution [15]. The main characteristic of this gel was its macroporous structure consisting of large interconnected pores separated by thick and dense pore walls with a high polymer concentration, which provide structural support to the material. The porous structure of the PIB gels formed in benzene was irregular and consisted of unshaped pores with a broad size distribution ranging from tens of micrometers to millimeters. This irregular pore structure of the gels is probably due to the poor solvating power of benzene for PIB chains with an upper critical solution temperature of 24.5 °C [16–18]. Thus, both liquid–liquid phase separation and separation of solvent crystals at low temperatures are expected to be responsible for the formation of irregular pores.

In contrast to benzene, cyclohexane–PIB system did not show significant temperature effect [18,19]. Thus, by replacing benzene with cyclohexane as the crosslinking solvent, liquid–liquid phase separation could be prevented during the cryogelation reactions of PIB. Further, both benzene and cyclohexane have similar freezing and melting properties; they both form high temperature orientationally disordered crystals and their melting temperatures in the bulk are close (5.5 versus 6.5 °C for benzene and cyclohexane, respectively) [20]. This motivated us to investigate the possibility of formation of macroporous organogels with a regular structure. The preparation of aligned porous materials with micrometer-sized pores is of particular importance for applications such as tissue engineering, microfluidics, and organic electronics [21,22]. Here, we report that macroporous organogel networks based on butyl rubber with an aligned pore structure could be prepared in cyclohexane at relatively high subzero temperatures, i.e., at −2 °C. The solution crosslinking reactions of PIB were carried out in cyclohexane at a polymer concentration of 5 w/v%. Macroporous organogels of high toughness and superfast responsivity were prepared under various experimental conditions. The size of the pores in these materials could be regulated by changing the freezing rate of the reaction solution.

2. Experimental section

2.1. Materials

Butyl rubber (Butyl 365, Exxon Chem. Co.) with 2.3 mol% isoprene units and a Mooney viscosity of 33 was used in the gelation experiments. It was dissolved in toluene followed by precipitation into methanol and drying at room temperature under vacuum to constant mass. The crosslinking agent sulfur monochloride, S_2Cl_2, was purchased from Aldrich Co. Cyclohexane, benzene, toluene, and methanol (all Merck grades) were used as the solvent for the solution crosslinking reactions, swelling and deswelling experiments.

The gels were prepared by solution crosslinking technique at a butyl rubber concentration of 5 w/v% according to the following scheme: butyl rubber (5 g) was first dissolved in 100 mL of cyclohexane at room temperature (20 ± 1 °C) overnight. Then, portions of this solution, each about 25 mL, were transferred to volumetric flasks and different amounts of sulfur monochloride were added under rigorous stirring. The homogeneous reaction solutions were transferred into plastic syringes and glass tubes of 16.4 mm and 3.7 mm internal diameters, respectively. The crosslinking reactions were carried out in a cryostat as well as in a freezer at predetermined temperatures for 1 and 3 days. The cooling profiles of the reaction solutions to attain the final temperature T_{prep} were measured by immersing a thermocouple into the reaction solutions. The crosslinker concentration in the reaction solution, S_2Cl_2%, was expressed as the volume of S_2Cl_2 added per 100 g of butyl rubber.

2.2. Methods

PIB gels were taken out of the syringes and 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 one 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 overnight 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

$$W_g = \frac{m_{\text{dry}}}{0.05 m_o} \tag{1}$$

where m_{dry} and m_o are the weights of the gel samples after drying and just after preparation, respectively. For all PIB gels reported here, gel fraction was close to unity except those obtained after a reaction time of 1 day and at a gel preparation temperature below −7 °C and above −2 °C. For these gel samples W_g was found to be 0.7 ± 0.1. The equilibrium volume and the equilibrium weight swelling ratios of the gels, q_v and q_w, respectively, were calculated as

$$q_v = \left(D/D_{\text{dry}}\right)^3 \tag{2a}$$

$$q_w = \left(m/m_{\text{dry}}\right) \tag{2b}$$

where D and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively, m is the weight of gel after drying. Note that Eq. (2a) assumes isotropic swelling of the porous gels.

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 $m_{\text{rel}} = m_t/m$, where m_t is the mass of the gel sample at time t. The temperature dependent swelling measurements of gels were conducted in situ by following the diameter of the gel samples immersed in cyclohexane and in benzene under microscope using the image analyzing system mentioned above. The results were given as the relative volume swelling ratio $V_{\text{rel}} = (D_T/D_o)^3$ where D_T and D_o are the gel diameters at a given temperature and after preparation, respectively.

Uniaxial compression measurements were performed on equilibrium swollen gels in toluene. All the mechanical measurements were conducted in a thermostated room of 20 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [23,24]. 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 α is the deformation ratio (deformed length/initial length).

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 (mL pores in one gram of dry polymer network) was calculated as

$$V_p = \left(m_M - m_{dry}\right) / \left(d_M m_{dry}\right) \qquad (3)$$

where m_M is the weight of the network immersed in methanol after 2 h and d_M is the density of methanol (0.792 g/mL).

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 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. For this purpose, the samples were first immersed into liquid nitrogen for 1 min and then, they were cut into thin slices of about 1 mm in thickness. After adding a few drops of oil for contrast enhancement, the measurements were conducted at magnifications between 10 and 100 times.

3. Results and discussion

3.1. Porosity formation

The solution crosslinking of butyl rubber (PIB) in cyclohexane was carried out in plastic syringes of 16.4 mm internal diameter immersed in a cooling liquid at various temperatures T_{prep} between −22 and 20 °C. We first fixed the reaction time at one day. The variation of the internal morphology of the organogels depending on the gel preparation temperature T_{prep} was monitored by electron microscopy. Previous works show that, in crosslinking copolymerization of hydrophilic monomers in frozen aqueous solutions, macroporous structures start to appear at polymerization temperatures about 8 °C below the freezing point of the reaction system [13,14]. Assuming this condition is also valid for the solution crosslinking of PIB, macroporous organogels should form at about −1.5 °C in cyclohexane. Indeed, we observed formation of macroporous PIB gels at or below −2 °C. Scanning electron micrographs (SEMs) of the gel networks formed at temperatures T_{prep} close to this upper temperature limit for cryogel formation showed oriented porous structure of the materials. For example, the micrograph in Fig. 1 evidences the alignment of the pores in the gel network formed at $T_{prep} = -2$ °C. The structure consists of brick-shaped pores of about 100 μm in length and 50 μm in width, separated by polymer domains (pore walls) of 10–20 μm in thickness (see Fig. 3A for a larger magnification). The aligned porous structure of the sample indicates directional freezing of the solvent crystals in the direction from the surface to the interior, i.e., in the direction of the temperature gradient. Note that experiments carried out by decreasing the reactor diameter from 16.4 mm to 3.7 mm partially destroyed the regularity of the pore structure, probably due to the increasing rate of freezing of the reaction solution.

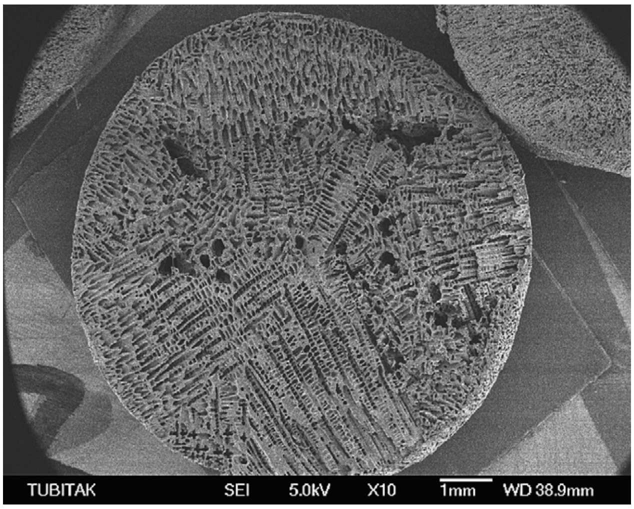

Fig. 1. SEM of PIB network formed in cyclohexane at $T_{prep} = -2$ °C. Reaction time = 24 h. S_2Cl_2 = 5.7%. The scaling bar is 1 mm. Magnification = 10×.

Because of the poor thermal conductivity of the reaction solution, a temperature gradient is formed in the radial direction and freezing of the solvent cyclohexane starts from the surface of the cylindrical reactor which is in contact with the cooling liquid at −2 °C. As the solvent freezes, both the PIB chains and the crosslinker S_2Cl_2 are excluded from the solvent crystals due to the freeze concentration and aggregate around the growing crystals to form unfrozen part of the system. This is illustrated schematically in Fig. 2. As the freezing progresses a polymer concentration gradient, as well as a temperature gradient establish across the moving freezing front. This leads to macroscopic instabilities due to which the moving freezing front collapses, leaving behind pockets of unfrozen concentrated polymer solution [21,22]. Further, due to the relatively high temperature T_{prep}, the freezing rate is slow so that the growing solvent crystals can be encapsulated in the concentrated solution and cannot grow further. Thus, directional freezing under a temperature gradient causes a crystallization of many isolated solvent crystal phases, leaving an unfrozen gel phase with high polymer content. After the crosslinking reactions, the polymer phase becomes insoluble and, after thawing, preserves the structure that had been conferred to it by the surrounding solvent crystals.

Fig. 3 shows SEM images of the networks formed at various T_{prep} between −2 and −18 °C at a larger magnification than in Fig. 1. It is seen that decreasing the temperature destroys the regularity of the porous structure of the network and the pores of 10^1–10^2 μm in

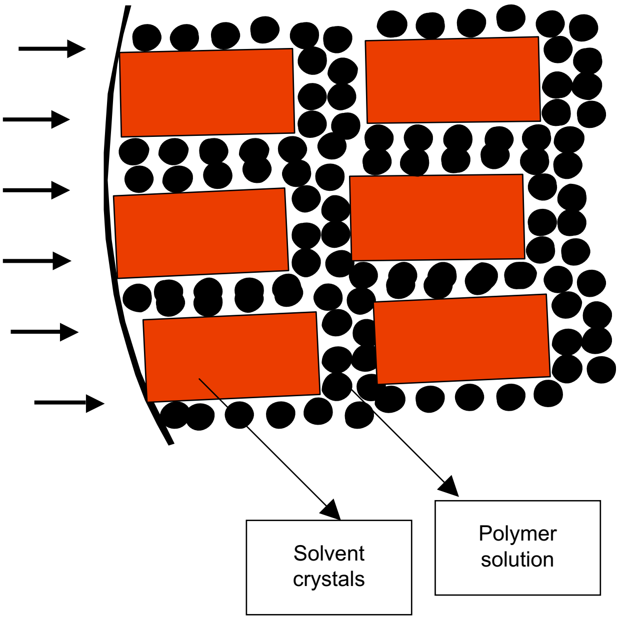

Fig. 2. Scheme showing the directional freezing of PIB solution from the surface to the interior at low cooling rates, i.e., at high temperatures T_{prep}.

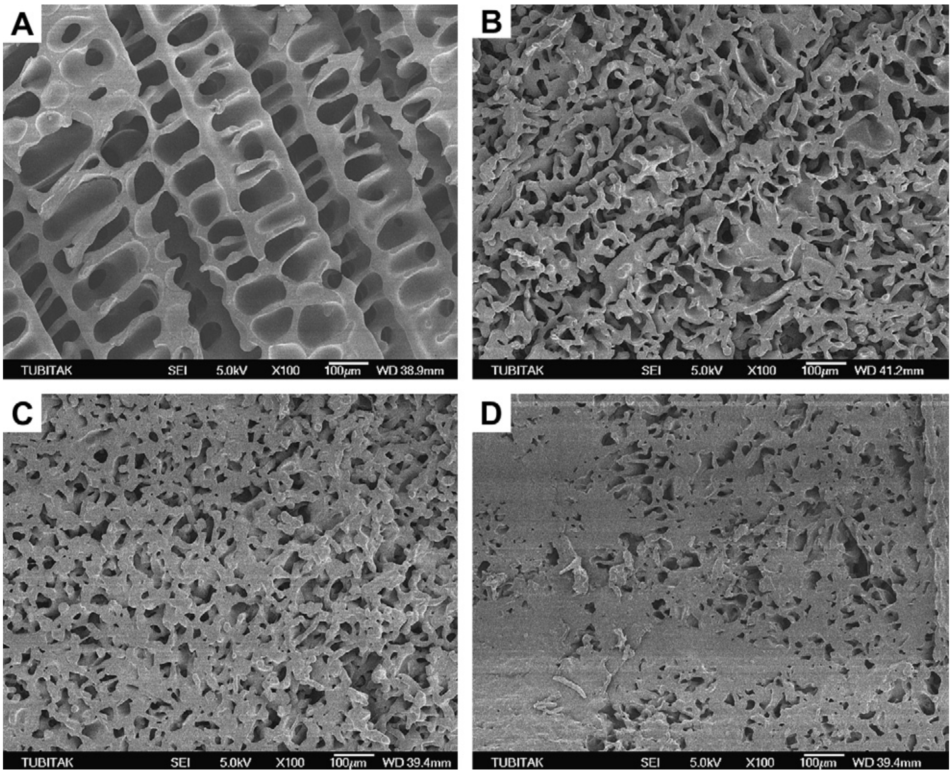

Fig. 3. SEM of PIB networks formed in cyclohexane. $T_{prep} = -2$ (A), −7 (B), −10 (C), and −18 °C (D). Reaction time = 24 h. $S_2Cl_2 = 5.7\%$. The scaling bars are 100 μm. Magnification = 100×.

sizes formed at −2 °C becomes increasingly irregular as T_{prep} is decreased. The collapse of the pores in PIB gels formed at low temperatures is also evidenced by the porosity measurements. The filled symbols in Fig. 4 show the total volume of the pores V_p estimated from the uptake of methanol (poor solvent) by the gel network plotted against the temperature T_{prep}. In accordance with Fig. 3, the total pore volume V_p is largest in gels formed at −2 °C while it decreases as the temperature is decreased. Further, increasing T_{prep} above −2 °C also decreases the pore volume and no macroscopic gel forms at or above 5 °C. To increase the stability of the porous structure of gels formed at lower temperatures, the reaction time was increased from 1 to 3 days. The crosslinking reactions were carried out under various experimental conditions, i.e., at two different crosslinker contents (5.7 and 10%), in reactors of 3.7 and 16.4 mm internal diameters as well as under various freezing rates. The results of the porosity measurements conducted on these gel samples are shown in Fig. 4 by the open symbols. The pore volume of all low temperature gels are about 2.5 mL/g indicating that increasing reaction time stabilizes the pore structure of the organogels. In contrast, however, SEM images of the networks show that the regularity of the porous structure is largely destroyed by increasing the reaction time (not shown). Increasing the crosslinker content from 5.7 to 10% did not recover the regular pore structure of gels obtained after a reaction time of one day.

Results of the equilibrium swelling measurements are collected in Fig. 5A, which shows the weight q_w (filled symbols) and the volume swelling ratios q_v of the organogels in toluene (open symbols) plotted against the gel preparation temperature T_{prep}. The triangles and the circles are the data points obtained from gels formed after a reaction time of 1 and 3 days, respectively. After 1 day, no gel formation was observed at temperatures below −18 °C, while the gels formed between −18 and −10 °C were too soft and fragile. In this range of T_{prep}, volume swelling ratio q_v is larger than the weight swelling ratio q_w due to the collapse of the gel samples during drying. Typical cryogels with a good mechanical performance were obtained between −7 and −2 °C. As T_{prep} is further increased, the gels become again too soft and no gel formation was observed at or above 5 °C. Since the reaction rates are slow at very low temperatures, one day of the reaction time is insufficient to produce strong gels. On the other hand, if T_{prep} is above −2 °C, the

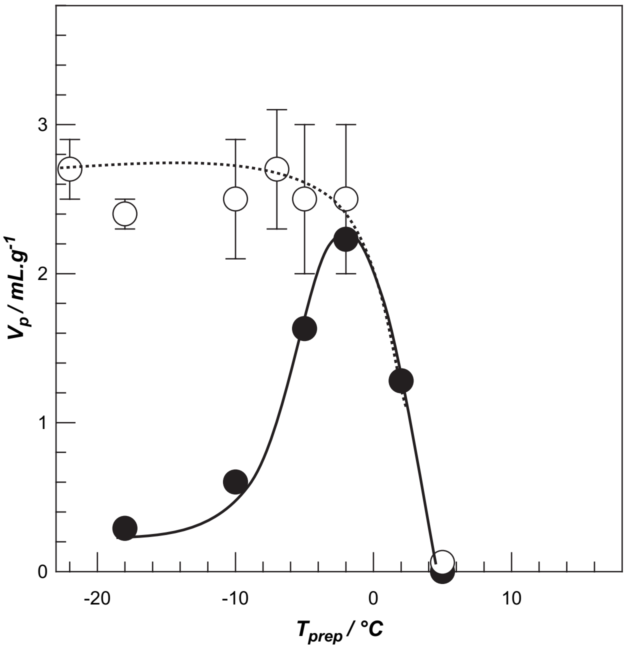

Fig. 4. The total volume of the pores V_p in PIB gels estimated from the uptake of methanol by the gel networks plotted against the temperature T_{prep}. Reaction time = 1 day (filled symbols, solid curve) and 3 days (open symbols, dashed curve).

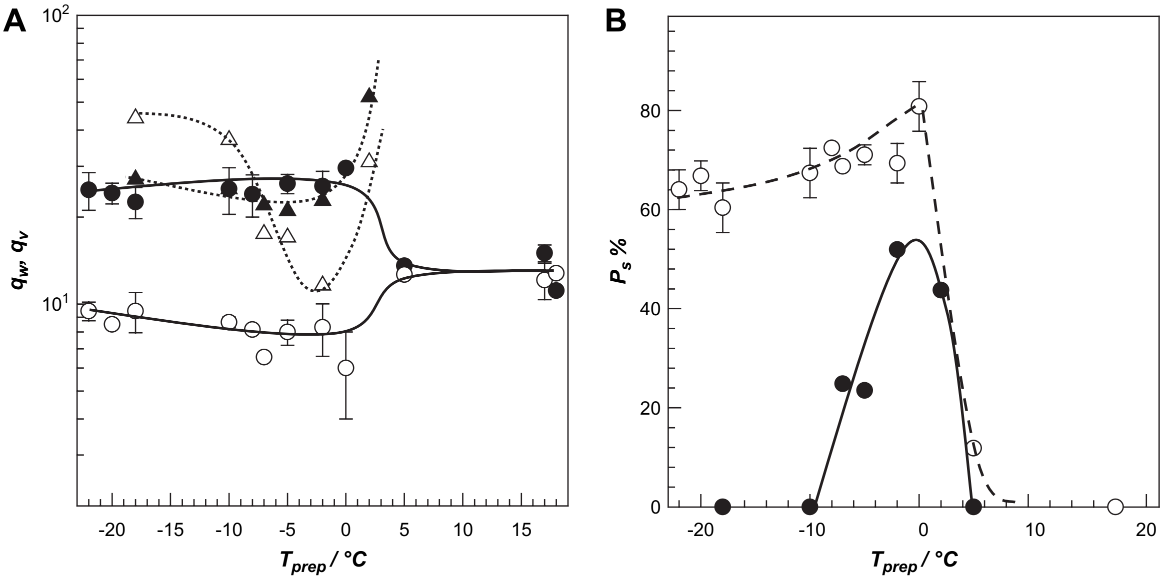

Fig. 5. (A): The equilibrium weight (q_w, filled symbols) and the equilibrium volume swelling ratios (q_v, open symbols) of PIB gels in toluene shown as a function of T_{prep}. Reaction time = 1 day (triangles) and 3 days (circles). (B): The swollen state porosities P_s of the organogels are calculated by using Eq. (4). Reaction time = 1 day (filled symbols, solid curve) and 3 days (open symbols, dashed curve).

reaction system remains unfrozen and the freeze concentration of the solution did not occur so that the reaction rates again slow down due to the low polymer concentration. The gels isolated after a reaction time of 3 days are prepared under various experimental conditions. The data points shown in Fig. 5A by the circles are average values of the measurements on these gel samples. It is seen that the swelling characteristics of the gels are largely independent on the crosslinker concentration, freezing rate and the reactor size. The general trend is that, $q_w = 25 \pm 3$ and $q_v = 8 \pm 1$ for $T_{prep} \leq 0\,°C$ while at higher gel preparation temperatures, the gel exhibits the same weight and volume swelling ratios which are equal to 13 ± 1.

The relative values of q_w and q_v of gels provide information about their internal structure due to the fact that the weight swelling includes the solvent locating in both pores and in the polymer region of the gel, while the volume swelling only includes the solvent in the polymer region [7]. 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 total volume of pores. From the weight and volume swelling ratios of the organogels, their swollen state porosities P_s can be estimated using the equation [7]

$$P_s\% = \left(1 - \frac{q_v}{1 + (q_w - 1)d_2/d_1}\right) \times 10^2 \tag{4}$$

where d_1 and d_2 are the densities of the swelling agent (toluene) and the polymer, respectively. Assuming that $d_1 = 0.867$ g/mL and $d_2 = 0.92$ g/mL, the swollen state porosities P_s were calculated and are shown in Fig. 5B plotted against the temperature T_{prep}. The results are in good agreements with those of the total pore volume of gels given in Fig. 4; after a reaction time of 3 days, all the gel samples formed at or below 0 °C are porous and exhibit swollen state porosities between 60 and 80%, slightly increasing function of

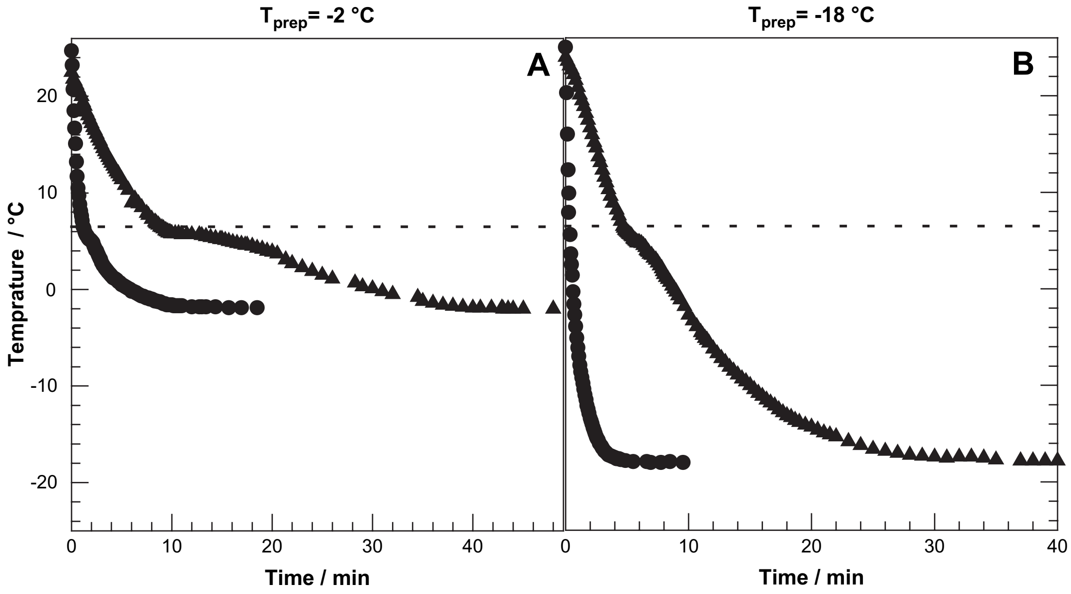

Fig. 6. Cooling profiles of the reaction solutions of 10 mL volume to attain $T_{prep} = -2$ (A) and -18 °C (B) under slow (triangles) and fast cooling (circles) conditions.

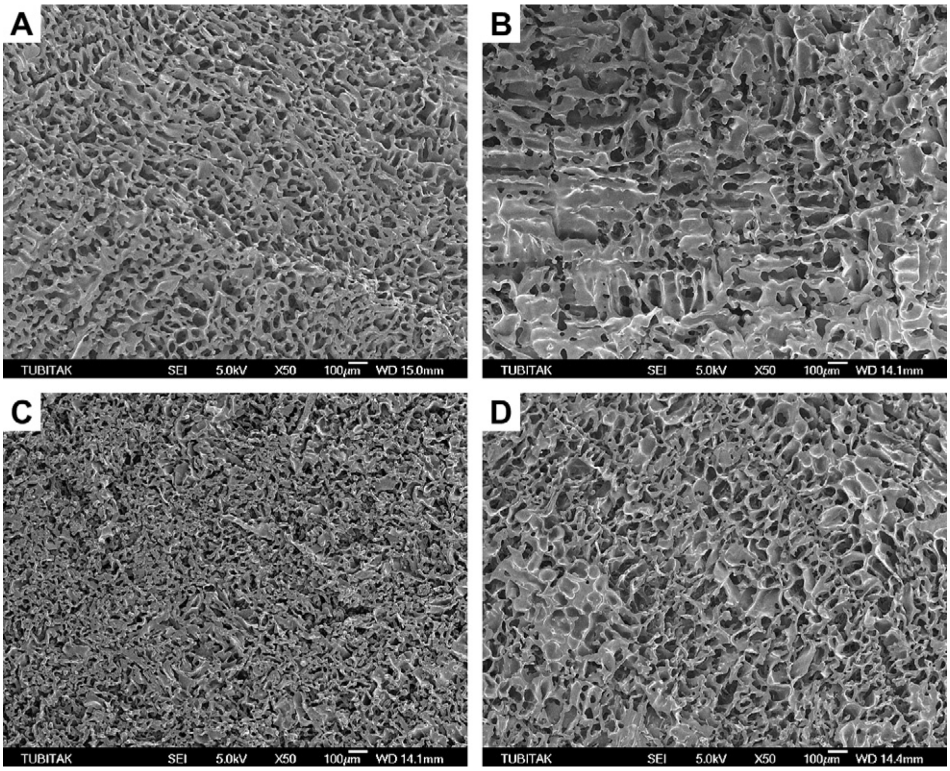

Fig. 7. SEM of PIB networks formed $T_{prep} = -2$ (A, B) and −10 °C (C, D). Freezing rate = fast (left panel), slow (right panel). Reaction time = 3 days. $S_2Cl_2 = 5.7\%$. The scaling bars are 100 μm. Magnification = 50×.

T_{prep} while those formed above 0 °C exhibit negligible porosities in the swollen state. For short reaction time, the porosity attains the maximum value of about 50% at −2 °C. It should be mentioned that both P_s and V_p represent the pore volume of PIB gels normalized with respect to the volume and mass of dry polymer network, respectively. P_s relates to V_p by the equation: $P_s = V_p d_o$, where d_o is the apparent density of porous polymer [7].

3.2. Effect of the freezing rate

Experiments were designed to study the effects of rapid and slow freezing on the morphology of the gel networks. For this purpose, one part of the reaction solution was slowly frozen in a freezer in contact with air, while the other part was fast frozen in a cryostat in contact with a liquid. Fig. 6A and B shows the cooling profiles of the reaction solutions quenched in liquid (circles) and in air (triangles), both set to $T_{prep} = -2$ and −18 °C, respectively. The dotted horizontal lines represent the freezing point of the solvent cyclohexane. The type of cooling as well as the final temperature T_{prep} significantly affect the duration of the initial non-isothermal period of the reactions and thus, the freezing rate of the system. The initial cooling rate decreases from 54 to 4 °C/min as the cooling liquid is replaced with cooling air at −18 °C. The initial cooling rate also decreases from 54 to 21 °C/min as the temperature of the cooling liquid is increased from −18 and −2 °C. Thus, increasing T_{prep} or replacing liquid with air in the surrounding bath of the reaction solution decreases the freezing rate of the solution.

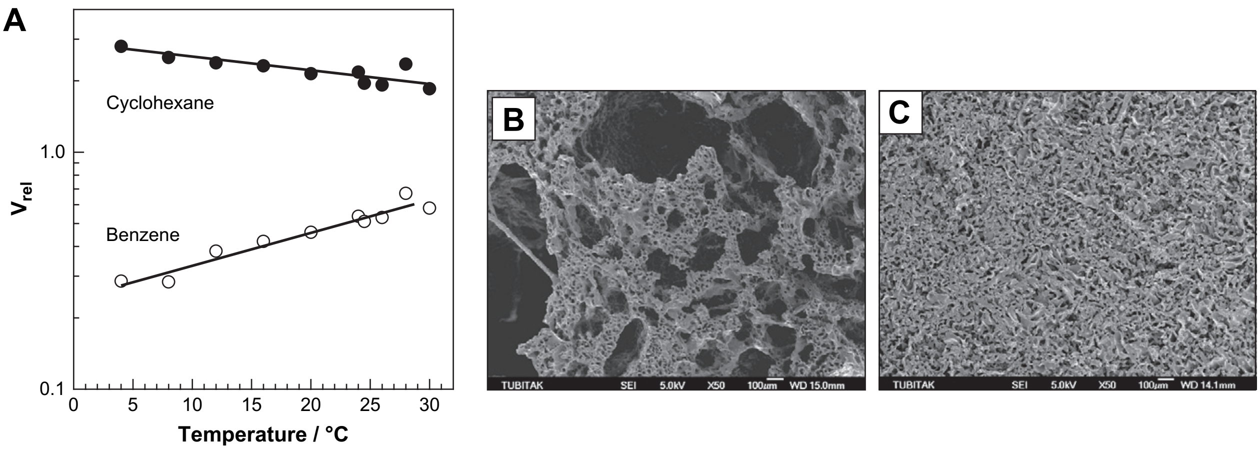

Fig. 8. (A) Normalized volume swelling ratio V_{rel} of PIB gel in cyclohexane (filled symbols) and in benzene (open symbols) shown as a function of the temperature. The gel was prepared at 17 °C in cyclohexane. Reaction time = 3 days. $S_2Cl_2 = 5.7\%$. (B) SEM images of PIB networks formed at $T_{prep} = -10$ °C in benzene (B) and in cyclohexane (C) under fast freezing condition. Reaction time = 3 days. $S_2Cl_2 = 5.7\%$. The scaling bars are 100 μm. Magnification = 50×.

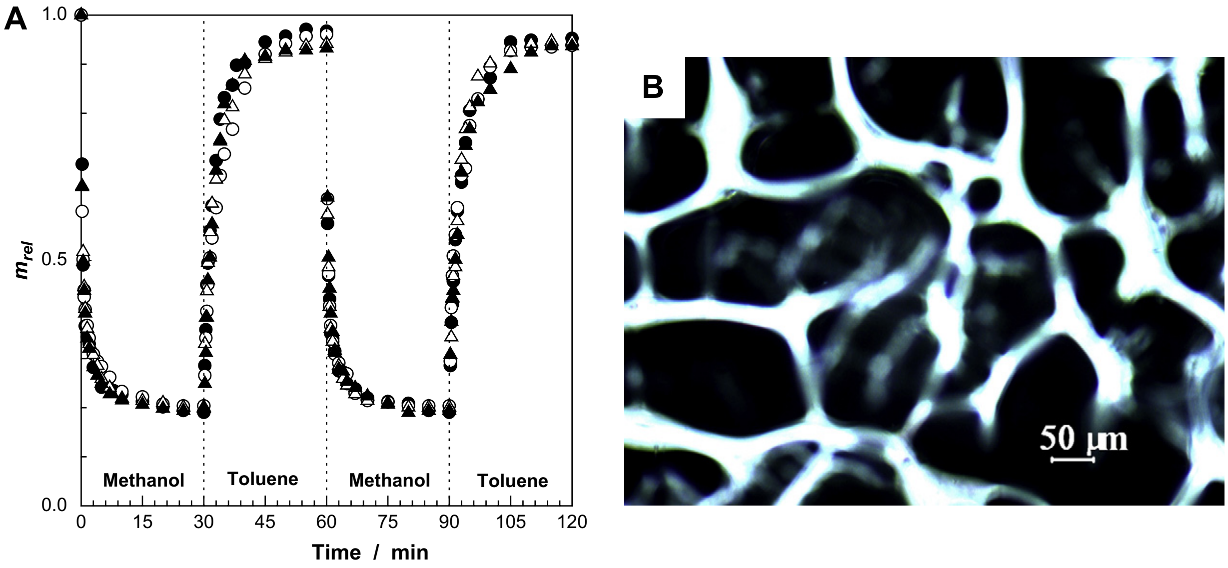

Fig. 9. (A) The normalized mass m_{rel} of PIB gels shown as a function of the time of deswelling in methanol and re-swelling in toluene. $S_2Cl_2 = 5.7\%$. $T_{\text{prep}} = -2$ °C. Reaction time = 1 day, freezing rate = slow (○), fast (△). Reaction time = 3 days, freezing rate = slow (●), fast (▲). (B) Optical microscopy image of a PIB gel sample prepared at −2 °C under fast freezing. $S_2Cl_2 = 5.7\%$. Reaction time = 1 day.

As mentioned in the previous section, swelling and porosity data of PIB gels given in Figs. 4 and 5 are the average values measured from gels after a reaction time of 3 days under various experimental conditions. The error bars in the figures mainly arise from different freezing rates of the reaction solutions. The general trend is that, as the freezing rate increases, both the porosity and the weight swelling ratio of gels increase. However, this increase is not significant and limited by the length of the error bars shown in the figures. In contrast, the rate of freezing significantly affects the structure of the organogels. Fig. 7 shows SEM images of the gel network prepared under fast (left panel) and slow (right panel) freezing conditions. It is seen that the size of the pores increases as the freezing rate decreases. This behavior was observed in all gel samples formed at subzero temperatures. Increasing the freezing rate of the reaction solution necessarily reduces the time available for solvent crystals to grow which would inhibit the formation of large crystals. Thus, small solvent crystals form under fast freezing conditions which lead to, after thawing, small pores. Further, increasing freezing rate shortens the duration of the initial non-isothermal period of the reactions so that the crosslinking mainly occurs in the unfrozen microzones of the apparently frozen reaction system. This may also decrease the size of the pores [25]. Fig. 7 also shows that, for a given cooling condition (air or liquid cooling), the pore size increases as T_{prep} is increased due to the simultaneously decrease in the freezing rate (Fig. 6). Thus, to obtain PIB gels with larger pores, the freezing temperature should be as high as possible, and the time for crystallization of the solvent cyclohexane should be extended.

3.3. Effect of the solvent

In this section, the internal morphologies of PIB gels formed in cyclohexane were compared with those prepared in benzene under identical conditions. Besides their molecular sizes, benzene and cyclohexane have similar freezing and melting properties. However, since the chemical structure of cyclohexane is close to that of the repeating unit of polyisobutylene, it is a good solvent for PIB [18,19]. This behavior is also seen in Fig. 8A, which shows the normalized volume swelling ratio V_{rel} of PIB gels in cyclohexane and in benzene plotted against the swelling temperature. In contrast to cyclohexane, benzene is a poor solvent for PIB and, the gel further deswells as the temperature is decreased.

Fig. 8B and C shows SEM images of PIB networks formed in benzene and in cyclohexane, respectively. In contrast to the regular morphology of the networks prepared in cyclohexane, the networks formed in benzene exhibit a broad size distribution of pores from micrometer to millimeter sizes. Further, the total volume of pores V_p in PIB gels formed in benzene was found to increase from 6 to 9 mL/g as T_{prep} is decreased from −2 to −18 °C, in contrast to the value of about 2.5 mL/g for all low temperature gels formed in cyclohexane (Fig. 4). The differences observed in the morphology of the gels are due to the cooling induced phase separation of the PIB chains in benzene. As seen in Fig. 8A, V_{rel}, that is the gel volume normalized with respect to the after preparation state, is below unity for PIB gels immersed in benzene. This means that the gel cannot absorb all the available solvent during gelation so that a phase separation should occur during the initial non-isothermal period of the reactions. Thus, the polymer chains are not only expelled from the solution due to freeze concentration but also undergo cooling induced phase separation to form agglomerates of various sizes. Larger pore volumes of gels formed in benzene also support that two mechanisms are operative in the formation of the porous structure in this solvent. Thus, during the crosslinking

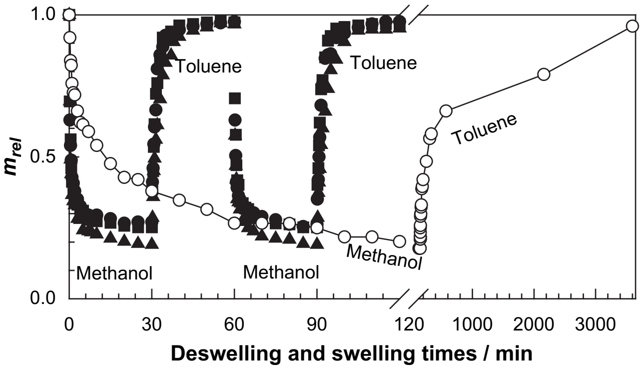

Fig. 10. The normalized mass m_{rel} of PIB gels shown as a function of the time of deswelling in methanol and re-swelling in toluene. $S_2Cl_2 = 5.7\%$. Reaction time = 3 days. Freezing rate = slow. $T_{\text{prep}} = -2$ (▲), −10 (●), −18 (■), and 17 °C (○).

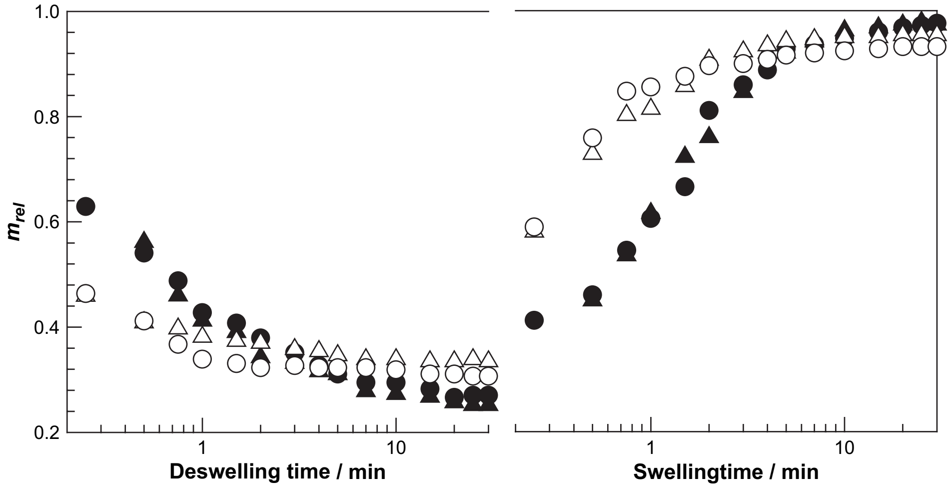

Fig. 11. The normalized mass m_{rel} of PIB gels shown as a function of the time of deswelling in methanol and re-swelling in toluene. $S_2Cl_2 = 5.7\%$. Reaction time = 3 days. Freezing rate = slow. $T_{\text{prep}} = -10$ (○, ●) and −18 °C (△, ▲). Crosslinking solvent = benzene (open symbols) and cyclohexane (filled symbols).

reaction of PIB in benzene the polymer component phase separates at low temperatures and undergoes crosslinking after phase separation.

3.4. Response rates and the degree of toughness

PIB gels were subjected to swelling and deswelling processes in toluene and in methanol, respectively. Fig. 9A shows the response rate of PIB gels formed at $T_{\text{prep}} = -2$ °C under fast and slow freezing conditions as well as at the two different reaction times. Here, the normalized gel mass m_{rel} (mass of gel at time t/equilibrium swollen mass in toluene) is plotted against the time t of deswelling in methanol and re-swelling in toluene. Independent on the reaction time or the freezing rate, the gels attain their equilibrium collapsed and swollen states within 10 min; they also exhibit reversible swelling–deswelling cycles, i.e., the gels return to their original shape and original mass after a short re-swelling period. The image shown in Fig. 9B was taken from −2 °C gel network using the optical microscope at a partially swollen state in the oil used for the contrast enhancement. It is seen that the gel has a fishnet-like structure with numerous large micrometer-sized pores. These pores provide the motion of the solvent in and out of the gel phase by convection, without undergoing a diffusion process through the gel phase. Fig. 10 compares the response rate of gels formed at various temperatures T_{prep}. Both the swelling and deswelling rates of the gel prepared at subzero temperatures are much faster than those prepared at 17 °C; the low temperature gels undergo two successive deswelling–swelling cycles before the room

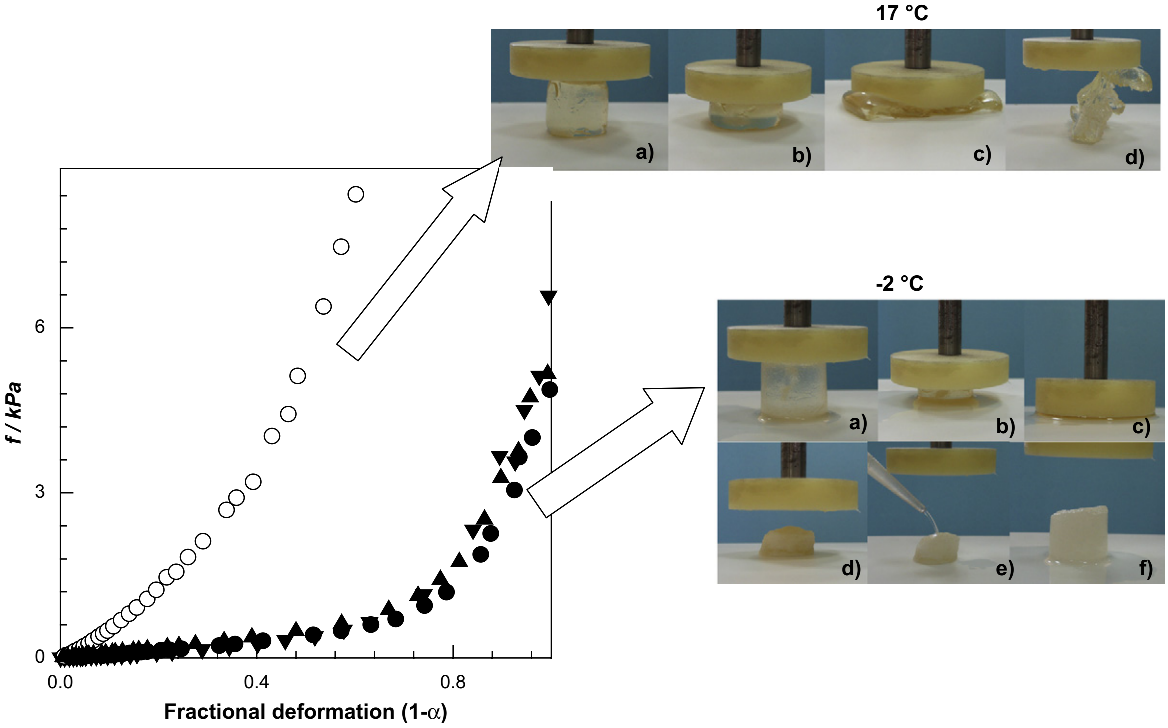

Fig. 12. Typical stress–strain data of PIB gels as the dependence of f on $1-\alpha$. $S_2Cl_2 = 5.7\%$. Reaction time = 3 days. Freezing rate = slow. $T_{\text{prep}} = 17$ (○), −2 (▲), −10 (●), and −18 °C (▼). Photographs show the gels formed at 17 °C (upper panel) and at −2 °C (lower panel) during the compression test. After compression of −2 °C gel, addition of toluene converts the gel back to its initial state.

temperature gel assumes its equilibrium collapsed conformation in methanol. The collapsed gel formed at 17 °C reswells again within 3 days compared to 10 min found for low temperature gels. The results also show that the differences in the microstructure of the low temperature gels depending on the preparation temperature as well as on the freezing rate do not affect their response rate against the solvent changes. Fig. 11 compares the response rate of gels formed in cyclohexane with that formed in benzene. Semi-logarithmic plot was chosen for clearer representation of the changes in m_{rel} at short times. Both deswelling and re-swelling of gels formed in benzene occurs much faster than in cyclohexane due to existence of much large pores as well as due to the larger pore volumes in benzene.

The mechanical properties of PIB gels were investigated by the compression tests. Except the gels formed after a reaction time of one day and at temperatures below -7 °C, all the low temperature gel samples were mechanically stable under very large pressures. The initial slope of the stress f versus strain $(\alpha - \alpha^{-2})$ data gave a value of the modulus of elasticity G of 10^2 Pa for the swollen gels formed at or below -2 °C compared to 10^3 Pa of gels formed at higher temperatures. Thus, formation of macroporous structure drastically reduces the elastic modulus of the organogels. The degree of toughness of PIB gels was also investigated by the compression tests. For this purpose, the stress f was recorded as a function of the fractional deformation of swollen, cylindrical gel samples (deformed length/initial length, $1 - \alpha$). The results are shown in Fig. 12 for gels formed at various T_{prep}. The gels prepared from unfrozen PIB solution broke at a stress of 8 kPa and a strain of about 60%. However, all the low temperature gels did not break even at a strain of about 99%. Photographs in Fig. 12 also demonstrate how the low temperature PIB gel sustains a high compression. The swollen gels prepared from unfrozen solution fractured under low deformation suggesting that cracks develop easily in the gel. However, low temperature gels remain mechanically stable up to about complete compression. During compression, the gel releases all its toluene so that it can completely be compressed. After the release of the load and, after addition of toluene, the sample immediately recovers its original shape.

4. Conclusions

Macroporous PIB gels prepared in cyclohexane at subzero temperatures exhibit distinctly different internal morphology from those formed in benzene. The pores formed in cyclohexane appear very regular and are oriented along a common direction. The structure of the gel networks prepared at -2 °C consists of pores of about 100 μm in length and 50 μm in width, separated by polymer domains of 10–20 μm in thickness. The aligned porous structure indicates directional freezing of the solvent crystals in the direction from the surface to the interior, i.e., in the direction of the temperature gradient. This unique orientation disappears as the gelation temperature is decreased or, as the reaction time is increased. Formation of PIB gels with a regular morphology is due to the fact that cyclohexane is a good solvent for PIB chains so that the pores are only generated by the cryogelation mechanism. However, in benzene solutions, both cooling induced phase separation and the cryogelation are responsible for the porosity formation so that benzene as a crosslinking solvent produces irregular pores with a broad size distribution from micrometer to millimeter sizes. Macroporous organogels prepared at subzero temperatures are very tough and can be compressed up to about 100% strain without any crack development. The gels also exhibit superfast swelling and deswelling properties as well as reversible swelling–deswelling cycles in toluene and methanol, respectively.

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References

[1] Gong JP, Katsuyama Y, Kurokawa T, Osada Y. Adv Mater 2003;15:1155.
[2] Tanaka Y, Gong JP, Osada Y. Prog Polym Sci 2005;30:1.
[3] Okumura Y, Ito K. Adv Mater 2001;13:485.
[4] Miquelard-Garnier G, Demoures S, Creton C, Hourdet D. Macromolecules 2006;39:8128.
[5] Haraguchi K, Takehisa T. Adv Mater 2002;14:1120.
[6] Huang T, Xu H, Jiao K, Zhu L, Brown HR, Wang H. Adv Mater 2007;19:1622.
[7] Okay O. Prog Polym Sci 2000;25:711.
[8] Lozinsky VI. Russ Chem Rev 2002;71:489.
[9] Lozinsky VI, Plieva FM, Galaev IY, Mattiasson B. Bioseparation 2002;10:163.
[10] Arvidsson P, Plieva FM, Lozinsky VI, Galaev IY, Mattiasson B. J Chromatogr A 2003;986:275.
[11] Ivanov RV, Babushkina TA, Lozinskii VI. Polym Sci Ser A 2005;47:791.
[12] Lozinskii VI, Kalinina EV, Grinberg VY, Grinberg VY, Chupov VV, Plate NA. Polym Sci Ser A 1997;39:1300.
[13] Dinu MV, Ozmen MM, Dragan ES, Okay O. Polymer 2007;48:195.
[14] Ozmen MM, Okay O. Polymer 2005;46:8119.
[15] Ceylan D, Okay O. Macromolecules 2007;40:8742.
[16] Krigbaum WR, Flory PJ. J Am Chem Soc 1953;75:5254.
[17] Erman B, Flory PJ. Macromolecules 1986;19:2342.
[18] Eichinger BE, Flory PJ. Trans Faraday Soc 1968;64:2053.
[19] Okay O, Durmaz S, Erman B. Macromolecules 2000;33:4822.
[20] Dosseh G, Xia Y, Alba-Simionesco C. J Phys Chem B 2003;107:6445.
[21] Zhang H, Cooper AI. Adv Mater 2007;19:1529.
[22] Zhang H, Edgar D, Murray P, Rak-Raszewska A, Glennon-Alty L, Cooper AI. Adv Funct Mater 2008;18:222.
[23] Sayil C, Okay O. Polymer 2001;42:7639.
[24] Gundogan N, Melekaslan D, Okay O. Macromolecules 2002;35:5616.
[25] Plieva F, Huiting X, Galaev IY, Bergenstahl B, Mattiasson B. J Mater Chem 2006;16:4065.