ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SUPERFAST RESPONSIVE, TOUGH ORGANOGELS BASED ON BUTYL RUBBER

M. Sc. Thesis by
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Programme: **Polymer Science and Technology (PST)**

Supervisor: Prof. Dr. Oğuz OKAY

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BUTİL KAUÇUK ESASLI HIZLI CEVAP VEREN DAYANIKLI ORGANOJELLER

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January, 2008 Deniz CEYLAN

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LIST OF SYMBOLS

n_1, n_2	:	Number of solvent and polymer molecules
n_o	:	Total number of lattice sites
x	:	Number of segments of a polymer chain
V_1	:	Molar volume of solvent
i	:	Number of chains added to the lattice
z	:	Coordination number of the lattice
Ω	:	Total number of conformations
v_1, v_2	:	Volume fractions of solvent and polymer molecule
ΔS_m	:	Entropy change of mixing
w_{ij}	:	Energy of the formation of a contact between a pair of segments of molecules i and j
ΔH_m	:	Enthalpy change of mixing
χ	:	Polymer-solvent interaction parameter
k	:	Boltzman's constant
T	:	Absolute temperature (K)
ΔG_m	:	Free energy change of mixing
p	:	Probability of a one end of the chain located within a small element
s	:	Entropy of the chain
λ	:	Deformation ratio (deformed length/initial length)
$\alpha_1, \alpha_2, \alpha_3$	:	Macroscopic deformation ratios of the network chains
r_o	:	End to end distance of an individual chain in the unstrained state
r	:	End to end distance after deformation
ΔS_{el}	:	Entropy change during deformation
ΔH_{el}	:	Enthalpy change during deformation
ΔG_{el}	:	Free energy change during deformation
v_2^0	:	Volume fraction of the crosslinked polymer after the gel preparation
ΔG	:	Free energy change during swelling
V_o, V	:	Gel volumes after the gel preparation and after swelling
μ_1, μ_1^o	:	Chemical potentials of solvents inside and outside the gel
v_2	:	Volume fraction of crosslinked polymer in the gel
v_e	:	Number of chains per unit volume of the network
ρ	:	Polymer density
$\overline{M_c}$	:	Molecular weight of the network chains
ΔA_{el}	:	Helmholtz free energy
W	:	Work of deformation

ν	:	Concentration of the network chains.
R	:	Gas constant
D , D_o	:	Diameter of the hydrogels after equilibrium swelling and after preparation
q_v	:	Volume swelling ratio
g	:	Gravitational acceleration
l_o , l	:	Initial undeformed and deformed lengths
A	:	Cross-sectional area of the specimen
c_p	:	Initial linear polymer concentration
G_o	:	Elastic modulus of gel after preparation
G	:	Elastic modulus of gel
$M_{c,chem}$	:	Chemical molecular weight of the network chains
X	:	Crosslinker ratio

SUPERFAST RESPONSIVE, TOUGH ORGANOGELS BASED ON BUTYL RUBBER

SUMMARY

The aim of this thesis is to prepare an ideal gel from the point of view of application, that is, a soft material exhibiting both a high degree of toughness, i.e., a mechanical stability up to about 100 % strain and a fast response rate against the external stimuli.

To achieve this aim, macroporous organogels were prepared by crosslinking of butyl rubber (PIB) in frozen benzene solutions using sulfur monochloride (S_2Cl_2) as a crosslinking agent. Our strategy to synthesize such fast responsive PIB gels with unique mechanical properties is the application of the so-called "cryogelation technique" to the present gelling system. Thus, the crosslinking reactions of butyl rubber were conducted at temperatures much below the freezing point of the reaction system. Effects of the crosslinker concentration, gel preparation temperature and the rate of cooling of the gelation system on the gel properties were investigated. The gels were characterized by means of their mechanical and swelling properties.

S_2Cl_2 was found to be an efficient crosslinking agent even at very low reaction temperatures up to -22^oC and at crosslinker ratios down to about 0.9 mol S_2Cl_2 / mol internal vinyl group on PIB. The gels prepared at subzero temperatures have a porous structure with irregular large pores of about 10^1-10^2 μm in diameter, separated by pore walls of about 10 μm in width with a high polymer concentration, which provide structural support to the material. The rate of cooling of the gelation system was found to be an important parameter determining the gel properties.

The results of the mechanical tests showed that, the gels prepared from frozen PIB solutions are very tough; they can be compressed up to about 100 % strain without any crack development. Further, the compressed gel immediately swells in contact with good solvents to recover its original shape. It was also found that the gels exhibit completely reversible swelling-deswelling cycles in toluene and methanol, respectively, i.e., they return to their original shape and mass after a short reswelling period.

BUTİL KAUÇUK ESASLI HIZLI CEVAP VEREN DAYANIKLI ORGANOJELLER

ÖZET

Bu tezin amacı, uygulama odaklı yüksek derecede dayanıklılığa sahip yani 100 % mekanik deformasyona dayanıklı ve dışardan gelen uyarılara hızlı cevap veren yumuşak bir malzeme olarak tanımlanan ideal bir jel hazırlamaktır.

Bu amaçla, donmuş benzen çözeltilerindeki butil kauçuğunun (PIB) kükürt monoklorür (S_2Cl_2) ile çapraz bağlanmasıyla makrogözenekli organojeller hazırlandı. Bu şekilde benzersiz mekanik özelliklere sahip hızlı cevap veren jelleri sentezlerken stratejimiz kriyojelleşme tekniğinin varolan jelleşme sistemine uygulanmasıdır. Böylelikle butil kauçuğunun çapraz bağlanma reaksiyonları, reaksiyon sisteminin donma noktasının altındaki sıcaklıklarda gerçekleştirildi. Çapraz bağlayıcı konsantrasyonunun, jel hazırlama sıcaklığının ve jelleşme sisteminin soğutma hızının jel özellikleri üzerine etkisi araştırıldı. Jeller, mekanik ve şişme özellikleri yoluyla karakterize edildi.

Kükürt monoklorürün -22^oC' ye kadar düşük sıcaklıklarda ve çapraz bağlayıcı oranı 0.9 mol S_2Cl_2 / mol "PIB üzerindeki vinil grup" varlığında etkili bir çapraz bağlama ajanı olduğu bulunmuştur. Sıfırın altındaki sıcaklıklarda hazırlanan jeller yaklaşık 10^1-10^2 μm çapındaki düzensiz yapıda büyük gözeneklere sahiptir. Bu gözenekler malzemeye yapısal destek sağlayan, yüksek polimer konsantrasyonuna sahip ve yaklaşık 10 μm genişliğindeki por duvarlarıyla ayrılmıştır. Jelleşme sisteminin soğutma hızı, jel özelliklerine karar vermede önemli bir parametre olarak bulundu.

Mekanik test sonuçlarına göre, donmuş PIB çözeltilerinden hazırlamış jeller çok dayanıklı; herhangi bir kırılma gerçekleşmeden 100 % deformasyona kadar sıkıştırılabilirler. Üstelik, sıkıştırılmış jel iyi çözücü ile temas ettiğinde hemen orijinal şeklini alıyor. Jellerin ayrı ayrı toluen ve metanoldeki şişme- büzülme döngülerinin tersinir olduğu yani kısa bir tekrar şişme periyotundan sonra orijinal şekline ve ağırlığına döndüğü de görülmüştür.

1. INTRODUCTION

A polymer gel is a multi-component system consisting of a polymer network and a solvent as a swelling agent [1]. The liquid prevents the polymer network from collapsing into a compact mass, whereas the network prevents the liquid from flowing away. Considering the technological importance and scientific richness, the unique properties of gels allow them to be useful in various applications as ion-exchange resins, sorbents, artificial lenses, actuators, optical devices, etc. In these application areas, design of the gels with a good mechanical performance together a fast response rate is crucially important. 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 [2, 3]. A number of techniques for toughening of gels have recently been proposed including the double network gels [4, 5], topological gels [6], gels formed by hydrophobic associations [7], gels made by mobile crosslinkers such as clay nanoparticles (nanocomposite hydrogels) [8], and microsphere composite hydrogels [9]. 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 [10].

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 non-porous 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 [11]. It is obvious that the response rate of gels is inversely coupled with their mechanical performance. 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, i.e., a mechanical stability up to about 100 % strain and a fast response rate against the external stimuli.

In this thesis, 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. The starting material of the organogel is a linear poly(isobutylene) containing small amounts of internal unsaturated groups (isoprene units), known as butyl rubber. Previous work within this department has shown that the dilute solutions of butyl rubber can easily be crosslinked using sulfur monochloride (S_2Cl_2) as a crosslinking agent [12]. Sulfur monochloride, a liquid at room temperature and soluble in organic solvents, was found to be an efficient crosslinking agent for the solution crosslinking processes of butyl rubber in toluene solutions, even at low polymer concentrations. 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 [12]. 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. Benzene was selected as the solvent due to the relatively high freezing point (5.5^{o}C) compared to toluene (-95^{o}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^{o}C 14 % of benzene remains unfrozen in the apparently frozen system. Thus, as benzene freezes, the polymer

chains are excluded from the ice 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^{o}C. The solution crosslinking of butyl rubber at temperatures below the freezing point of the reaction system, followed removal of ice crystals produced macroporous organogels containing pores with the approximate shape and dimensions of the ice crystals.

2. BACKGROUND

2.1. General Properties of Polymeric Gels

2.1.1 Swelling of Gels

Polymeric gels absorb large quantities of suitable solvents without dissolving. As more and more solvent is absorbed by the polymer network, the network expands progressively. During the swelling process, the network chains are forced to attain more elongated, less probable configurations. As a result, like pulling a spring from both ends, a decrease in chain configurationally entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies the swelling. In addition, enthalpy of mixing also controls the extent of swelling.

The equilibrium swelling theory developed by Flory and Rehner treats simple polymer networks in the presence of small molecules. The theory considers forces arising from three sources [13]:

1. The entropy change caused by mixing of polymer and solvent. The entropy change from this source is positive and favors swelling.
2. The entropy change due to the reduction in the number of possible chain conformations on swelling. The entropy change from this source is negative and opposes swelling.
3. The heat of mixing of polymer and solvent, which may be positive, negative or zero. Usually, it is slightly positive and opposing mixing.

2.1.1.1 Entropy of Mixing in Polymer Solutions

The polymer solutions show deviation from ideal solution behavior because of the wide difference in molecular size between the two components. Lattice theory of polymer solutions was developed first by Flory and independently by Huggins in 1942 in order to explain the very large deviations from ideality exhibited by polymer

solutions, shown in Figure 2.1. They found expressions for the total number of configurations of a mixture formed from n_1 solvent and n_2 polymer molecules. They assume that:

- **i.** Volume is unchanged during mixing.
- **ii.** Mixing entropy is strongly influenced by the chain connectivity of the polymer component.
- **iii.** Mixing enthalpy for polymer-small molecule mixtures is similar to that for regular solutions.

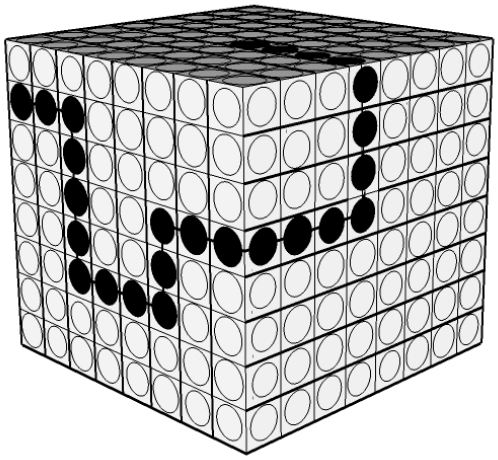


Figure 2.1: Lattice Theory suggested by Flory-Huggins. Polymer chain and solvent molecules are represented by the filled and open symbols, respectively.

According to the Flory-Huggins theory, polymer molecules are added one by one to the lattice before adding the solvent molecules and simultaneously, the number of possible arrangements is calculated for each segment of the chain. The number of different ways of arranging the (i+1)th molecule in the lattice ν_{i+1} is obtained:

$$\nu_{i+1} = \left\{ \frac{(n_0 - xi)!}{[n_0 - x(i+1)]!} \right\} \left[\frac{z-1}{n_0} \right]^{x-1} \tag{2.1}$$

where z is the coordination number of the lattice. The total number of distinguishable spatial arrangements of placing the n_2 polymer molecules on n_o sites is given by:

$$\Omega_{12} = \frac{1}{n_2!}\prod^{n_2-1} \nu_{i+1} \tag{2.2}$$

The number of ways Ω_2 by which chains can be placed on xn_2 sites is obtained by setting $n_1 = 0$ in Equation (2.2).

The configurational entropy of mixing is;

$$\Delta S_m = k\, ln \frac{\Omega}{\Omega_2} = -k\left[n_1 ln \nu_1 + n_2 ln \nu_2\right] \tag{2.3}$$

where k is the Boltzman's constant, ν_1 and ν_2 are the volume fractions of solvent and polymer, i.e.,

$$\nu_1 = \frac{n_1}{n_1 + xn_2}, \qquad \nu_2 = \frac{xn_2}{n_1 + xn_2} \tag{2.4}$$

2.1.1.2 Enthalpy and Free Energy of Mixing in Polymer Solutions

There are three types of contacts in polymer solutions shown in the figure which are solvent-solvent (w_{11}), solvent-segment (w_{12}) and segment-segment (w_{22}) interactions, shown in Figure 2.2.

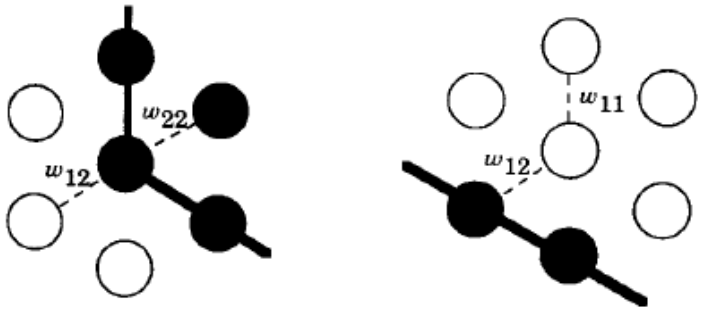


Figure 2.2: Schematic illustration of the interactions between solvent (unfilled) and polymer (filled) molecules.

The energy change for the formation of a polymer-solvent pair from solvent-solvent and polymer-polymer pairs is given as:

$$\Delta w_{12} = w_{12} - 1/2(w_{11} + w_{22}) \tag{2.4}$$

where w_{ij} is the energy of $i - j$ contacts.

The expression for the enthalpy of mixing was then written [13]:

$$\Delta H_m = z n_1 \nu_2 \Delta w_{12} \tag{2.5}$$

To eliminate the coordination number z and the energy parameter Δw_{12} from the above equation, Flory (or polymer-solvent) interaction parameter χ was introduced:

$$\chi = \frac{z\Delta w_{12}}{kT} \tag{2.6}$$

The expression for the enthalpy of mixing can then rewritten by combining equations (2.5) and (2.6):

$$\Delta H_m = kT\chi n_1 \nu_2 \tag{2.7}$$

The quantity $kT\chi$ represents the difference in energy of a solvent molecule immersed in pure polymer $(\nu_2 \cong 1)$ compared with one surrounded by molecules of its own kind, i.e., in the pure solvent.

Having calculated the entropy (2.3) and entalpy (2.7) contributions to mixing, these can be combined to give the expression for the free energy of mixing, $\Delta G_m = \Delta H_m - T\Delta S_m$ *as*:

$$\Delta G_m = kT(n_1 \nu_1 + n_2 \nu_2 + \chi n_1 \nu_2) \tag{2.8}$$

2.1.2. Elastic Deformation of Gels

The understanding of the polymer network elasticity began in the early 1930s. The forms of the stress-strain relationships were developed beginning in 1942 with Wall

[14], Treloar [15], Flory-Rehner [16], James-Guth [17]. The first molecular theory of rubber elasticity provided the first absolute prediction of mechanical modulus from network structure with the following assumptions:

- **i.** The polymer network contains v chains per unit volume.
- **ii.** The mean square end-to-end distance for the chains consisting of N segments with each bond having a length l equals to $\langle r^2 \rangle = Nl^2$.
- **iii.** There is no change of the volume on the deformation.
- **iv.** The junction points between the chains move on deformation as if they were embedded in an elastic continuum. As a result of the components of length of each chain change in the same ratio as the corresponding dimensions.
- **v.** The entropy of the network is the sum of the entropies of the individual chains.

Elasticity of the polymer networks refers to two aspects: very high deformability and essentially complete recoverability. The crosslinked materials can undergo large deformations under tensions without rupturing. When the deforming force is removed, they spontaneously recover their original dimensions [18].

There are several theories in order to derive the entropy change during deformation (ΔS_{el}) [19, 20, 21]. According to the simplest affine network model, crosslinking points are embedded in the network; thus, components of each chain vector transforms linearly with macroscopic deformation. The entropy change during elastic deformation of an affine network is given by [13]:

$$\Delta S_{el} = -\frac{1}{2} \nu k \left(\alpha_1^{\,2} + \alpha_2^{\,2} + \alpha_3^{\,2} - 3 \right) \tag{2.9}$$

where ν is the number of network chains and α_1, α_2 and α_3 are the deformation ratios. This equation is basic to molecular theories of rubberlike elasticity and can be used to obtain the elastic contribution to the free energy of the polymer network (ΔG_{el}).

$$\Delta G_{el} = \Delta H_{el} - T.\Delta S_{el} \tag{2.10}$$

Assuming, in accordance with the basic principles of the kinetic theory, that there is no change of internal energy on deformation and so, $\Delta E_{el} = 0$. According to the rubber elasticity assumptions there is no change of volume on deformation and hence, $\Delta V_{el} = 0$. Also the interactions do not much change upon deformation ($\Delta H_{el} = \Delta E_{el} + p.\Delta V_{el}$) and this results for $\Delta H_{el} = 0$. Substituting ΔH_{el} and Eq. (2.10) for ΔS_{el} in the Eq. (2.9) gives the elastic contribution to the free energy of the polymer network (ΔG_{el}):

$$\Delta G_{el} = -T.\Delta S_{el} = \frac{1}{2}\nu kT\left(\alpha_1^{\,2} + \alpha_2^{\,2} + \alpha_3^{\,2} - 3\right) \tag{2.11}$$

Since work of deformation W equals to ΔA_{el}, using Equation (2.11), the following equation for W can be written:

$$W = \frac{1}{2}\nu kT\left(\alpha_1^{\,2} + \alpha_2^{\,2} + \alpha_3^{\,2} - 3\right) \tag{2.12}$$

For uniaxial deformation (Fig. 2.3), since $\alpha_2^{\,2} = \alpha_3^{\,2} = \frac{1}{\alpha}$ and $\alpha_1^{\,2} = \alpha^2$, Equation (2.12) reduces to:

$$W = \frac{1}{2}\nu kT\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \tag{2.13}$$

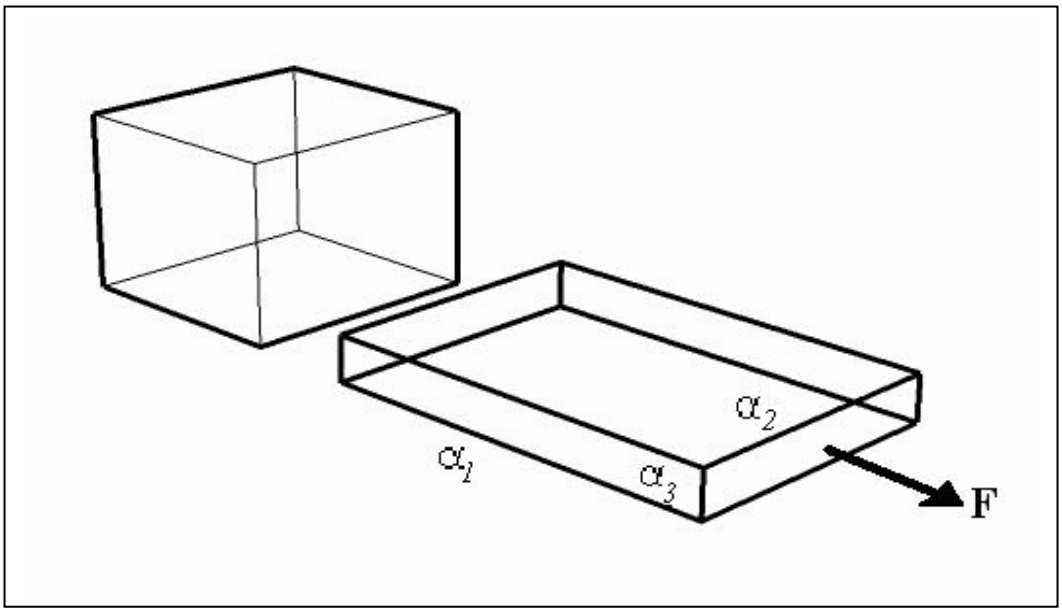


Figure 2.3: The uniaxial deformation of polymer network.

By using Equation (2.12), the force F acting on the gel sample can be calculated:

$$F = \left(\frac{\partial W}{\partial \alpha}\right)_{T,V} = \frac{1}{2}\nu kT\left(2\alpha - \frac{2}{\alpha^2}\right) = \nu kT\left(\alpha - \frac{1}{\alpha^2}\right) \tag{2.13}$$

Equation (2.13) involves a single physical parameter νkT, which is only dependent on the crosslink density of the material. This is called the elastic modulus G of the gel in dried state:

$$G_{dry} = \nu kT = \frac{\rho}{Mc}RT \tag{2.14}$$

As the gel swells, the elastic modulus decreases due to the decrease in the concentration of the network chains ν. The elastic modulus of swollen gels is given by the following equation:

$$G = A\frac{\rho}{Mc}RT\left(\nu_2{}^0\right)^{2/3}\left(\nu_2\right)^{1/3} \tag{2.15}$$

where R is gas constant and T is temperature. The front factor A equals to 1 for an affine network and $1-2/\Phi$ for a phantom network, where Φ is the functionality of

the crosslinks. Since $\nu_2^0 = \nu_2$ for the hydrogels just after preparation, the modulus G_0 after preparation becomes:

$$G_0 = A\frac{\rho}{Mc}RT\nu_2^0 \tag{2.16}$$

2.2. Macroporous Gels

Polymeric gels are useful materials for drug delivery systems, artificial organs, actuators, on–off switches, separation operations in biotechnology, and processing of agricultural products. In these applications, the response rate of the conventional gel is not as fast as required due to the rate- limited diffusion process. In order to increase the response rate of these gels, several approaches were reported, such as reducing the size of the gel particles [22], creating dangling chains on the gel samples [23-25], or, constructing an interconnected pore structure within the polymeric matrices which is called macroporous gels [26,27,10]. There is an increasing both fundamental and technological interest to macroporous polymeric materials.

Macroporous polymers emerged in the late 1950s as a result of the search for polymeric matrices suitable for the manufacture of ion-exchange resins with better osmotic shock resistance and faster kinetics [28]. In contrast to the polymers that require solvent swelling to become porous, macroporous polymers are characterized by a permanent porous structure formed during their preparation that persists even in the dry state. Their internal structure consists of numerous interconnected cavities (pores) of different sizes, and their structural rigidity is secured through extensive crosslinking.

Macroporous polymer networks are mainly prepared by free-radical crosslinking copolymerization of vinyl and divinyl monomers in the presence of an inert diluent. The network synthesized without inert diluent consists of a continuous polymer phase while the network synthesized with inert diluent consists of voids (pores). In order to form macroporous structure in dried state, a phase separation must occur during the crosslinking process [10, 29]. The structures obtained at high crosslinker

contents have nanometer to micron-sized pores and they look like cauliflowers, typical for macroporous networks [29]. As a result of this macroporous structure, these materials respond to the external stimuli very rapid. The uncontrollable size distribution and the high crosslinker needed which results in low swelling ratios are the main disadvantages of this method.

A new route for the preparation of macroporous gels with micrometer pores is so-called cryogelation or, cryostructuration [30]. In this case, gelation proceeds in the medium of a frozen monomer solution.

2.2.1 Low Temperature Gels

As is well known, in sea ice, pure hexagonal ice crystals are formed and the various impurities, e.g., salts, biological organisms, etc. are expelled from the forming ice and entrapped within the liquid channels between the ice crystals [31, 32]. This natural principle was used by Lozinsky for the preparation of porous gels [33]. As in nature, during the freezing of a monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the polymerization reactions only take place in these unfrozen liquid channels. After polymerization and, after melting of ice, a porous material is produced whose microstructure is a negative replica of the ice formed (Figure 2.4) [34-37].

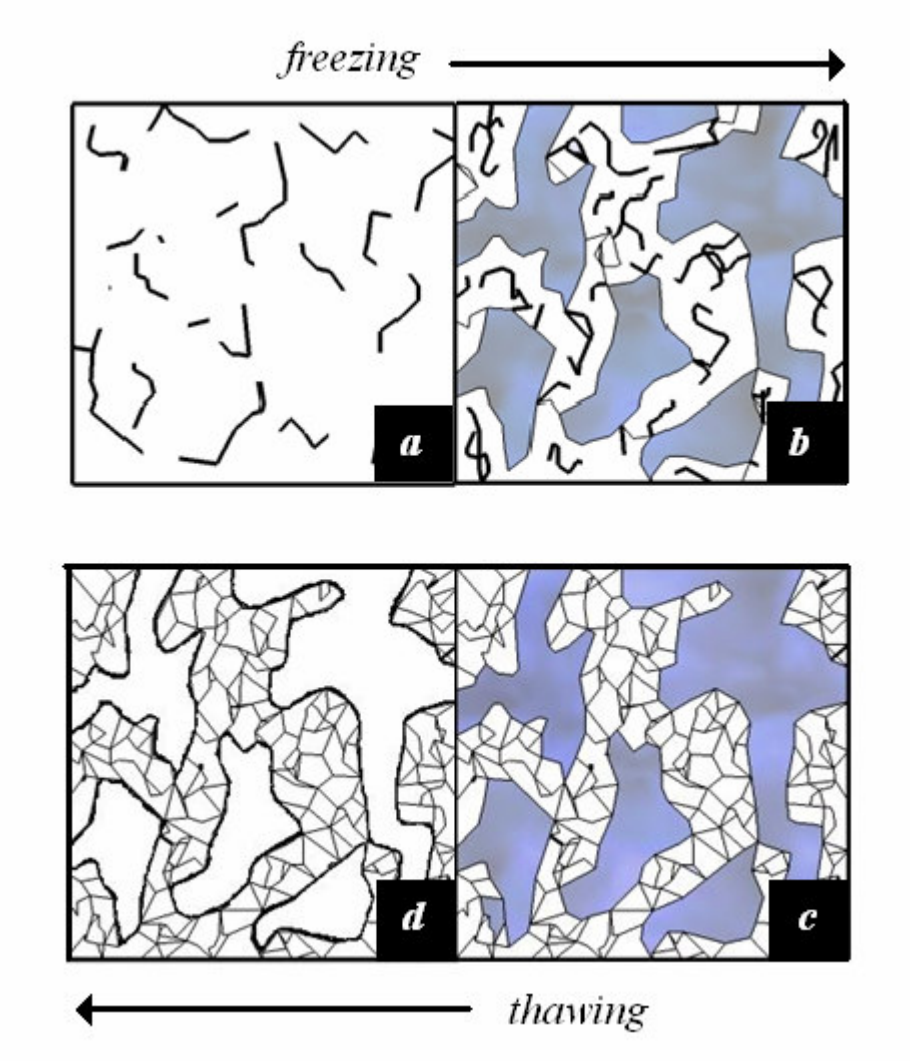


Figure 2.4: Schematic presentation of polymerization of apparently-frozen monomer solutions and formation of macroporous structure in a continuous polymer matrix. a) monomer solution; b) benzene crystals in blue colour and monomer solution in the unfrozen liquid channels; c) crosslinked polymer and benzene crystals; d) crosslinked polymer with macropores (cryogel).

In these cryogelation systems, although there is no phase separation during the course of the network formation, the frozen zones (benzene crystals) of the reaction system act as template during gelation, which is removed from the gel by thawing leading to a porous structure [33].

The main characteristic features of the cryotropic gelation processes can be summarized as below:

1-The reaction mixture containing gel-forming agents (e.g., monomer or polymer solution containing a crosslinker) is frozen at temperatures at least a few degrees centigrade below the solvent freezing point. The frozen system, despite looking as a single solid block, remains essentially heterogeneous and contains so-called unfrozen liquid microphase (UFLMP) along with the crystals of the frozen solvent.

2-Gel-forming reagents are concentrated in UFLMP, that is, cryoconcentration takes place. As UFLMP presents only a small portion of total initial volume, the concentration of gel precursors increases dramatically promoting the gel-formation.

3- The crystals of frozen solvent act as a pore-forming agent. When melted, they leave voids, macropores, filled with the solvent. The surface tension between solvent and gel phase rounds the shape of the pores, making pore surface smoother.

4- When freezing, the solvent crystals grow till they meet the facets of other crystals, so after thawing a system of interconnected pores arises inside the gel. The dimensions and shape of the pores depend on many factors; the most important are the concentration of precursors and the regimes of cryogenic treatment.

5- The polymer phase of the cryogel has, in turn, micropores formed in between the polymer chains. Thus, cryogels have both heterophase and heteroporous structure (Figure 2.2).

In the present work, the cryogelation technique was applied to the crosslinking reactions of butyl rubber solutions. Therefore, in the following section, some characteristics of butyl rubber are summarized.

2.3. Vulcanization of Butyl Rubber

Vulcanization refers to a specific crosslinking (curing) process of rubber invented by Charles Goodyear in 1844, involving high heat and the addition of sulfur [38]. A method of cold vulcanization (treating rubber with a bath or vapors of a sulfur compound) was developed by Alexander Parkes in 1846. It is a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulfur atoms, the properties of the latter are decisively influenced by the course of vulcanization, as shown in Figure 2.5. In particular the modulus, hardness, elastic properties, resistance to swelling, etc. are considerably modified during the

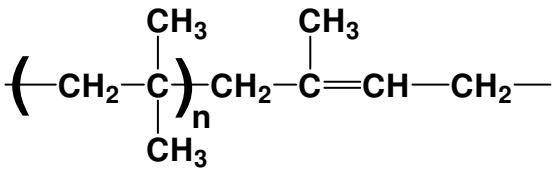
progress of vulcanization [39]. The invention of vulcanization made possible the wide use of rubber and aided the development of such industries as the automobile industry [40].

Raw rubber Vulcanised rubber

Figure 2.5: Schematic representation of a raw rubber (left) and vulcanised rubber.

Types of rubber in common use today are natural and synthetic. Even though only one chemical type of natural rubber, there are approximately twenty different chemical types of synthetic rubber, and within each type there are many distinguishable grades. The different types of rubber, each with its own properties and advantages, allow industry to choose the rubber that most clearly meets the demands of an intended use.

Butyl rubber (PIB) also known as polyisobutylene is a type of synthetic rubber consisting of poly(isobutylene) chains containing small amounts of (about 0.5 to 3 mol %) isoprene units. The structure of PIB may be represented as follows, where n is a number between 30 and 200:



butyl rubber

To obtain rubber products with the best possible properties which greatly differ according to the application concerned, it is necessary to use the most suitable

combination of vulcanization conditions and auxiliaries [39]. Due to the low degree of unsaturation in butyl rubber, its vulcanization (crosslinking) requires much powerful accelerators than the natural rubber. Butyl rubber can not be vulcanised with peroxides due to the chain scission reactions. 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.

2.3.1. Vulcanization in Bulk

In general vulcanization of butyl rubber in bulk can be performed by three methods:

2.3.1.1. Using elemental sulfur and an organic accelerator

As mentioned above, butyl rubber is considerably more reluctant to vulcanize than natural rubber. The grades with the lowest degree of unsaturation are so inert they can only be vulcanized with difficulty when sulfur and accelerators are employed. The more unsaturated types can be vulcanized more easily with elemental sulfur.

2.3.1.2. Using polyfunctional nitroso compounds

Nitroso compounds such as p-benzoquinone dioxime has a crosslinking effect on many types of rubber because of their radical action. It is best known and most useful as a crosslinking agent for butyl rubber. As already mentioned, the vulcanization of buyl rubber with sulfur and organic accelerators does not give particularly good heat resistance. In this respect, however, p-benzoquinone dioxime and dibenzoyl-p-benzoquinone dioxime have proved particularly useful.

2.3.1.3. Using reactive methylol phenol resins

In a dissertation published in 1947, Van der Meer examined the vulcanizing action of numerous phenol formaldehyde condensates including the halogen methyl phenols. Since then, many crosslinking mechanisms associated with the resin crosslinking. The results of the work described above have been applied methodically to the vulcanization of butyl rubber [41].

2.3.2 Vulcanization in Solution

Although a large number of publications and patents have been reported on the vulcanization of butyl rubber in bulk, the first successful study concerned with the vulcanization of rubber in solution was published in 2000. According to this study, butyl rubber can easily be crosslinked in an organic solution using sulfur monochloride as a crosslinking agent [42]. Sulfur monochloride, S_2Cl_2, 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. The crosslinking reaction between the PIB chains via sulfur monochloride is believed to proceed in steps as in the reaction between ethylene and sulfur monochloride [42, 42] (Figure2.6).

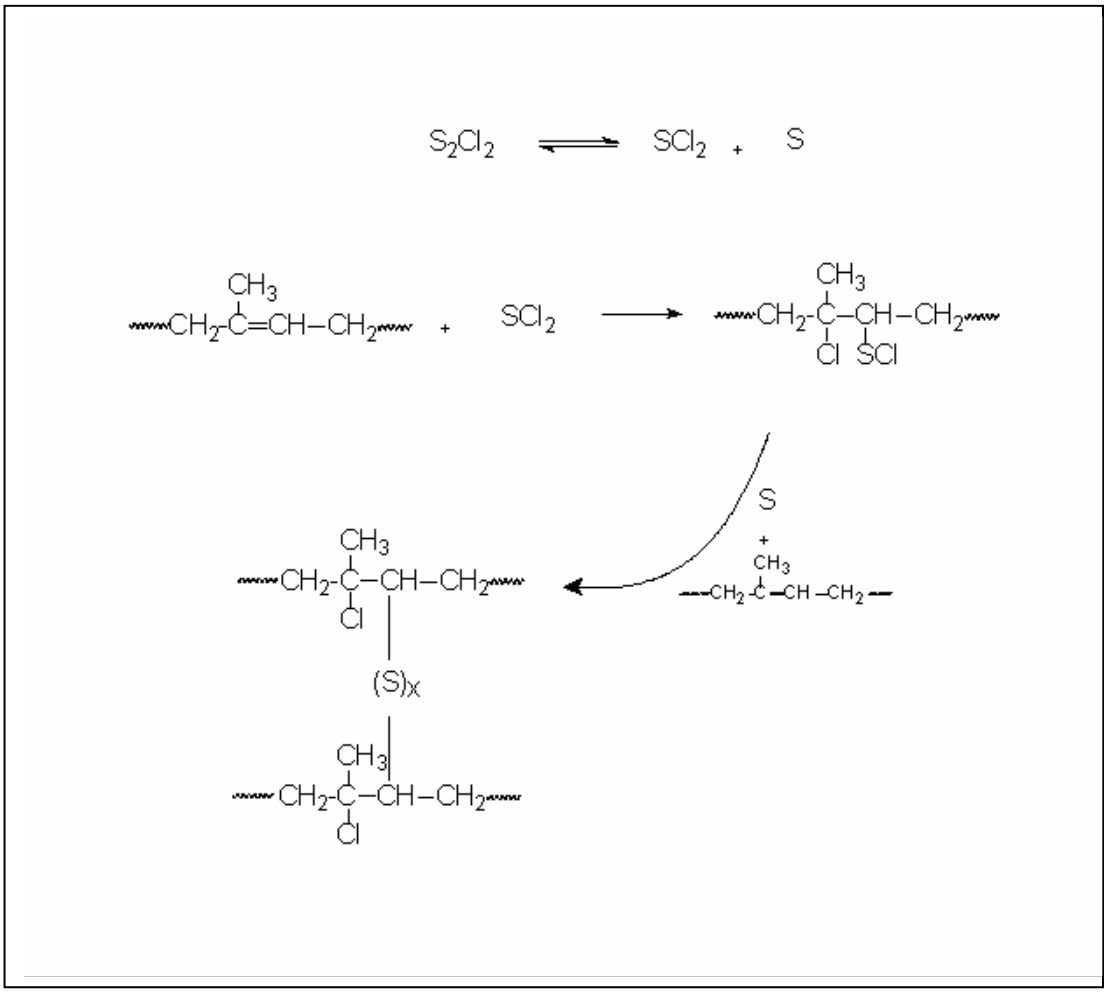


Figure 2.6: The crosslinking reactions between the PIB chains via sulfur monochloride

According to this scheme, attack of sulfur dichloride to the internal vinyl group of the polymer leads to the formation of pendant sulfur chloride groups on the PIB chains acting as potential crosslink points. Reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective crosslinks. In the work mentioned above, dried PIB gels were also subjected to sulfur analysis. The results show that, increasing crosslinker concentration in the feed also increases the sulfur content of the networks.

3. EXPERIMENTAL

3.1 Materials

The materials used in the preparation of the organogels are described below.

a) Linear Polymer : Butyl Rubber

The main component in the gel synthesis is butyl rubber, which was purchased from Exxon Chem. Co. The butyl rubber sample Butyl 165 used in this work contained 1.3 – 1.8 mol % isoprene units. Its weight-average molecular weight $\overline{M}_w$ was determined to be 3.9×10^5 g/mol on a gel permeation chromatograph with polystyrene standards. The polydispersity index $\overline{M}_w / \overline{M}_n$ was 2.5.

b) Crosslinker : Sulfur monochloride (S_2Cl_2)

The crosslinking agent sulfur monochloride was purchased from Aldrich Co.

c) Solvent : Benzene, toluene and methanol

Benzene (Merck) was used as the solvent for the solution crosslinking process. In the swelling- deswelling experiments, reagent grade toluene and methanol (Merck) were used without further purification.

3.2 Synthesis of the Organogels

The gels were prepared by solution crosslinking technique according to the following scheme: 0.01-5 g of butyl rubber was first dissolved in 100 mL of benzene at room temperature (20 ± 1^oC) overnight. After bubbling nitrogen for 20 min, different amounts of sulfur monochloride were added under rigorous stirring, and the homogenous solutions were transferred with a pasteur pipette into several glass tubes of 8 mm internal diameters and about 100 mm length. For mechanical tests, the gel samples were prepared in glass tubes of about 16 mm internal diameter. The glass tubes

were sealed and immersed in a freezer at predetermined temperatures T_{prep} for 24 h. The following variables were used for defining the composition of the gel forming system:

a) Gel preparation temperature T_{prep}: The temperature of the reaction solution at thermal equilibrium.

b) Butyl rubber concentration c_P:

$$c_P = \frac{mass\ of\ butyl\ rubber\ in\ gram}{volume\ of\ benzene\ in\ mL} x10^2 \quad (1)$$

c) Crosslinker concentration S_2Cl_2 %:

$$S_2Cl_2\% = \frac{volume\ of\ S_2Cl_2\ in\ mL}{mass\ of\ butyl\ rubber\ in\ gram} x10^2 \quad (2)$$

Three sets of gelation experiments were carried out (Table 3.1). In the first set, butyl rubber concentration c_P was varied between 0.01 and 5 % while T_{prep} and S_2Cl_2 % were set to -18°C and 6 %, respectively. In the second set, the temperature T_{prep} was varied between -22°C and 21°C. In the third set, the crosslinker concentration was varied between 2 and 10 % at T_{prep} = -22°C and c_P = 5 %.

Table3.1. Three sets of gelation experiments conducted as various reaction conditions.

Sets	c_P (w/v %)	T_{prep} (°C)	S_2Cl_2 (v/w%)
1	0.01 ⟶ 5	-18	6
2	5	−22 → +21	6
3	5	-22	2 ⟶ 10

4. CHARACTERIZATION METHODS

4.1 Equilibrium Swelling Measurements

The swelling behavior of gels was investigated in toluene. After the preparation, the organogels in the form of rods of approximately 8 mm in diameter were immersed in an excess of toluene and toluene was washed out every other day over a period of at least one week to wash out the soluble polymer and unreacted crosslinker (Fig 4.1).

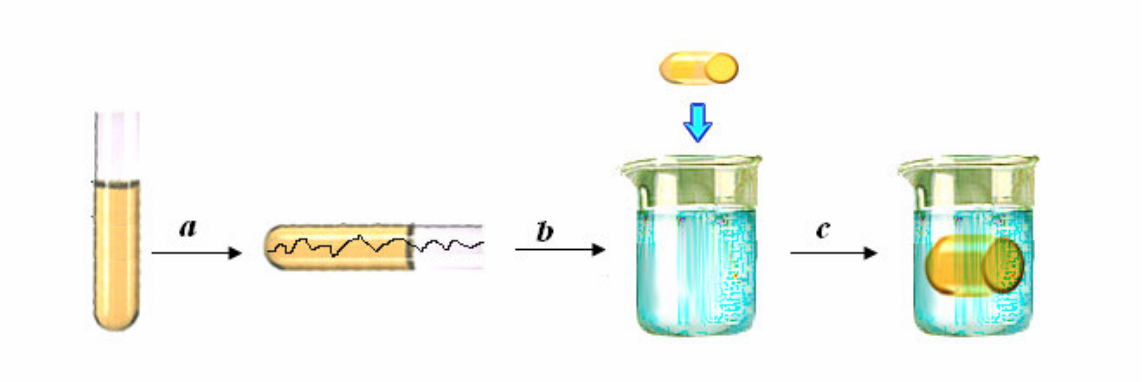


Figure 4.1: Schematic representation of the swelling period. a) breaking of the tube after synthesis; b) immersing the gel into the good solvent toluene; c) equilibrium swelling state of the gel.

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. 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:

$$W_g = \frac{m_{dry}}{m_o \; c_P \; /100} \tag{4.1}$$

where m_{dry} and m_o are the weights of the gel samples after drying and just after preparation, respectively. The swelling equilibrium was also tested by weighing the

gel samples. For good precision, three measurements were carried out on samples of different length taken from the same gel.

For gravimetric measurements, the weights of the gel rods after drying m_{dry} and after swelling m_{sw} were measured on an electronic balance. The equilibrium weight swelling ratio of the gel samples with respect to the after their dry state was calculated as:

$$q_w = \frac{m_{sw}}{m_{dry}} \tag{4.2}$$

For volumetric measurements, the diameters of the gel rods after swelling D and after drying D_{dry} were measured by a calibrated digital compass as well as by the image analyzing system (Fig. 4.2). The equilibrium volume-swelling ratio of the gel samples with respect to the after drying state was calculated as:

$$q_v = \frac{V}{V_{dry}} = \left(\frac{D}{D_{dry}} \right)^3 \tag{4.3}$$

where V_{dry} is the volume of the dry gel and D_{dry} and m_{dry} are the diameter and the mass of dry gels, respectively.

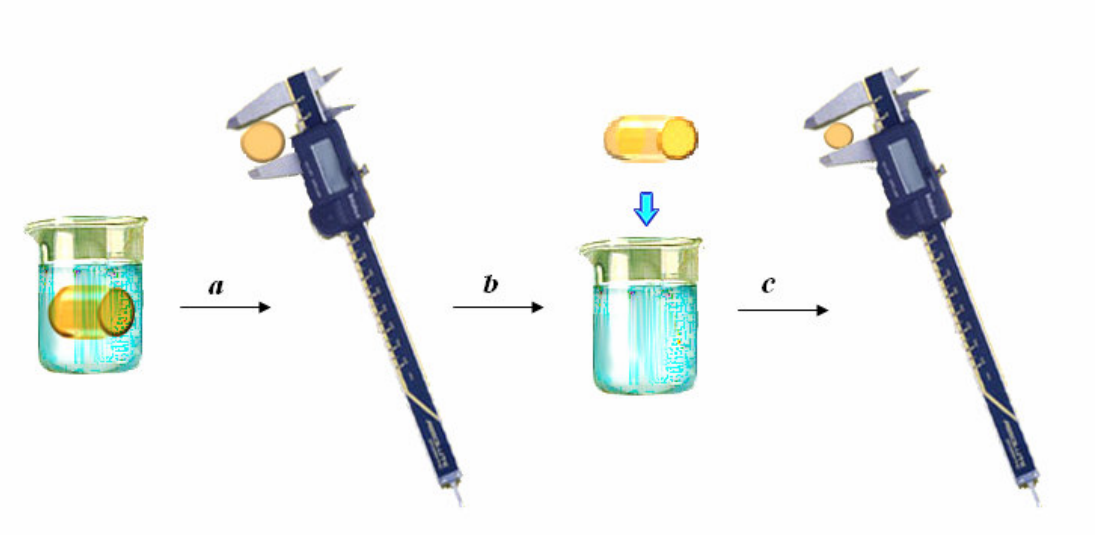


Figure 4.2: Schematic representation of the swelling measurements. a) measuring the diameter of the equilibrium swollen gel; b) immersing the gel to the bad solvent (methanol); c) measuring the diameter of the collapsed gel by a digital compass.

4.2 Swelling-Deswelling Kinetics Measurements

For the deswelling kinetics measurements, the equilibrium swollen organogel 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 relative weight swelling ratio $m_{rel} = m_t / m$, 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 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.

4.3 Mechanical Measurements

For the mechanical measurements, the organogels were prepared in several glass tubes of about 10-15 mm internal diameters and about 100 mm length. After the reaction, the hydrogels were cut into specimens of approximately 15 mm in length. Uniaxial compression measurements were performed on equilibrium swollen gels in toluene and in a thermostated room of 20 ± 0.5°C by using an apparatus which is schematically shown in Figure 4.3.

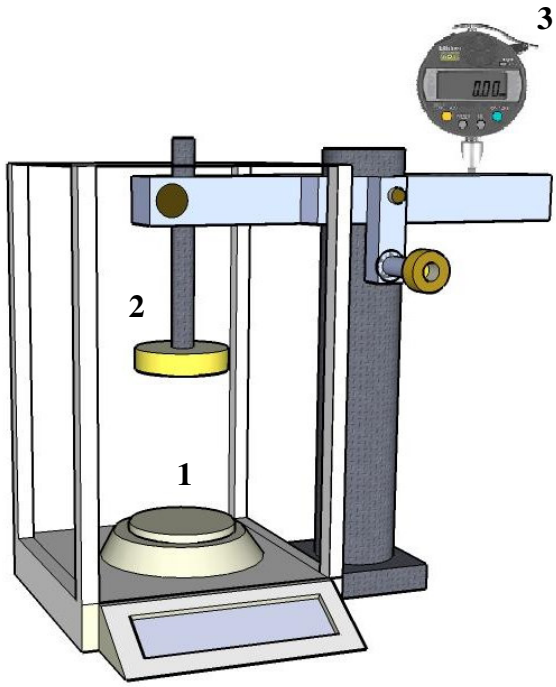


Figure 4.3: Apparatus for carrying out stress-strain measurements. 1. Digital electronic balance, 2. PTFE end plate and, 3. Digital comparator.

A cylindrical gel sample of 10-15 mm in diameter and 15 mm in length was placed on a digital electronic balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE (Teflon) end-plate. The force acting on the gel F was calculated from the reading of the balance m as F = mg, where g is gravitational acceleration (g = 9.8030 $m.s^{-2}$). The elastic modulus G was determined from the slope of linear dependence, $f = G\left(\alpha - \alpha^{-2}\right)$, 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). Deformation ratio was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo) which was sensitive to displacements of 10^{-3} mm. The force and deformation ratio were recorded after 15 sec of relaxation.

4.4 Texture Determination by Scanning Electron and Optical Microscopy

The internal morphology of the gels was investigated by Scanning Electron Microscopy (SEM). The gels were dried by gradually replacement of toluene with

methanol (0→ 40 % →60 % → 80 % →100 %) and were kept at vacuum for one week without heating. After that gels were coated with gold using Sputter-coater S150 B Edwards. Then, JEOL JSM 6335F Field Emission Scanning Electron Microscope instrument was used for obtaining the SEM images of the gels.

The morphology of the gels was also investigated by optical microscopy (Fig. 4.4). An Olympus Biological Microscope Model CX31 was used to monitor the interior morphology of the organogels in their swollen state. The gels were cut to thin slices using a razor blade. The slices were then transferred to object slides and the gel samples were studied at various magnifications. Microphotographs taken from the gels were captured by Q Imaging Camera, MicroPublisher 3.3 RTV connected to PC with software Image-Pro PlusVersion 6.0.

Figure 4.4: Photograph of the image analyzing system. Optical microscope (right), PC monitors (middle) and imaging camera (left).

4.5 Differential Scanning Calorimetry Measurements

For the determination of the non-freezable benzene content of the gels, DSC measurements were carried out on Perkin-Elmer Diamond DSC. 5 % solutions of butyl rubber in benzene were first frozen at -18^{o}C for 48 h and then, portion of this solution (about 0.01 g) was placed in the aluminum sample pan of the instrument. The pan with solution was sealed and weighted. Then, it was held within the

instrument at -18°C for two hours and then heated to 20°C with a scanning rate of 1°C/min. In this way, the transition enthalpy ΔH for the melting of frozen benzene was determined. After the scans, the pans were punctured and dried at 80°C to constant weight. The total benzene content of the gel sample $m_{benzene}$ was calculated as $m_{benzene} = m_1 - m_2$, where m_1 is the weight of pan with solution and m_2 is the same weight but after drying. The mass fraction of non-freezable benzene in the solution, $f_{benzene}$ was estimated as

$$f_{benzene} = 1 - (\Delta H/\Delta H_m) / m_{benzene} \quad (4.4)$$

where ΔH_m is the heat of melting of benzene.

4.6 Pore Volume and Porosity Calculations

4.6.1 Pore Volume

Total volume of the pores in a porous material (with an open-pore structure) can be estimated from the uptake of poor solvents. In the present work, 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 while the polymer will not absorb the solvent. Thus, V_p (mL pores in one gram of dry polymer network) in the material can be estimated from the amount of the absorbed poor solvent.

$$V_p = (m_M - m_{dry}) / (d_M\, m_{dry}) \quad (4.5)$$

where m_M is the weight of the network immersed in methanol after 2h and d_M is the density of methanol.

5. RESULTS AND DISCUSSION

As mentioned in the Introduction, solution crosslinking of butyl rubber (PIB) using sulfur monochloride as a crosslinker leads to the formation of organogels with a slow rate of response against the external stimuli. For example, the swelling process of these gels in a good solvent such as toluene requires at least one day attaining the swelling equilibrium [12]. The purpose of this thesis is to obtain tough, superfast responsive PIB gels by modification their internal structure. The gels should swell or deswell immediately in good and poor solvents, respectively. Moreover, the gels should be able to release all the absorbed solvent under a mechanical force of a few kilopascals, so that they should exhibit sponge-like properties specific for the sorption of organic solvents.

Our strategy to prepare such fast responsive PIB gels with unique mechanical properties is the application of so-called "cryogelation technique" to the present gelling system. As reported in the literature [33-37], during the freezing of a monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the polymerization reactions only take place in these unfrozen liquid channels. After polymerization and, after melting of ice, a porous material is produced whose microstructure is a negative replica of the ice formed. Recently, our research group has shown that by conducting the copolymerization-crosslinking reactions below $-8^{o}C$, hydrogels based on 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as well as acrylamide monomer with superfast swelling properties could be obtained [44]. This was achieved by using gelation reactions occurring in the apparently frozen reaction system, which allowed for the formation of a bicontinuous morphology in the polymer networks. The free water molecules freezing in the gel causes the network chains to gather and condense so that a heterogeneous network forms after removing the ice.

In the present work, we applied this procedure for the preparation of organogels based on butyl rubber (PIB), a linear poly(isobutylene) containing small amounts of internal unsaturated groups (isoprene units). The organogels were prepared starting from apparently frozen butyl rubber solutions in benzene. Benzene was selected as the solvent due to the relatively higher freezing point (5.5°C) compared to toluene (-95°C) so that the crosslinking reactions in the frozen state can be conducted at much higher temperatures. Sulfur monochloride was used as the crosslinking agent. For comparison, conventional organogels were also prepared starting from the same butyl rubber solutions, but at usual reaction temperatures (+17°C). In the following sections, the preparation of PIB gels under various reaction conditions and their properties will be described. The following gel synthesis parameters were varied:

1) Crosslinker (S_2Cl_2) concentration,

2) Gel preparation temperature (T_{prep}),

3) Cooling rate

5.1 Gel Fractions

We first determined the gel fractions after the solution crosslinking reactions by use of the gravimetric measurements, as mentioned in the Experimental Part. This is due to the fact that, decreasing the reaction temperature below the freezing point of the reaction system will decrease the rate of the crosslinking reactions, which may lead to a decrease in the yield of the crosslinked polymers. For this and other experiments, the reaction time was set to one day. The gel fraction W_g was defined as the amount of crosslinked (insoluble) polymer obtained from one gram of butyl rubber. Fig. 5.1 shows the gel fraction W_g plotted as a function of the gel preparation temperature T_{prep}. For this set of experiments, the concentrations of PIB and S_2Cl_2 were set to 5 and 6 %, respectively. It is seen that W_g is higher than 0.85 for all the gels prepared at or above -22°C. Thus, reducing T_{prep} below the bulk freezing temperature of the reaction system does not decrease the amount of the crosslinked polymer in the crude gels. Experiments carried out at various (S_2Cl_2) concentrations between 2 and 10 % also gave a W_g value larger than 0.85. Assuming that the butyl rubber contains 1.5 - 1.8 mol % isoprene units, the molar masses of isobutylene, isoprene units and S_2Cl_2 are 56, 68, and 135 g/mol, respectively, and the density of

S_2Cl_2 is 1.68 g/mL, a multiplication factor of 0.43 ± 0.04 converts S_2Cl_2 % into the molar ratio of the crosslinker S_2Cl_2 to the vinyl group in the polymer. 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_2Cl_2 / mol internal vinyl group of PIB. The temperature independence of W_g is due to the high polymer concentration in the unfrozen regions of the reaction system.

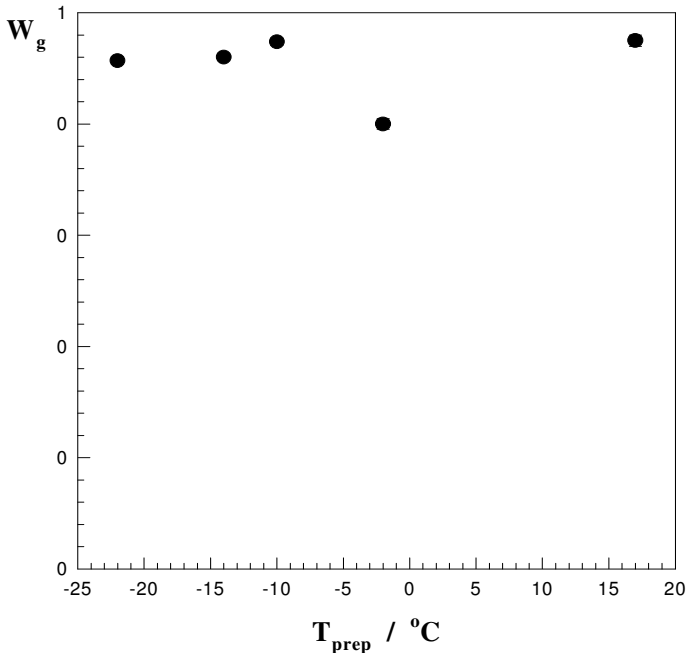


Figure 5.1: Gel fraction W_g shown as a function of the gel preparation temperature. c_P = 5 w/v %, S_2Cl_2 = 6 %.

In order to find out the critical initial butyl rubber concentration required for the onset of gelation, a series of experiments were carried out at PIB concentrations c_P between 0.01 and 5 %. The temperature T_{prep} and the crosslinker content were set to -18°C and 6 % S_2Cl_2, respectively. In Fig. 5.2, the weight fraction of gel, W_g, is plotted against the polymer concentration c_P. It can be seen that, in the range of c_P between 2 and 5 %, the gel fraction is around 0.90 while it starts to decrease as c_P is decreased below the 2 %, indicating increasing number of PIB chains remains unattached to the gel after the reaction. It should be noted that at c_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_P = 0.05 %, the reaction

system dissolved completely in toluene. Thus, the critical butyl rubber concentration for the onset of gelation is 0.08 ± 0.02 %, compared to the reported value of 4 % at T_{prep} = 20°C [12].

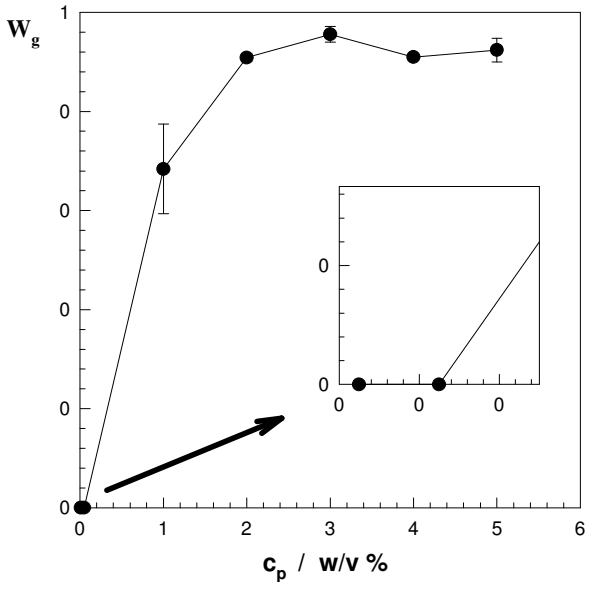


Figure 5.2: Gel fraction W_g plotted against the initial PIB concentration c_P. S_2Cl_2 = 6 %, T_{prep} = -18°C.

It is seen that, decreasing the reaction temperature from 20°C 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. By DSC measurements mentioned in the Experimental Part, 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. 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 [33, 44, 45]. Although the usual polymer concentrations can lower the freezing point by only a few degrees, once ice is present, the effect is enhanced. This is because polymer

chains are excluded from the ice 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 is required to keep the liquid phase in equilibrium with the pure ice phase. It was shown that, in frozen poly(ethyl acrylate) gels swollen in benzene, up to about 30 % benzene remains unfrozen at low temperatures [46].

5.2 Effect of the Crosslinker Concentration

In this section, effect of the crosslinker (S_2Cl_2) concentration on the properties of the PIB gels was investigated. For this purpose, several series of PIB gels in the form of rods were prepared at various S_2Cl_2 concentrations by the solution crosslinking technique. In all the experiments, butyl rubber concentration and the gel preparation temperature were set to 5 w/v % and -22^{o}C, respectively.

5.2.1 Equilibrium Swelling Properties of PIB gels

In Fig. 5.3**,** the equilibrium weight (q_w) and the equilibrium volume swelling ratios (q_v) of PIB gels in toluene are shown as a function of the crosslinker concentration. The gel preparation temperature was set to –22^{o}C (open symbols) and +17^{o}C (closed symbols). It is seen that, for the PIB gels formed at +17^{o}C, both q_w and q_v are slightly decreasing functions of the crosslinker concentration. As the S_2Cl_2 concentration is increased from 2 to 10 %, the swelling ratio decreases from 25 to 20. This is expected since an increasing amount of the crosslinker S_2Cl_2 in the reaction system also increases the number of crosslinks in the PIB network, so that its capacity to absorb liquids decreases. Another point shown in Fig. 5.3 is that, for all the gels prepared at +17^{o}C, the weight swelling ratio q_w is equal to the volume swelling ratio q_v. In contrast, the gels prepared at –22^{o}C swell in toluene about between 2 and 4-fold more by weight than by volume. The weight swelling ratio q_w of PIB gels does not change much with the experimental parameters and remains around 30. However, the volume swelling ratio qv increases and approaches to q_w as the crosslinker concentration is increased.

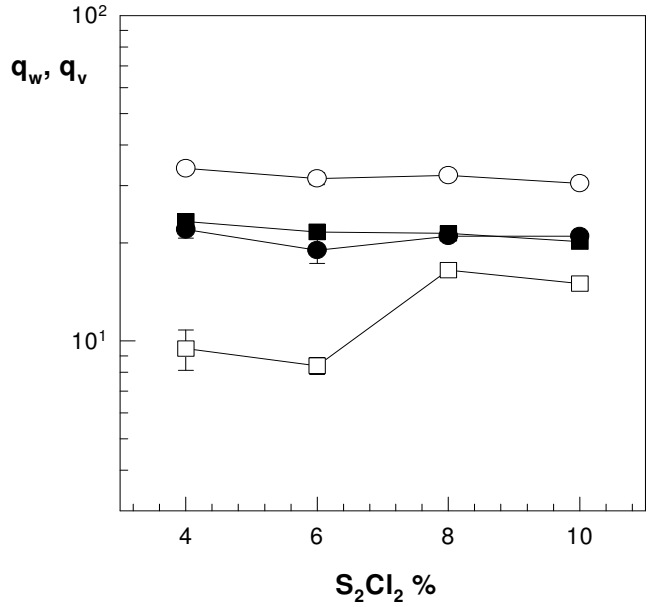


Figure 5.3: The equilibrium weight (q_w) and the equilibrium volume swelling ratios (q_v) of PIB gels in toluene shown as a function of the crosslinker (S_2Cl_2) concentration. Gel preparation temperature = –22°C (open symbols) and +17°C (closed symbols).

5.2.2 Pore Volume and Porosity of PIB gels

The relative values of the weight and the volume swelling ratios of the gels provide information about their internal structure in the swollen state [10]. This is due to the fact that the weight swelling ratio includes the solvent locating in both pores and in the polymer region of the gel. On the contrary, if we assume isotropic swelling, that is the volume of the pores remains constant upon swelling, volume swelling ratio q_v of porous networks only includes the amount of solvent taken by the gel portion of the network. 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. In Figure 5.4, the scheme of a porous material is given, where black regions represent the pores while white regions represent the polymer domains. Filling of the solvent into the pore regions does not increase the volume of the material, but its weight will increase. However, swelling of polymer regions increases both the weight and the volume of the material (Figure 5.4).

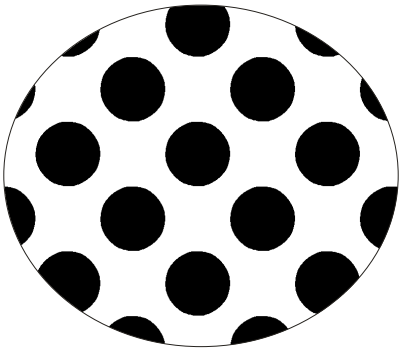


Figure 5.4: Scheme of a porous polymeric material

From the weight and volume swelling ratios of PIB gels, their swollen state porosities P_s can be estimated using the equation [10]:

$$P_s\,\% = \left(1 - \frac{q_v}{1 + (q_w - 1)d_2 / d_1}\right) x10^2 \qquad (5.1)$$

where d_1 and d_2 are the densities of swelling agent (toluene) and 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 Fig. 5.5 plotted against the crosslinker concentration. Open and filled symbols represent the gels prepared at -22 and +17^{o}C, respectively.

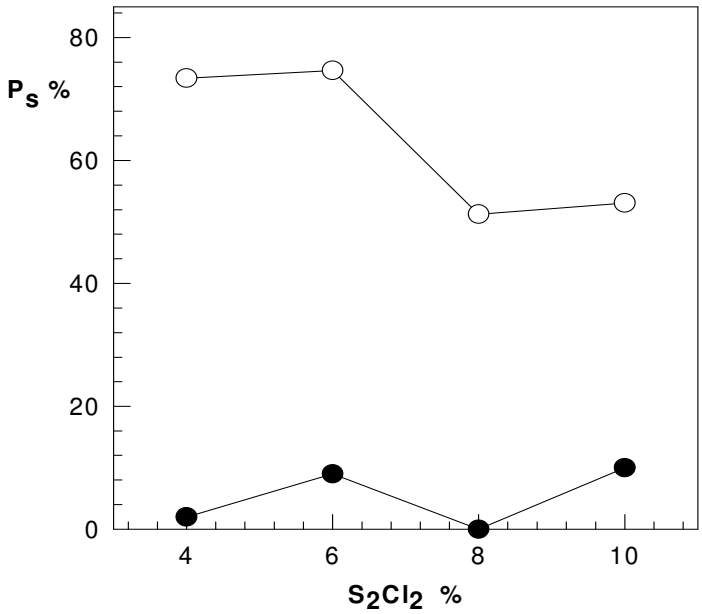


Figure 5.5: The swollen state porosity P_s of the networks prepared at +17°C (filled symbols) and -22°C (open symbols) plotted against the crosslinker (S_2Cl_2) concentration.

It is seen that the swollen state porosity P_s is almost zero for the gels formed at +17°C while those prepared at -22°C exhibit significant porosities. P_s is close to 80 % at low S_2Cl_2 contents while it slightly decreases to about 50 % as the crosslinker content is increased.. A P_s value of 80 % indicates that 80 % of the swollen gel volume consists of voids (pores) filled with the swelling agent.

The total volume of pores, V_p can also be estimated from the amount of the absorbed poor solvent. Here, the pore volume of PIB gels was estimated from the uptake of methanol, which is a poor solvent for the PIB chains. For the measurements, dried PIB gel samples were immersed into methanol for 2 h and then, the amount of absorbed methanol was determined gravimetrically. For the gels prepared at -22°C, V_p was found to be in the range of 7 – 8 mL /g while those formed at 17°C exhibited negligible pore volumes. Thus, one gram of dry PIB network prepared at -22°C contains pores with a total volume of 7-8 mL. Dry state porosity P_{dry} can be calculated from the total volume of pores together with the polymer density d_2 using the equation:

$$P_{dry}\,\% = \left(1 - \frac{{d_2}^2}{1 + d_2 V_p}\right) x10^2 \qquad (5.2)$$

In Fig. 5.6, the swollen (P_s) and the dry state porosities (P_{dry}) of the gels prepared at -22°C (open and filled circles, respectively) are plotted against the crosslinker concentration. P_s and P_{dry} values were calculated using equations 5.1 and 5.2, respectively. It is seen that the two different techniques to estimate the porosity of the organogels, namely one starting from the swelling ratios in a good solvent and the other from the uptake of a poor solvent gave similar results. The porosities are larger than 50 % for all the PIB gels formed at -22°C compared to the negligible porosity of the PIB gels formed at usual temperature.

A direct technique to investigate the internal structure and thus, the porosity of these organogels is the analysis of the dried gel samples under electron microscope. In the following section, the results of this analysis are given.

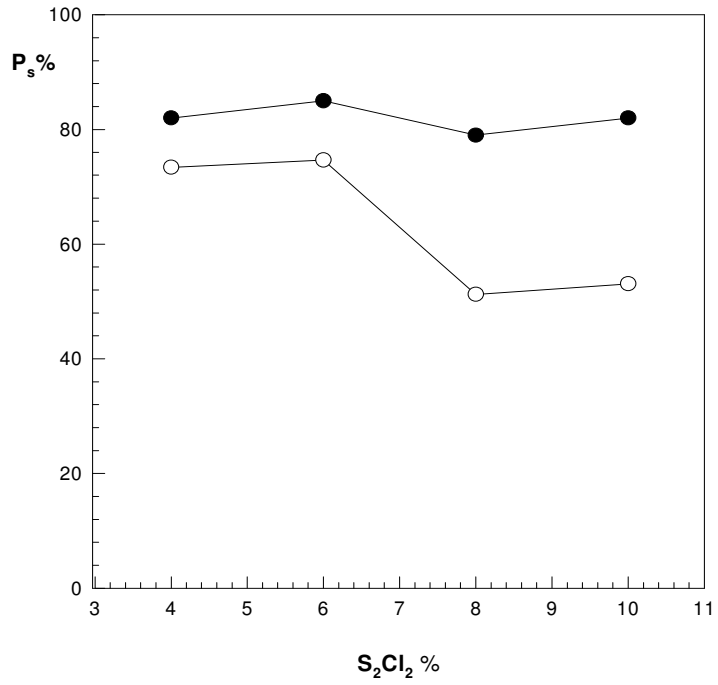


Figure 5.6: The swollen state (open symbols) and the dry state (filled symbols) porosities of the networks plotted against the crosslinker (S_2Cl_2) concentration.

5.2.3 Morphology of PIB Gels

The morpologies of dried gel samples were observed by scanning electron microscopy (SEM). In the scanning electron micrographs shown in Figure 5.7, the microstructure of the network formed at -22 (right) and +17°C (left) are given.

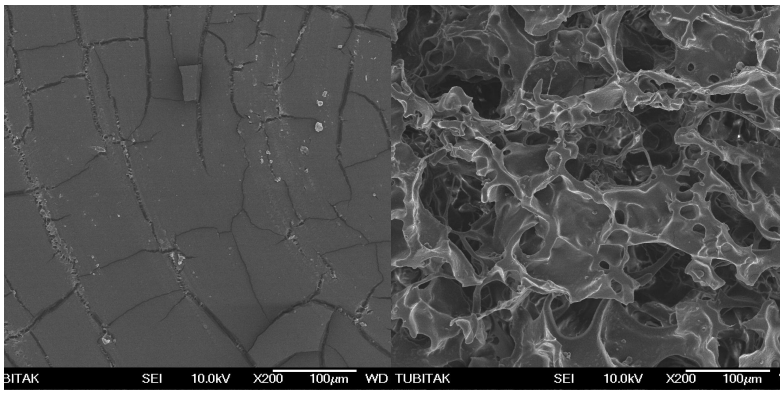


Figure 5.7: SEM of PIB networks formed at +17°C (left) and -22°C (right). S_2Cl_2 = 4 %, c_P = 5 w/v %. The scaling bars are 100 µm. Magnification = x200

It is seen that the network formed at +17°C exhibits a continuous morphology while that formed at –22°C have a porous structure demonstrating the presence of bicontinuous morphologies. Thus, the drastic change in the swelling behavior of the gels prepared at low temperatures as well as the large difference between the weight and volume swelling ratios are reflected with the difference in the internal morphology of the gel networks.

SEM images of low temperature PIB networks exhibit clearly different morphologies when one compares with macroporous networks formed by reaction induced phase separation, where the structure looks like cauliflower and consists of aggregates of various sizes [10]. The morphology of the present networks also significantly differs from the honeycomb morphology of cryogels obtained from hydrophilic monomers [33, 44, 45]. The characteristic of the texture of PIB networks is thick pore walls of about 10 µm in width which provide structural support to the material.

The influence of crosslinker concentration on the network microstructure is shown in the Figure5.8. Here, SEM images of dried PIB gels formed at various crosslinker concentrations are shown. The gel preparation temperature was -22°C. It is seen that the architecture or morphology of the networks essentially does not depend on the crosslinker concentration, whereas the size of the structure responds sensitively: The higher the crosslinker concentration, the smaller the pore diameters and the thicker the pore walls. Increasing size of the pores with decreasing crosslinker concentration can be explained as a result of the weak network structure formed at low crosslinker concentrations. Since the structure is weak, it collapses upon drying of PIB gels so that the small pores combine each other to form large pores.

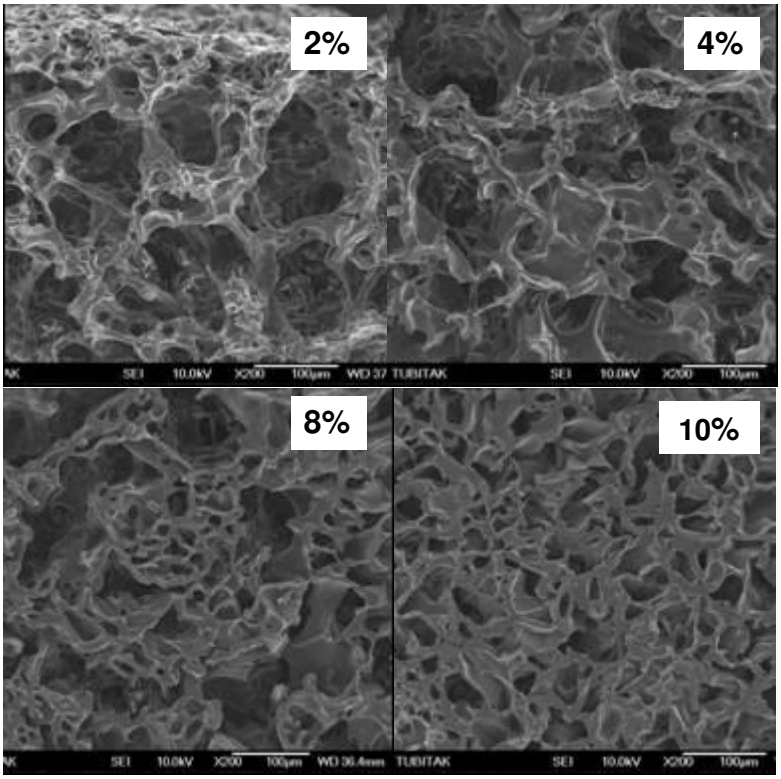


Figure 5.8: SEM of PIB networks formed at various crosslinker (S_2Cl_2) concentration, as indicated in the images. T_{prep} = -22°C, c_P = 5 w/v %. The scaling bars are 100 μm. Magnification = x200

5.2.4 Deswelling-Swelling Kinetics of PIB Organogels

PIB gels formed at various crosslinker concentrations were subjected to swelling and deswelling processes in methanol and in toluene, respectively. For this purpose, the gel sample equilibrium swollen in toluene was first immersed in methanol (poor solvent) and the weight change of gel was determined as a function of the deswelling time. After reaching the equilibrium collapsed state in methanol, the collapsed gel was immersed in toluene (good solvent) and the reswelling process was monitored by recording the weight increase with time. In order to check the durability of the gel sample against the weight changes, this swelling-deswelling cycle was repeated two times.

We first compared the swelling and deswelling behavior of two gels containing 4 % crosslinker S_2Cl_2; namely one prepared at -22^oC (low temperature gel) and the other at +17^oC, which is the conventional gel reported in the literature. The semilogaritmic plots in Figure 5.9 compares the response rate of two PIB gel samples prepared at -22^oC (open symbols) and 17^oC (filled symbols). 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. Comparison shows that both the swelling and deswelling rates of the gels obtained at -22^oC are much faster than those of the gels obtained at room temperature. Low temperature gel attains its equilibrium collapsed state in methanol within 2 min while the conventional gel requires 80 min for this deswelling process. On the other hand, the swelling times in toluene are 2 min and 200 min for the low temperature and conventional gels, respectively. Thus, the cryogelation technique was successfully applied for the preparation of fast responsive PIB gels.

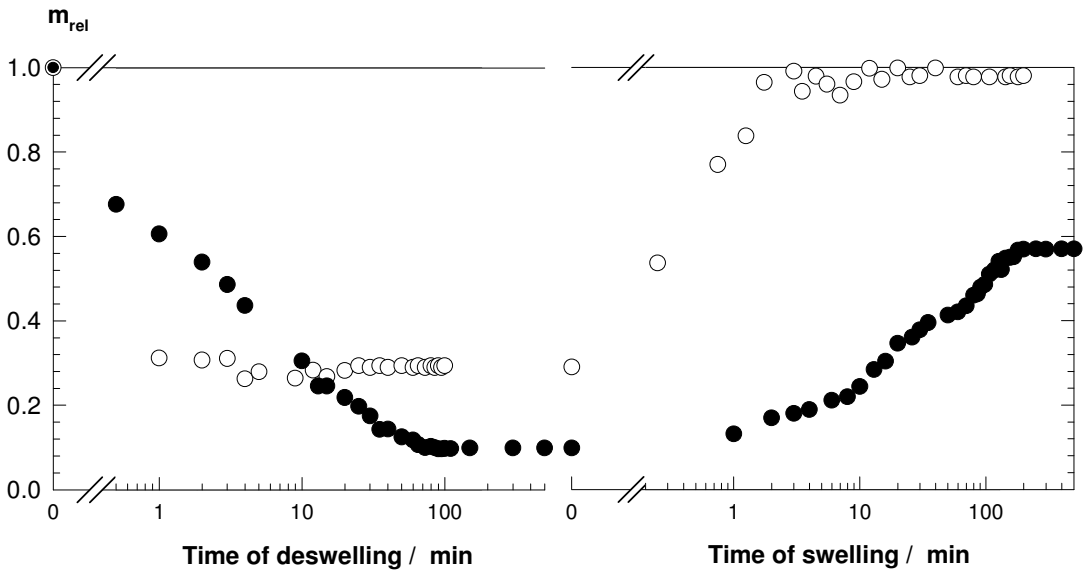


Figure 5.9: The normalized mass m_{rel} of PIB gels shown as a function of the time of deswelling in methanol and re-swelling in toluene. T_{prep} = 17°C (filled symbols) and -22°C (open symbols). S_2Cl_2 = 6 w/v %, c_P = 5 w/v %. .

Effect of the crosslinker concentration on the swelling-deswelling behavior of PIB gels are collected in Figure 5.10. Here, the relative weight swelling ratio m_{rel} is plotted against the time of deswelling or reswelling for the gels formed at various crosslinker concentrations. The gel preparation temperature was –22°C and +17°C for Fig. 5.4A and 5.4B, respectively.

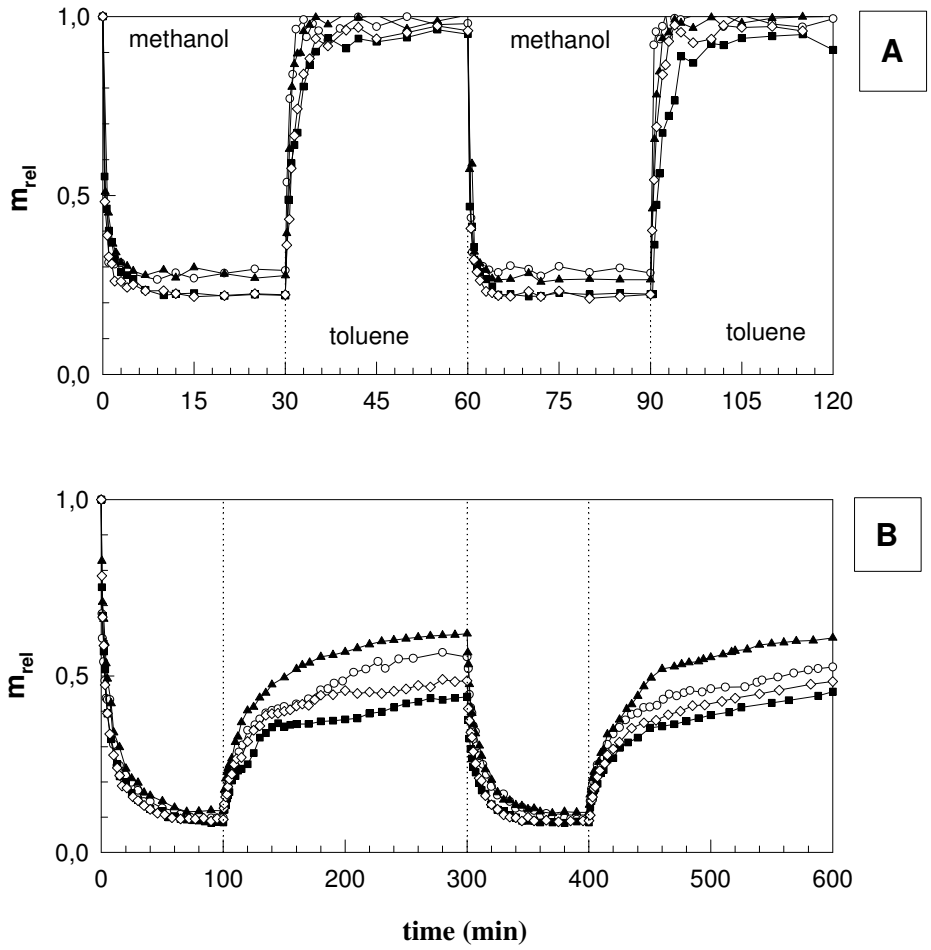


Figure 5.10: Swelling and deswelling kinetics of PIB gels in toluene and in methanol, respectively, shown as the variation of the relative weight swelling ratio m_{rel} with the time of swelling or deswelling. c_P = 5 w/v %. Gel preparation temperature T_{prep} = -22°C (A) and +17°C (B). Crosslinker (S_2Cl_2 %) concentration = 4 (○), 6 (▲), 8 (■), and 10 w/v % (◇).

Independent of the amount of the crosslinker, all the PIB gels prepared at –22°C attain their equilibrium collapsed and equilibrium swollen states in less than two minutes. 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. Only the response rate of the gel containing 4 % crosslinker is slightly faster than the others. 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. Thus, all the PIB gels which are prepared at -22°C exhibit fast response rates.

5.3 Effect of the Gel Preparation Temperature

In this section, both the crosslinker (S_2Cl_2) content and the butyl rubber concentration were fixed at 6 % and 5 w/v %, respectively. The gel preparation temperature, T_{prep}, was varied between -22°C and 17°C. It should be noted that T_{prep} is the temperature of the thermostated bath in which the reactions were carried out. Since the addition of the crosslinker S_2Cl_2 into the butyl rubber solution occurred at room temperature the crosslinking reactions proceed non-isothermally from the moment of the crosslinker addition to the moment when the temperature of the reaction system reaches to T_{prep}.

5.3.1 Equilibrium Swelling Properties and Porosities of PIB gels

Equilibrium swelling measurements of PIB gels formed at various temperatures were performed at room temperature in toluene. In Figure 5.11A, the equilibrium weight q_w and the volume swelling ratios q_v of the gels are shown as a function of the gel preparation temperature T_{prep}. In Fig. 5.11B, the swollen state porosities P_s of the gels, calculated as described in section 5.1.1 by use of equation 5.1 are plotted against T_{prep}. The gels prepared below the freezing point of benzene exhibit weight and volume swelling ratios, which are decreasing function of T_{prep}. For example, q_w decreases from 33 to 27 as T_{prep} is decreased from -2 to -18°C. This decrease in the swelling ratio may be related to the decreasing rate of the crosslinking reactions at lower temperatures. Further, these gels exhibit weight swelling ratios which are much larger than their volume swelling ratios, indicating the existence of a porous structure in these gel networks. Indeed, Fig. 5.11B shows that, while the swollen state porosities of the gels prepared below the freezing point of benzene is between 25 and 80 %, swollen state porosities of the gels prepared at room temperature is considerable lower (about 4 %). Further, as the gel preparation temperature is decreased, the swollen state porosity increases. This is in accord with the mechanism suggested in the previous section for the formation of porous structure in such networks. The lower the gel preparation temperature, the larger is the amount of ice formed in the reaction system, so that the porosity of gels increases.

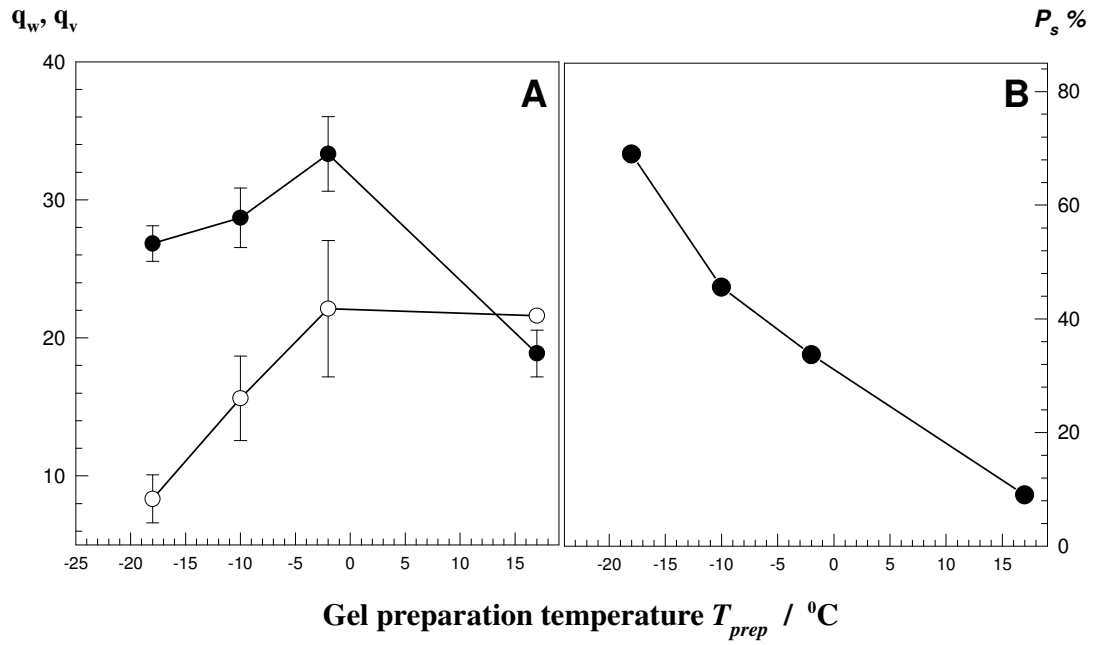


Figure 5.11: The equilibrium weight (q_w, filled symbols) and volume swelling ratios (q_v, open) of the gels shown as a function of the gel preparation temperature T_{prep}. (B): The swollen state porosity P_s of the gels plotted against T_{prep}. S_2Cl_2 = 5 w/v % and c_P = 6 w/v %.

5.3.2 Morphology of PIB Gels

The morphologies of dried gel samples formed at various T_{prep} were also investigated by the optical microscopy and scanning electron microscopy (SEM). In the scanning electron micrographs shown in Figure 5.12, the microstructures of the network formed at different temperatures are given.

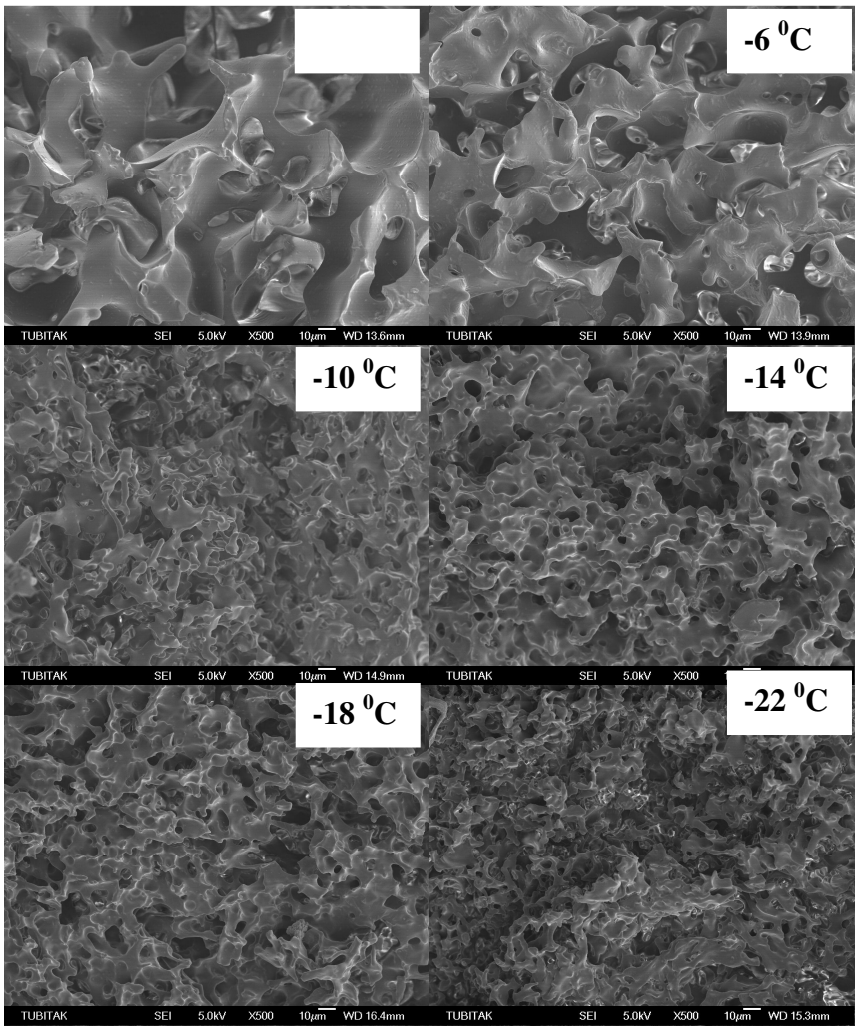


Figure 5.12: SEM of PIB networks formed at various gel preparation temperatures (T_{prep}), as indicated in the images. c_P = 5 w/v %, % S_2Cl_2 = 6. The scaling bars are 10 μm. Magnification = x500

In Figure 5.13, the images taken from the optical microscope are shown. It is seen that all the PIB gels formed below the freezing point of benzene have a porous structure. The shape of the pores is rather irregular and they are relatively polydisperse. In order to characterize the pore structure, a large number of images were taken from each gel sample and their sizes 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 ± 12 μm and 58 ± 17 μm, respectively, independent of $T_{prep.}$ The average diameter of the pore walls was calculated as 17 ± 16 μm.

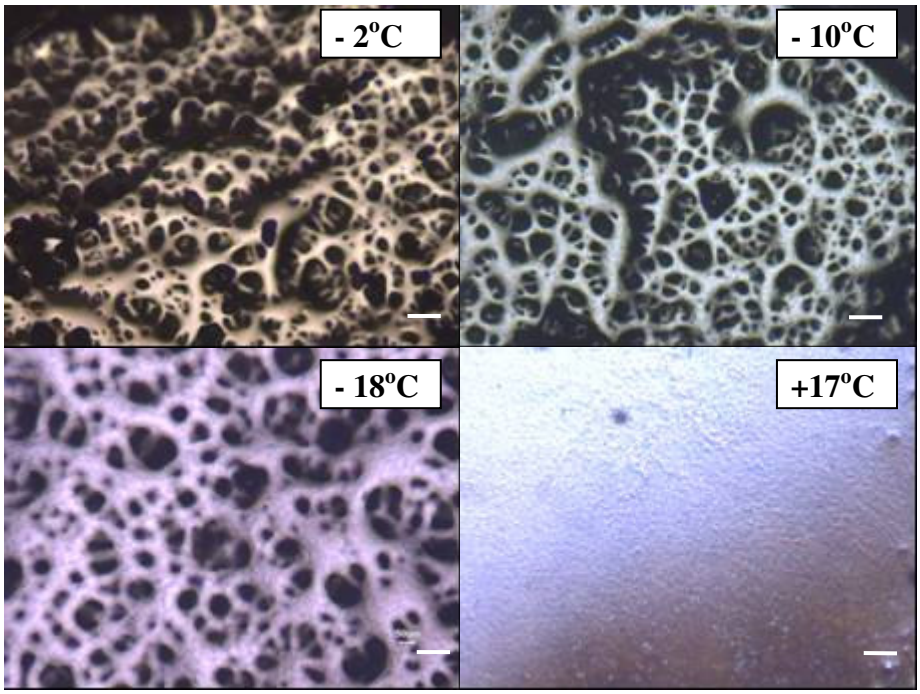


Figure 5.13: Images taken from the optical microscope of the network samples prepared at various T_{prep} as indicated in the figures. c_P = 5 w/v %, S_2Cl_2 = 6 %. The scaling bar is 50 μm.

5.3.3 Deswelling-Swelling Kinetics of PIB Gels

At a fixed crosslinker and butyl rubber concentration, we varied the gel preparation temperature T_{prep} between -22°C and 17°C in order to observe the effect of T_{prep} on the swelling-deswelling kinetics of PIB gels. In Figure5.14**,** the relative weight swelling ratio m_{rel} is plotted against the time of deswelling in methanol or reswelling in toluene for PIB gels prepared at various T_{prep}.

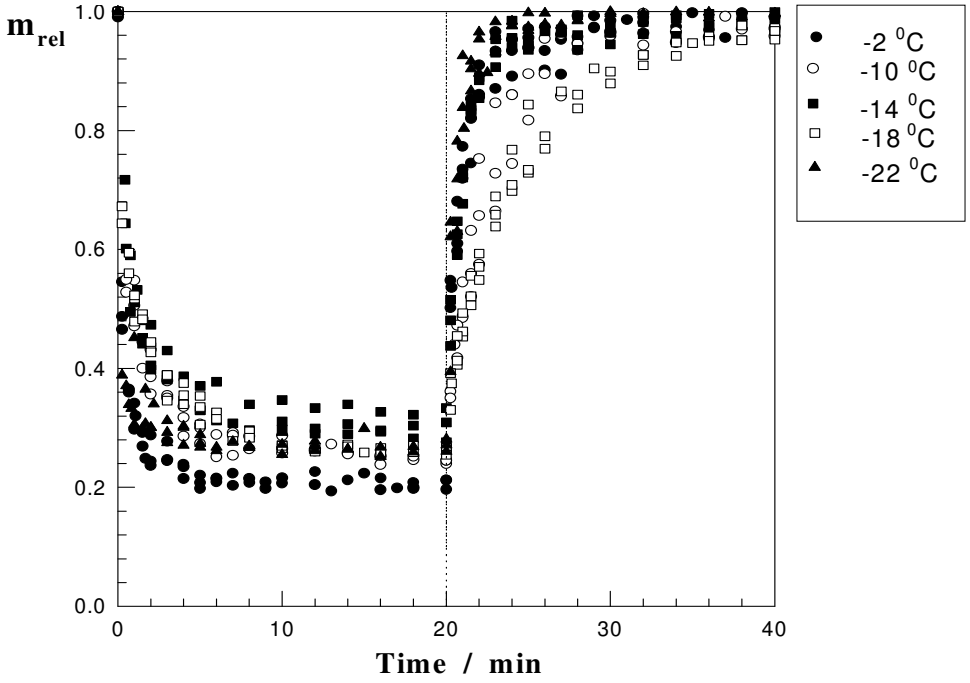


Figure 5.14: Swelling and deswelling kinetics of PIB gels in toluene and in methanol, respectively, shown as the variation of the relative weight swelling ratio m_{rel} with the time of swelling or deswelling. c_P = 5 w/v %, S_2Cl_2 = 6 %. The gel preparation temperature T_{prep} which was varied between -22°C and -2°C as indicated in the figure.

In accord with the previous results, all the PIB gels formed below -2°C exhibit completely reversible swelling-deswelling cycles. Further, no systematic variation of the rate of deswelling or reswelling of gels depending on T_{prep} was observed. The difference in the swelling and deswelling rates of gels is too small and this is within the limits of the experimental error. It should be noted that, for the measurement of swelling-deswelling kinetics of the gels, gravimetric method was used. Thus, the gel samples were taken out of the solvent in certain time intervals and their masses were determined. This technique may be inaccurate since the gel sample is not in continuous contact with the solvent. In order to check the accuracy of the gravimetric technique, we also monitored the deswelling-swelling kinetics of PIB gels by measuring their diameters using the optical microscopy as a function of time. For this purpose, the diameter of the gel samples immersed in a solvent is on-line monitored using the image analyzing system connected with the microscope. The details of the measurement technique were given in the experimental Part.

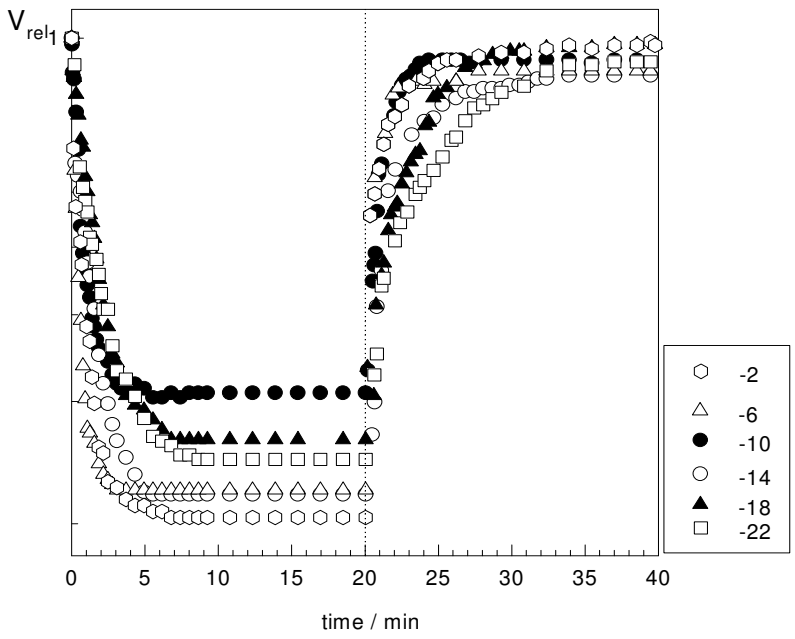


Figure 5.15: Swelling and deswelling kinetics of PIB gels in toluene and in methanol, respectively, shown as the variation of the relative volume swelling ratio V_{rel} with the time of swelling or deswelling. c_P = 5 w/v %, S_2Cl_2 = 6 %. Gel preparation temperatures are indicated in the figure (in ^oC)

Fig. 5.15 shows the results of the measurements in terms of the relative volume swelling ratio V_{rel} plotted as a function of time of swelling or deswelling. The two different techniques to observe the effect of the gel preparation temperature on the swelling-deswelling kinetics of PIB gels, namely one starting from the relative weight swelling and the other from the relative volume swelling gave similar characteristic cycles. The only difference between the data points shown in Figs. 5.14 and 5.15 is the time interval to reach the equilibrium state in toluene or methanol. Using the gravimetric technique, the gel reaches its equilibrium collapsed or equilibrium swollen states in 5 min. However, by the volumetric technique, this time interval was found to be 2 min. One may expect that, since the gel samples are taken out of the solvent at certain time intervals for the gravimetric measurements, this technique leads to longer equilibration time than the on-line volumetric technique.

5.4 Effect of the Cooling Rate

In this section, all the above mentioned experimental parameters were fixed while the cooling rate of the reaction solution to attain the final temperature T_{prep} was changed.

It should be mentioned that, all the 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 1- 7°C/min, depending on the final temperature T_{prep}. The lower the final temperature T_{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_{prep}, we may conclude that both the final freezing temperature T_{prep} and the rate of cooling between 1 and 7°C/min or combination of both do not affect the properties of PIB gels. However, as will be seen below, cooling rates outside of this range significantly affect the properties of PIB gels.

5.4.1 Deswelling-swelling Kinetics of PIB Gels

To highlight the effect of cooling rate on the gel properties, a series of experiments were carried out at high cooling rates in the range 10 – 50°C/min. This was achieved by immersion the reaction system in a cryostat filled with an antifreeze solution. The cooling rates were measured by dipping a thermocouple into the reaction solutions. The cooling profiles of the gelation systems immersed in a cryostat (open symbols) and in a freezer (filled symbols) are shown in Figure 5.16. The final temperature that is the gel preparation temperature T_{prep} was adjusted to -22 °C in both systems.

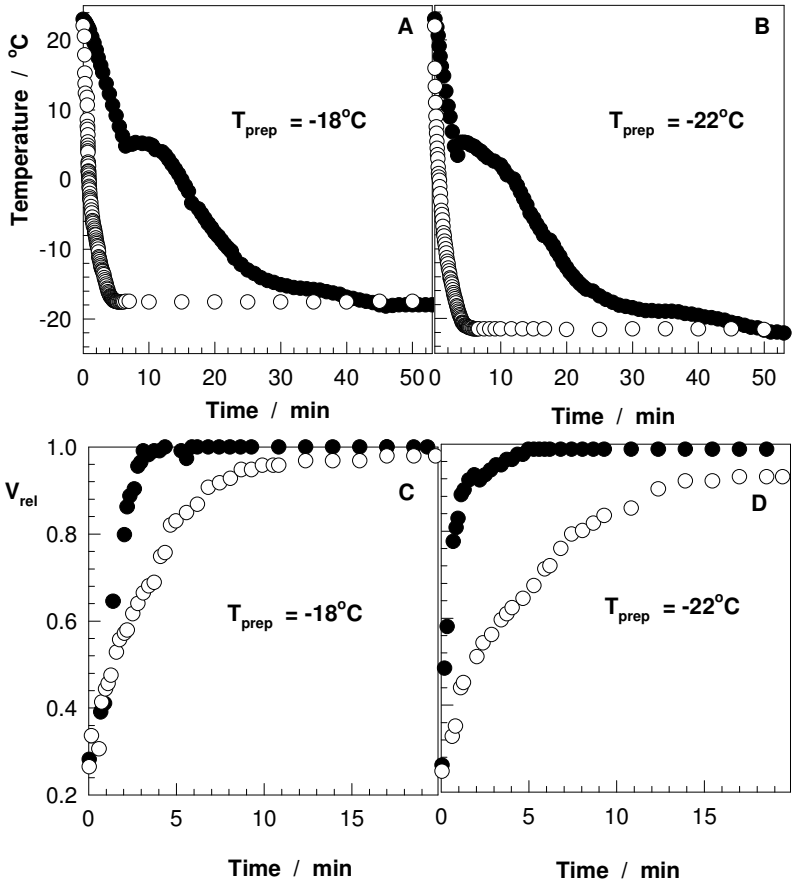


Figure 5.16 (A and B): The temperature of the gelation solutions immersed in a cryostat (open symbols) and placed in a freezer (filled symbols) shown as a function of the reaction time. **(C and D)**: The relative volume swelling ratio V_{rel} of gels prepared in a cryostat (open symbols) and in a freezer (filled symbols) shown as a function of the swelling time in toluene. c_P = 5 %. S_2Cl_2 = 6 %. The final temperature is -22°C.

According to the Figure 5.16A, 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 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 re-swelling of the collapsed gels in toluene showed great differences. Figure 5.16B illustrate the swelling behavior of the gels prepared in the cryostat (open symbols) and in the freezer (filled symbols), where their relative volume swelling ratios V_{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 rapidly cooled solution swell in toluene much slower than those obtained from slowly cooled solutions.

5.4.2 Morphology of PIB Gels

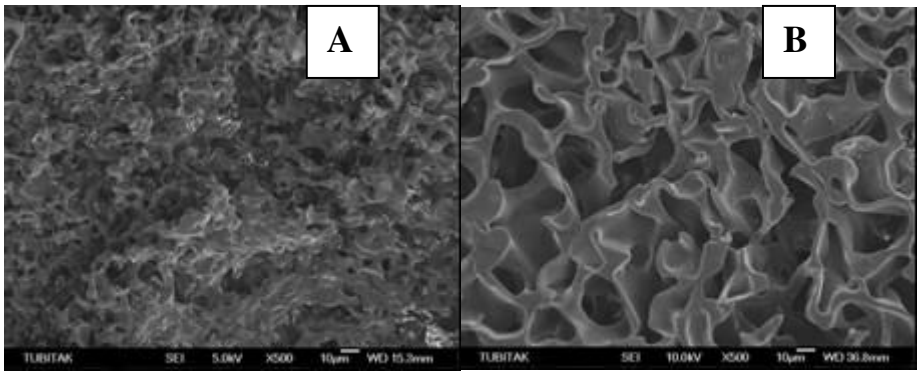


Figure 5.17: SEM of PIB networks prepared at T_{prep} = -22°C at initial cooling rates of 50°C/min (A) and 6°C/min (B). c_P = 5 %. S_2Cl_2 = 6 %. The scaling bars are 10 µm. Magnification = x500

In Figure 5.17, SEM images of the gels prepared at T_{prep} = -22°C with fast (50°C/min, A) and slow cooling rates (6°C/min, B) are given. It is seen that, the gel network formed at a fast cooling rate consists of agglomerates of large polymer domains; the interstices between these domains constitute the porous structures. 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 χ-induced syneresis [10]. The phase separated polymer particles agglomerate into larger clusters and 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 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. PIB gels with a fast response rate were obtained at cooling rates ranging between 1 – 7°C/min.

5.5 Mechanical Properties of PIB Gels

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 5.18A. All the gels prepared below the freezing point exhibited moduli of elasticity of about 2 x 10^2 Pa, one order of magnitude lower than the moduli 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 5.18B where the stress-strain curves in the form of *f* versus 1-α (fractional deformation) plots are given. The gels prepared at room temperature broke at a stress of 8kPa and a strain of about 40 %. However, all the low temperature gels did not break even at a strain of 100 %.

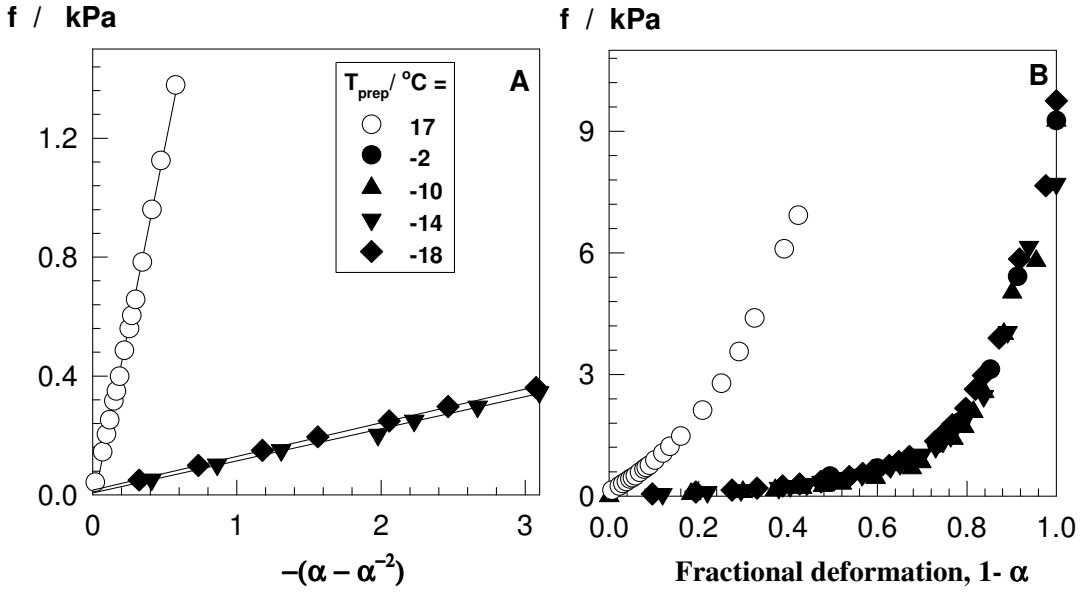
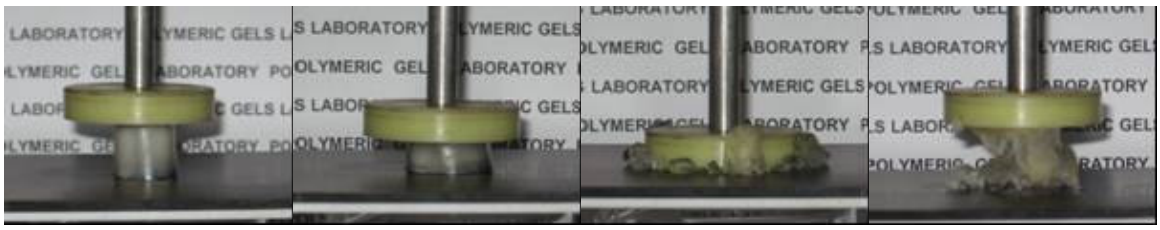


Figure 5.18: Typical stress – strain data of PIB gels as the dependence of f on ($\alpha - \alpha^{-2}$) (A) and 1-α, (B). Gel preparation temperatures are indicated. c_P = 5 %. S_2Cl_2 = 6 %.

Photographs in Figure 5.19 also demonstrate how the low temperature PIB gel sustains a high compression. As shown in the upper panel of Figure 9, the 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 5.19). Important point is that, as the low temperature gel is squeezed under the piston, the gel releases its solvent content so that it can completely be compressed. After the release of the load and, after addition of the solvent toluene, all the gel samples immediately recovered their original shape, as also shown in Figure 5.19.

T_{prep} = +17°C



T_{prep} = -2°C

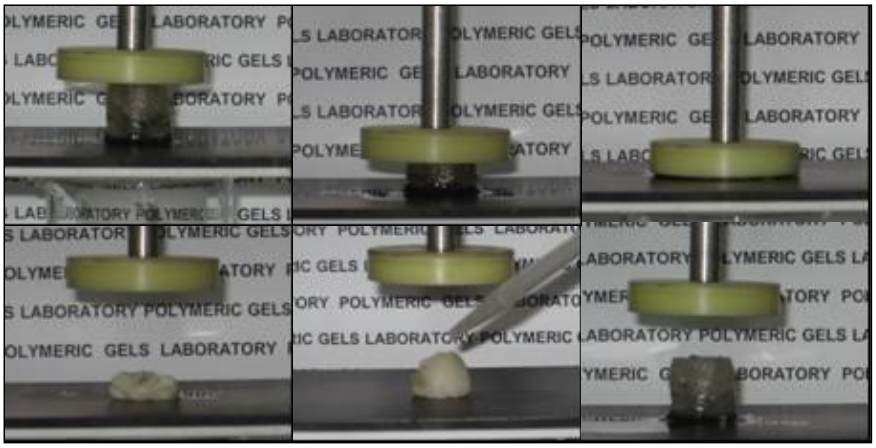


Figure 5.19: Fotographs of PIB gels formed at 17°C and at -2°C during the compression test. After compresion of -2°C gel, addition of toluene converts the gel back to its initial state. c_P = 5 %. S_2Cl_2 = 6 %.

5.6 Phase Transition of PIB gels in toluene/methanol mixtures

Polymer gels are known to exhibit a first order volume-phase transition when a gel network is brought into contact with a solvent [47]. In such a transition, a change in a variable like pH, solvent composition or temperature can induce a discontinuous change in the volume of the swollen gel. For example, a hundred-fold change in the gel volume can be observed as a function of an infinitesimal change in the magnitude of the external variable. As Tanaka and others have shown, a small proportion of ionizable units on the polymer chains seem to be essential for a discontinuous shrinkage of the gel [48]. However, more detailed calculations indicate that a strong concentration dependence of the solvent - polymer interaction parameter χ may also induce a discontinuous shrinkage of the swollen network, irrespective of its ionic group content [49]. The solvent - polymer interaction parameter χ is usually represented as a function of composition by the empirical equation:

$$\chi = \chi_1 + \chi_2 \nu_2 + \chi_3 \nu_2^2 + ... \qquad (5.3)$$

where ν_2 is the volume fraction of the polymer. In ref. [49], it was shown that, for non-ionic gels, the requirement for the polymer collapse, i.e., for the coexistence of two gel phases in equilibrium with pure solvent is $\chi_1 \leq 1/2$ and $\chi_2 > 1/3$. Although the indicated requirement for the polymer collapse is rare for real polymer - solvent systems, the χ parameter reported for PIB - benzene system exhibits strong concentration dependence [12]. This suggests that the PIB gels are suitable candidates for the investigation of their swelling behavior in solvent - nonsolvent mixtures.

Recently, it was shown that the conventional PIB gels exhibit an abrupt deswelling behavior in toluene/methanol mixture at a critical amount of methanol, which is about 10 % by volume [12]. These data are shown in Figure 5.20A, where the equilibrium swelling degrees of the PIB gels in toluene / methanol mixtures are shown in terms of the polymer volume fraction v_2 plotted as a function of the toluene content of the external solution. For these swelling experiments, the gels were prepared at room temperature by solution crosslinking process at four different crosslinker contents (4, 8, 17, and 24 % S_2Cl_2), but at a fixed butyl rubber

concentration of 5 w/v %. In all cases, the PIB gels in toluene / methanol mixtures with less than 3 % methanol are in a swollen state. They rapidly deswell if the toluene content of the external solution is decreased from 97 to 90%. For instance, the loosely crosslinked gel with 4 % S_2Cl_2 swells in toluene 61 times of its dry mass. Addition of methanol in toluene as a poor solvent decreases its swelling capacity significantly and a seven-fold decrease in gel volume was observed with a further increase in the methanol content of the solution, as seen from Figure 5.14. This swelling behavior is similar to that of acrylamide - based hydrogels in solvent / nonsolvent mixtures. The shape of the swelling curve for the gel with 4 % crosslinker shown in Figure 5.20 indicates that this gel is in a critical state.

The experimental data shown in Fig. 5.14A were obtained within 4-5 months due to the slow rate of response of the conventional PIB gels. This slow rate of response may also be responsible for the fact that the collapse transition does not occur discontinuously. Since the gels prepared in the present study exhibit superfast response rate against the external stimuli, we measured their swelling behavior in this solvent-nonsolvent mixture. The experimental results obtained with a PIB gel sample prepared at -22^{o}C are shown in Fig. 5.20B. All the data points were obtained within a few hours due to the fast responsivity of the PIB gels. However, as seen in the figure, the low temperature gel does not exhibit a volume transition in this solvent mixture. This may be related to the relatively low swelling capacity of low temperature gels in good solvents.

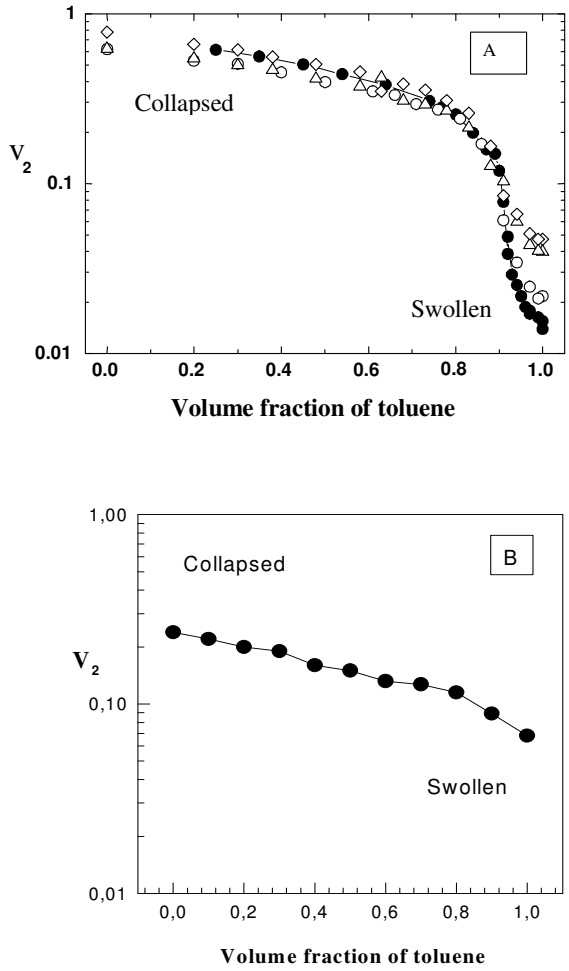


Figure 5.20: Dependence of the volume fraction of polymer in the swollen gels v_2 on the amount of toluene in toluene/methanol mixture. (A): The data were taken from Ref. [12]. c_P = 5 %. Crosslinker contents used in the gel synthesis are 4 (•), 8 (o), 17 (Δ), and 24 v/w % (◊). (B) Results of the measurements using PIB gels prepared at -22°C. c_P = 5 w/v %. Crosslinker content = 6 %.

6. CONCLUSIONS AND RECOMMENDATIONS

The present work was carried out to prepare an ideal gel defined as a soft material exhibiting both a high degree of toughness, i.e., a mechanical stability up to about 100 % strain and a fast response rate against the external stimuli. For this purpose, the crosslinking reactions of butyl rubber (PIB) using sulfur monochloride S_2Cl_2 as a crosslinking agent were carried out in benzene at subzero temperatures. The conclusions that can be drawn from the experimental results can be summarized as follows:

i. Low temperature crosslinking of PIB leads to a 50-fold decrease in the critical polymer concentration for the onset of gelation. This indicates that S_2Cl_2 is an efficient crosslinking agent even at very low reaction temperatures and at crosslinker ratios down to about 0.9 mol S_2Cl_2 / mol internal vinyl group of PIB.

ii. The crosslinking reactions conducted at or below -2^oC lead to the formation of porous organogels with irregular large pores of $10^1 – 10^2$ μm in diameter, separated by pore walls of about 10 μm in width with a high polymer concentration.

iii. PIB networks exhibit different morphologies when one compares with macroporous networks formed by reaction induced phase separation, where the structure looks like cauliflower and consists of aggregates of various sizes.

iv. The pore structure of PIB networks does not depend on the crosslinker concentration, whereas the size of the pores responds sensitively: The higher the crosslinker concentration, the smaller the pore diameters and the thicker the pore walls.

v. The swollen PIB gels prepared from frozen solutions contain 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.

vi. All the gels prepared at or below -2^{o}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.

vii. The cooling rate of the gelation system was found an important parameter determining the gel properties. Tough gels with fast responsivity were obtained at low cooling rates ranging between 1 – 7^{o}C/min

For the future studies, different solvents suitable for the solution crosslinking of butyl rubber at subzero temperatures may be investigated to highlight the effect of the freezing point as well as of the crystal structure of the solvent on the gel properties. Furthermore, polymer-clay nanocomposite systems exhbiting extraordinary mechanical properties may also be investigated by selecting butyl rubber as the polymer component and, by conducting the reactions in a frozen state of the system.

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