Preparation and Swelling Properties of Solution Crosslinked Poly(*cis*-1,4-butadiene) Gels

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ABSTRACT: Poly(*cis*-1,4-butadiene) (PCB) gels were prepared by the crosslinking polymerization of 4-*tert*-butylstyrene (tBS) and divinylbenzene (DVB) onto unvulcanized butadiene rubber with a solution polymerization technique with benzoyl peroxide (BPO) as an initiator. The effects of the reaction conditions, such as the amount of the solvent, the amount of DVB and tBS, and the initiator (BPO), on the equilibrium swelling ratio (Q_e) were also investigated. The highest oil absorbencies of crosslinked gels in xylene and cyclohexane were 51.35 and 32.98 g/g, respectively. A swelling kinetic equation was proposed for this system: $Q_t = Q_e - \{Kt + [1/(Q_e - Q_0)]\}^{-1}$, where Q_t is the swelling ratio at time t, Q_0 is the initial swelling ratio, and K is the swelling kinetic constant. This equation fit the experimental results quite well. The diffusion of organic solvents in PCB gels was Fickian. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2241–2245, 2003

Key words: gels; swelling kinetic; poly (*cis*-1,4-butadiene)

INTRODUCTION

Academically and technologically, polymer gels are considered important materials,[1] and they can swell hundreds of times beyond their original volume. On solvents in gel networks, they can be separated into two classes: hydrophilic gels, or hydrogels, and hydrophobic gels, or organic gels.[2] Hydrogels have been studied extensively by many research groups, especially with respect to the swelling kinetics[3–6] and sensitive behaviors in response to changes in the surroundings, such as the pH,[7] ionic strength,[8] solvent composition,[9] and temperature.[10] As for the study of organic gels, however, relatively little research has appeared in the literature. With industrial development all over the world, environmental pollution has attracted much attention because of the random discharge of oil and organic solvents in rivers and oceans; therefore, the investigation of the oil-absorption capacities of organic gels has gained considerable interest. Zhou and Cho[11] prepared an oil-absorptive network by the graft crosslinking reaction and examined the effect of the reaction conditions on the graft efficiency. They found that the highest oil absorbency of the network was 57.76 g/g in an oil solution (crude oil diluted with toluene, 10% oil). Zhou and Cho[12], using 4-*tert*-butylstyrene (tBS)/ethylene–propylene–diene terpolymer/divinylbenzene (DVB) graft polymers and fibers, sponges, and nonwoven fabrics as supporters, prepared oil-absorptive composites. They also investigated the oil absorbency of the composites. Jang and Kim[13] synthesized crosslinked styrene–acrylate copolymers by copolymerizing styrene monomers with various long-chain alkyl acrylates and found that their oil-absorption capacity was not desirable. The swelling mechanism of oil absorbents in oil or organic solvents, however, has not been found in previous studies.

Vulcanized butadiene rubber has excellent tensile strength, tear resistance, and abrasion resistance. In this study, poly(*cis*-1,4-butadiene) (PCB) gels were prepared by the crosslinking reaction of tBS and DVB onto unvulcanized butadiene rubber through a solution process with benzoyl peroxide (BPO) as an initiator. The effects of the reaction conditions on the equilibrium swelling ratio (Q_e) of PCB gels and the swelling kinetics were also investigated in detail.

EXPERIMENTAL

Materials

PCB, which was supplied by the Shanghai Institute of Rubber Products (China), was purified by dissolution in toluene, precipitation in excess methanol, and drying in a vacuum oven before use. The weight-average molecular weight was 5.2×10^5 (according to gel permeation chromatography with polystyrene stan-

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TABLE I
Compositions and Preparative Conditions of the Gels

Condition	Description					
Toluene (mL/g)	10	12	14	15	18	20
tBS (wt %)[a]	5	10	15	20	30	
DVB (wt %)[b]	2	4	6	8	10	
BPO (wt %)[c]	1	2	4	6	8	
Temperature (°C)			85			
Time (h)			24			

[a,b,c] The concentrations are based on the mass of the rubber, the mass of the rubber and tBS, and the total mass containing the monomers and rubber, respectively.

dards). The polydispersity index (weight-average molecular weight/number-average molecular weight) was 2.36. tBS (Aldrich Chemical, Milwaukee, WI) and DVB (Shanghai Chemical Co., Ltd., China) were purified by standard procedures. BPO (Shanghai Chemical) was recrystallized from a methanol solution before use. All other chemicals were analytical-grade and were used without further purification.

Synthesis of the PCB gels

The PCB gels were prepared by a crosslinking reaction as follows. A given amount of butadiene rubber was first dissolved in a certain volume of toluene at room temperature overnight. After nitrogen bubbled for 20 min, different amounts of BPO, DVB, and tBS, as shown in Table I, were added under rigorous stirring, and the homogeneous solutions were transferred into glass tubes with an internal diameter of 15 mm and a length of about 100 mm. The solution crosslinking reactions proceeded at 85°C. After predetermined reaction times, the resultant gels were taken out from the glass tubes, and they were cut into specimens approximately 10 mm long. Each gel sample was extracted with an excess of toluene several times. The samples were dried in a vacuum oven until a constant weight was reached and then were further extracted with tetrahydrofuran in a Soxhlet extractor for 1 day; they were finally dried at 45°C until the weight was constant.

Swelling degree measurements

Swelling studies for all gels were made gravimetrically. In a typical case, the prepared gel disc was weighed and immersed in the required medium. At regular time intervals, the disc was picked up from the medium, the excess medium of its surface was removed with tissue paper gently, and the disc was weighed on a balance and returned to the same bath. This procedure of swelling and weighing was continued until the sample achieved a constant final weight. After equilibrium swelling, the sample was taken out of the solvent and dried in a vacuum oven until a constant weight was obtained for another use.

The swelling capacities of the gels were expressed in terms of the swelling ratio, which was calculated as follows:

$$Q_t = W_t / W_d \tag{1}$$

$$Q_e = W_e / W_d \tag{2}$$

where Q_t is the swelling ratio at time t, W_t is the mass of the swollen gel at time t, W_d is the mass of the dried gel, and W_e is the final mass of the swollen gel.

RESULTS AND DISCUSSION

Effects of the reaction conditions on Q_e

Effects of the amount of the solvent

The effects of the amount of the solvent on Q_e are shown in Figure 1. The gels were prepared with 3 wt % BPO, 2 wt % DVB, and 30 wt % tBS at 85°C for 24 h, and the amount of the solvent added was 10–20 mL/g, based on the mass of the rubber. As Figure 1 shows, Q_e increases with an increase in the amount of the solvent monotonously in the solution polymerization system. However, the amount of the solvent should be lower than a critical value of 30 mL/g because there is no formation of gels over the critical value. These results can be explained by the concentration of the polymeric solution;[14–16] toluene is a good solvent for the polymerization system. As the amount of the solvent increases, the polymeric solution becomes dilute, and intermolecular distance is stretched by the solvent and a curl-like cloud. Only tBS and DVB can move to them and polymerize with them or further crosslink with them. As a result, it is easy to form intramolecular crosslinking or intramolecular cyclization. Therefore, a larger volume of pores

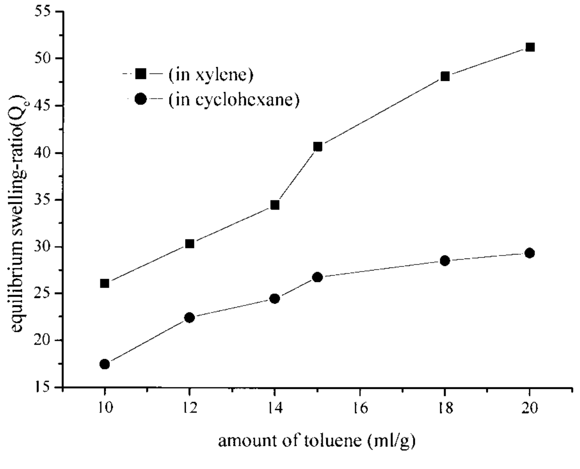


Figure 1 Effect of the amount of toluene in the reaction system on Q_e of PCB gels at room temperature.

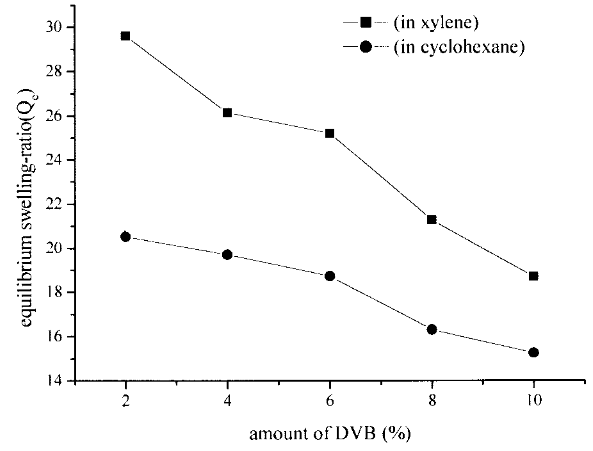


Figure 2 Effect of the amount of DVB in the reaction system on Q_e of PCB gels at room temperature.

is made in the gel network, and this leads to a decrease in the crosslink density and an increase in Q_e.

Effects of the concentration of the crosslinking agent

According to Flory's swelling theory,[15] the swelling behavior is affected by three factors: the rubber elasticity, the affinity to the solution, and the crosslinking density. The swelling behaviors of gels with different amounts of the crosslinking agent were studied. Various gels were prepared with different DVB contents (from 2 to 10% of the total monomer mass). Figure 2 shows the relationship between Q_e and the amount of the crosslinking agent (DVB). Q_e decreases with an increase in the amount of DVB because of the restricted relaxation of the polymer chain. An increase in the contents of the crosslinking agent leads to a denser network of the gel and reduces the average molecular weight between crosslinks (M_c). Generally, a lower M_c means a decreased swelling ratio.[13]

Effects of the concentration of the initiator

To investigate the effects of the initiator concentration on Q_e, we synthesized a series of gels, keeping all other variables constant. The concentrations of BPO as an initiator were 4, 6, 8, and 10%, based on the total mass containing the monomers and rubber. The results of the oil-absorption test are shown in Figure 3. It is well known that in free-radical chain polymerization, the initiation efficiency and conversion will be as high as the increasing initiator concentration. However, a further increase in the initiator concentration makes the radical concentration excessive, causing the rate of the termination reaction to increase and the conversion to decrease. This can affect the oil-absorption capacity of gels. As shown in Figure 3, there is a maximum point at 4% BPO. When the amount of BPO is smaller than that at the maximum point, Q_e increases with an increasing amount of the initiator. This arises from an increase in the concentration of radicals formed through the decomposition of the initiator. When the amount of BPO is larger than that at the maximum point, however, Q_e decreases with an increasing amount of the initiator (BPO) because of the excessive radicals. This can also be explained by the concept of the relative amounts of the polymer chain ends. The number-average degree of polymerization is inversely proportional to the square of the initiator concentration. When the initiator concentration increases, the molecular weight decreases and the polymer chain ends increase. Because the polymer chain ends do not contribute to the oil-absorption capacity, Q_e decreases.

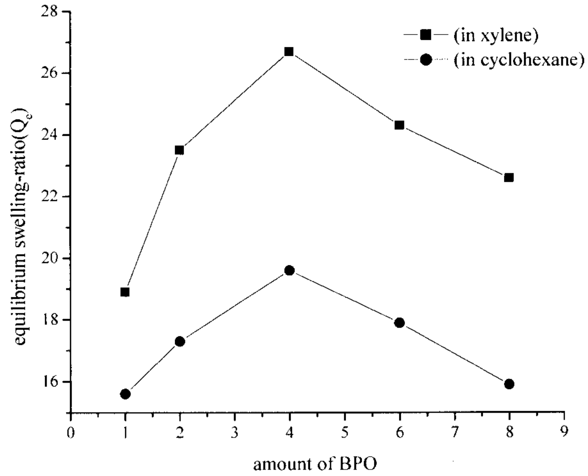


Figure 3 Effect of the amount of BPO in the reaction system on Q_e of PCB gels at room temperature.

Effects of the amount of tBS

The Q_e values for a series of PCB gels in different amounts of tBS, shown in Figure 4, indicate that if the tBS concentration is less than 20% (with respect to the

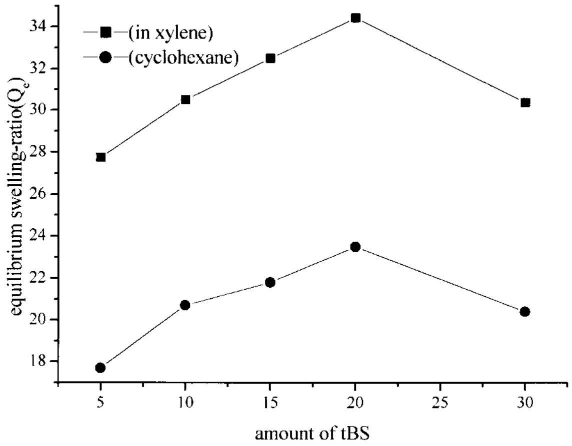


Figure 4 Effect of the amount of tBS in the reaction system on Q_e of PCB gels at room temperature.

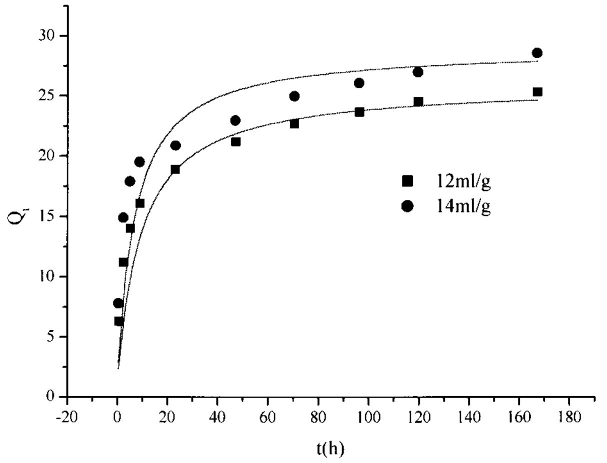


Figure 5 Swelling kinetic curves of PCB gels prepared with different amounts of toluene (used as a solvent) in xylene solutions: (●,■) experimental points and (—) theoretical results.

mass of the rubber), Q_e increases with an increase in the tBS concentration. This is probably due to the increased porosity in the gel networks due to the stereoeffect of tBS, as reported by other researchers.[11,12] However, with a further increase in the tBS concentration, Q_e attains a maximum point at 20% tBS. When the amount of tBS is higher than that at the maximum point, Q_e starts to decrease in xylene or cyclohexane. This phenomenon can result from the stiffness of segmental motion at higher tBS contents in the networks of PCB gels.

Swelling properties of the PCB gels

Swelling kinetics

Figure 5 shows the swelling kinetic curves of gels in xylene (used as a solvent). From the curves, it is clear that, at the initial stage, the ratio of swelling is remarkably increased. With more time, Q_t increases gradually until it reaches an equilibrium value. This phenomenon is similar to that of general gels reported in the literature.[11,12] The swelling procedure of PCB gels in organic solvents can also be predicted from theoretical aspects. If the swelling procedure is fit for a second-order kinetic equation, the swelling rate of PCB gels can be described by the following equation:

$$\frac{dQ_t}{dt} = K(Q_e - Q_t)^2 \tag{3}$$

where K is a swelling kinetic constant.

Integration from eq. (3) gives

$$\frac{1}{Q_e - Q_t} - \frac{1}{Q_e - Q_0} = Kt \tag{4}$$

Equation (4) may be written as

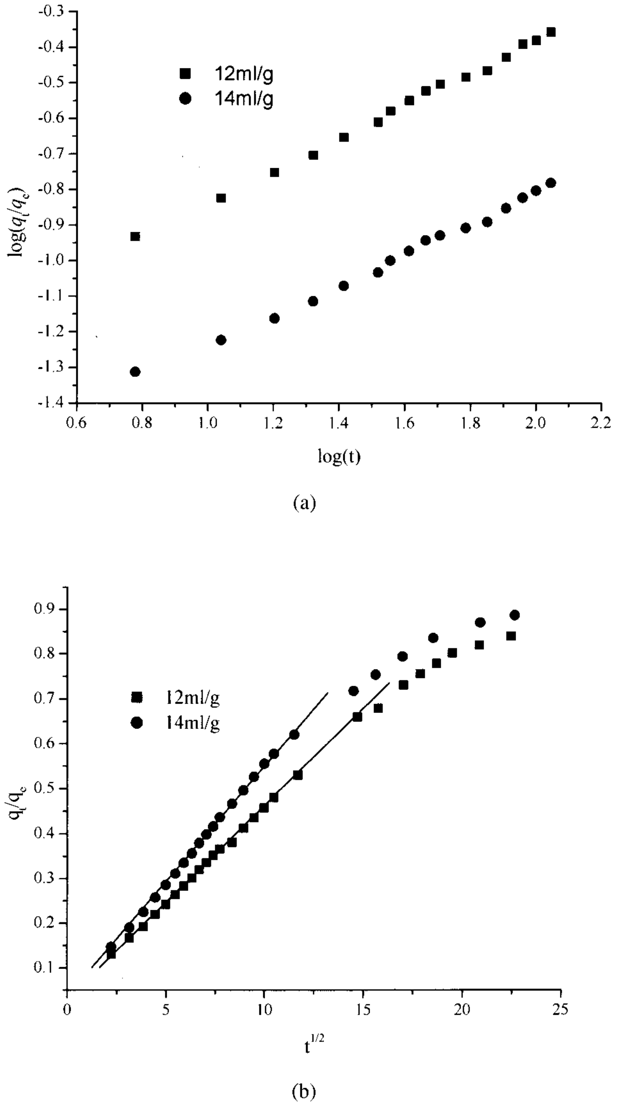
$$Q_t = Q_e - \left[Kt + \frac{1}{Q_e - Q_0}\right]^{-1} \tag{5}$$

where Q_0 is the initial swelling ratio and t is the characteristic time.

The following relation can also represent eq. (4):

$$\frac{1}{Q_e - Q_t} = Kt + \frac{1}{Q_e - Q_0} \tag{6}$$

Plots of $1/(Q_e - Q_t)$ versus t were made. K was obtained from the slope of the straight line. The results show that the swelling kinetic curves obtained from the calculation agree with the experimental values, proving that the proposed assumption is fairly reason-



(a)

(b)

Figure 6 (a) Log(q_t/q_e) versus log t and (b) q_t/q_e versus $t^{1/2}$ for gels prepared with different amounts of toluene (used as a solvent).

able. A second-order kinetic equation can describe the swelling behavior of PCB gels quite well.

Mechanism of swelling

To understand the nature of the diffusion of organic solvents in PCB gels, we can use the following equation:[17–19]

$$q_t/q_e = kt^n \tag{7}$$

where q_t is the molar percentage uptake at time t, q_e is the equilibrium molar percentage uptake, and k is a constant that depends on the structural characteristics of the polymer and its interaction with solvents. n is the diffusion exponent, and it is indicative of the transport mechanism. In the general equation[18] for transport phenomena, when n is 1/2, diffusion obeys Fick's law, which occurs when the segmental mobility of the polymer chains is faster than that of the diffusion of penetrant molecules. When n is 1, the diffusion is said to be non-Fickian; the segmental relaxation processes are the slowest steps and, therefore, the rate-determining steps. An intermediate situation ($1/2 < n < 1$) is called anomalous; the penetrant mobility and segmental relaxation are on comparable timescales.

This equation was applied to the initial stages of swelling, and plots of $\log(q_t/q_e)$ versus $\log t$ and q_t/q_e versus $t^{1/2}$ for PCB gels in xylene solutions are shown in Figure 6(a,b), respectively. In this system, n, obtained from a linear plot of $\log(q_t/q_e)$ versus $\log t$ (correlation coefficient > 0.98), is 0.5, and the two curves of the plots of q_t/q_e versus $t^{1/2}$ are straight up to about $q_t/q_e = 0.65$. Therefore, it can be concluded that the diffusion process can be treated as Fickian in nature and that the penetrant diffusion rate is the slowest step and, therefore, the rate-determining step.

CONCLUSIONS

A new type of highly oil-absorbent gel of PCB can be synthesized from tBS and DVB onto *cis*-1,4-butadiene rubber with BPO as an initiator through a solution polymerization technique. The highest oil absorbencies of PCB gels in xylene and cyclohexane are 51.35 and 32.98 g/g, respectively. Q_e is remarkably affected by the amount of the solvent. The contents of both DVB and BPO are also important factors during the polymerization, for which there is an optimum content for achieving a maximum value of Q_e. The swelling behaviors of PCB gels in solvents can be well described by a second-order kinetic equation. The diffusion mechanism of organic solvents into PCB gels seems to be Fickian in nature.

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