*Macromolecules* **1997,** *30,* 3507−3512

# Influence of the Copolymer Molar Mass on the Physical Gelation of Triblock Copolymers in a Selective Solvent of the Middle Block

**José R. Quintana, Esperanza Díaz,[†] and Issa Katime***

*Grupo de Nuevos Materiales, Departamento de Química Física, Facultad de Ciencias, Campus de Leioa, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain*

*Received October 29, 1996; Revised Manuscript Received March 11, 1997*[⊗]

ABSTRACT: The influence of the copolymer molar mass on the thermoreversible gelation of the triblock copolymer polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene in a paraffinic oil was studied. The solvent used is selective for the middle poly(ethylene/butylene) block of the copolymer. The thermal behavior as a function of copolymer concentration was investigated. The sol−gel transition temperature increased with the copolymer concentration and molar mass. The mechanical properties of the gels were examined through oscillatory shear and compressive stress relaxation measurements. The concentration dependences of the elastic storage modulus were established and were observed to be similar for the three copolymers. The relaxation rates observed were extremely high, indicating a considerable mobility in the gel over the measurement time. The relaxation rate decreased as the copolymer molar mass increased. The swelling behavior has also been examined. All gels swelled significantly. The copolymer concentration dependences of the swelling ratio were linear but their ordinates were not close to unity. Whereas the two copolymer with higher molar mass show a similar swelling behavior, the copolymer with the lowest molar mass shows a swelling capability markedly smaller.

## Introduction

Physical gels consist of chains which are "physically" cross-linked into networks. The cross-links have a small but finite energy and/or a finite lifetime. A special case of physical gels are the ones formed by block copolymers dissolved in selective solvents. The study of these gels has been only recently undertaken.[1−19]

In general two types of thermally reversible copolymer gels have been reported: (a) those formed in concentrated aqueous solutions of copolymers AB and ABA where A represents an oxyethylene unit and B an oxypropylene or oxybutylene unit;[1−8] (b) those formed in semidiluted solutions of triblock copolymers in a selective solvent of the middle block.[9−19] Whereas the former have been studied to a certain extent, few studies have been undertaken on the latter.

The thermally reversible gelation of semidiluted solutions of triblock copolymers in selective solvents of the middle block is not yet well established. Some authors[9−11] have considered the existence of micelles with one poorly solvated outer block extending into solution. This would be a consequence of the additional entropic penalty to the micelle formation arising from the formation of a loop by the middle block so that both outer blocks stay in the micelle core. If the copolymer concentration were large enough, this end block could form part of another micelle core or interact with another end block corresponding to a different micelle in the same condition. A physical network would be formed in this way. Tuzar et al.[10] suggest that not only unimers but also oligomers could assist with the attractive forces operative between the outer copolymer blocks placed outside the micelle shell. Other authors[14,15] proposed that branched or networklike structures due to the interchain association might exist. The lattice should consist of nodes of the poorly solvated outer blocks linked together by strands of the well-solvated middle blocks of the copolymer. The dynamics would be governed by the glass transition of the nodes.

In a previous paper[19] we studied the physical gels formed by a polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene copolymer in a paraffinic oil (*n*-alkane mixture). The solvent was a selective one of the poly(ethylene/butylene) block. We found that the copolymer formed viscoelastic and thermoreversible gels at concentrations as low as 2 wt %. The sol−gel transition and mechanical properties of the gels were studied. We concluded that the gel junctions do not consist only of proper micelles and that a fringed micellar structure characterized by a short mesh could be considered. We also found large relaxation rates that could be explained according to a classical network in which the junctions break and re-form.

The aim of the present paper was to analyze the influence of the copolymer molar mass on these physical gels. For this purpose we chose three polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene copolymers with a similar chemical composition (31 wt % PS) and molar masses ranging between 60 700 and 260 000 g·mol$^{-1}$. We have studied the sol−gel transition and the mechanical properties of the gels formed by the three copolymers. Oscilatory shear and compression measurements were carried out over concentration ranges for which the gels had enough consistency.

## Experimental Section

The polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene triblock copolymer (PS-*b*-PEB-*b*-PS) samples used, designated SEBS1, SEBS2, and SEBS3, are commercial products kindly provided by Shell España, S.A. The samples have been previously characterized in detail.[20] They are homogeneous in chemical composition and their weight average molar masses, polydispersities, and styrene contents are shown in Table 1. The paraffinic oil sample, Norpar 15, is an Exxon product consisting of an *n*-alkane mixture with an average carbon number of 15 and a distillation range of 252−272 °C.

Sample gels were prepared by dissolving the copolymer samples in Norpar 15 at 120 °C in sealed flasks. Once the

---

[†] Permanent address: Departamento Ingeniería Minera, Metalúrgica y Ciencia de Materiales, Escuela Superior de la Marina Civil de Bilbao, Universidad del País Vasco, C/M$\underline{a}$ Díaz de Haro, 68, 48920 Portugalete, Spain

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S0024-9297(96)01597-5 CCC: $14.00

**Table 1. Characteristics of the Block Copolymers: Mass Average Molar Mass of the Copolymer, $M_w$, of the Polystyrene Block, $M_{w,Ps}$, and of the Poly(ethylene/butylene) Block, $M_{w,PEB}$, Polystyrene Weight Percentage, and Polydispersity Index, $I$**

| | SEBS1 | SEBS2 | SEBS3 |
|---|---|---|---|
| $M_w$ | 60 700 | 87 300 | 260 000 |
| $M_{w,Ps}$ | 2 × 9100 | 2 × 14 000 | 2 × 39 000 |
| $M_{w,PEB}$ | 42 500 | 59 400 | 182 000 |
| % Ps by weight | 30 | 32 | 30 |
| $I$ | 1.09 | 1.11 | 1.18 |

solutions were clear, they were allowed to cool to room temperature in order to form the gels. In this study the concentrations are expressed in wt %. The solution concentrations range between 15−30 (SEBS1), 6−17 (SEBS2), and 2.5−11 wt % (SEBS3) for the analysis of the mechanical properties and swelling and 4−30 (SEBS1), 2−17 (SEBS2), and 2−9 wt % (SEBS3) for the sol−gel transition analysis. These concentrations ranges were chosen taking into account a sufficient consistency of the gels and a melting temperature low enough to avoid solvent evaporation.

Oscillatory shear measurements were performed in a Polymer Laboratories dynamic mechanical thermal analysis apparatus. The mechanical mode used was the torsion one with a fluid cup and a torsion plate whose diameters were 44 and 38 mm respectively. The temperature was controlled with a precision of 0.1 °C. Gel bits were introduced into the cup prior to increasing the chamber temperature to 120 °C in order to melt the gel. Once a homogeneous solution was obtained, the sample was quickly cooled to a prefixed temperature. The elastic storage modulus, $G'$, and loss modulus, $G''$, were measured as a function of frequency between 0.01 and 20 Hz at a maximun strain amplitude of 6.25 mrads. The main focus here was placed on the shear modulus as a function of temperature. A frequency of 1 Hz was employed. The heating rate used was 0.5 °C·min$^{-1}$.

The sol−gel transition was determined by two methods. The gelation temperatures were determined by tilting a test tube containing the copolymer concentration. The temperature at which the solution no longer flowed was taken as the gelation temperature, $T_{GL}$. The melting temperatures were determined measuring $G'$ and $G''$ as a function of temperature at a frequency of 1 Hz. The temperature at which $G' = G''$ was considered as the melting temperature, $T_m$, since it marks the transition from a solidlike state to a viscoelastic liquidlike state. It should be noted, however, that the transition temperature so defined is frequency dependent. A heating rate of 0.5 °C·min$^{-1}$ was confirmed to be slow enough to keep the gels in an equilibrium state and, therefore, independent of gel history.[19]

Compression measurements were made in a Perkin-Elmer dynamic mechanical analyzer, Model DMA 7. A cup and plate geometry cell (diameter 10 mm) was used for all measurements. The gels were formed in the cell in the same way described above, having a height of 3 mm. The temperature of the measuring chamber was 25.0 ± 0.1 °C. The stress relaxation measurements were performed by measuring the load as a function of time, keeping constant the gel deformation.

Samples used for the swelling experiments were immersed in an excess of Norpar 15 to achieve equilibrium swelling. The swelling kinetics were followed by measuring the sample weight until equilibrium was reached (or nearly reached). The equilibrium swelling ratio, $G^\infty$, is defined as the ratio of the final weight to the initial weight of the sample.

## Results and Discussion

In a previous paper[19] the frequency dependence of the storage, $G'$, and loss moduli, $G''$, was analyzed for the copolymer SEBS2. At temperatures below the gel point, the elastic properties dominate, $G' > G''$, and the logarithmic curves show a slight curvature. This curvature was found at every temperature studied. Near the gel melting temperature, $T_m$, both $G'$ and $G''$ curves crossed with a crossover frequency that increased as the temperature went up. Finally for $T > T_m$, $G' < G''$ at every frequency, with the sample having a liquid-like behavior. Taking into account the uncertainty found in this system to determine the temperature at which $G'$ and $G''$ follow approximately the known scaling relation[21−23]

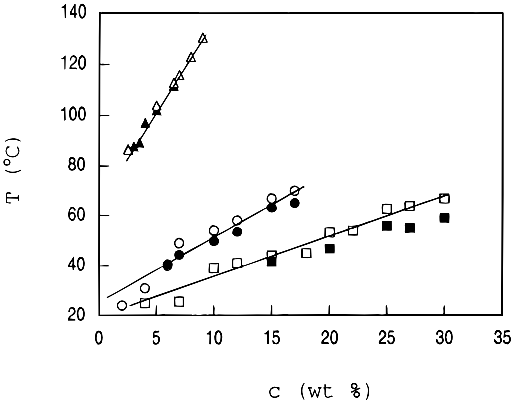

**Figure 1.** Dependence of the sol−gel transition temperature on the copolymer concentration for SEBS1 (□), SEBS2 (○), and SEBS3 gels (△). Gel formation temperatures were determined by the tilting method (unfilled symbols), and melting temperatures were determined by oscillatory shear measurements (filled symbols).

$$G'(\omega) \sim G''(\omega) \sim \omega^n \tag{1}$$

we chose as the gel melting temperature the temperature at which the crossover frequency becomes equal to unity. Thus to determine the gel melting temperature, oscillatory shear measurements were focused on the variation of $G'$ and $G''$ with temperature at a single frequency (1 Hz). A sharp drop of $G'$ and a slight drop of $G''$ are observed when the gel melting takes place. As mentioned above, the temperature at which $G' = G''$ was considered as the melting temperature since it marks the transition from a solidlike state to a viscoelastic liquidlike state. It should be noted, however, that the transition temperature so defined is frequency dependent.

The influence of the copolymer concentration on the sol−gel transition is shown in Figure 1 where the gel melting temperature, $T_m$, and the gelation temperature, $T_{GL}$, are plotted as a function of concentration for the three copolymer samples. There is not an appreciable difference between the gelation and melting temperatures for the three cases in spite of the different methods used. This behavior is coincident with that of other amorphous polymer gels[24] and contrary to the thermoreversible gelation of crystallizable polymers. The concentration dependence of the sol−gel transition temperature is linear over the concentration range studied for each copolymer sample. The concentration dependence increases with the molar mass of the copolymer.

To compare the sol−gel transition temperatures of the different copolymers, two concentrations were chosen (5 and 10 wt %). These temperatures are plotted in Figure 2 as a function of the molar mass of the copolymer. The sol−gel transition temperature varies linearly with the copolymer molar mass, becoming higher as the copolymer molar mass increases. Taking into account that the three copolymers have very similar chemical compositions and that the polystyrene block is the block solely responsible for the gel junctions, the

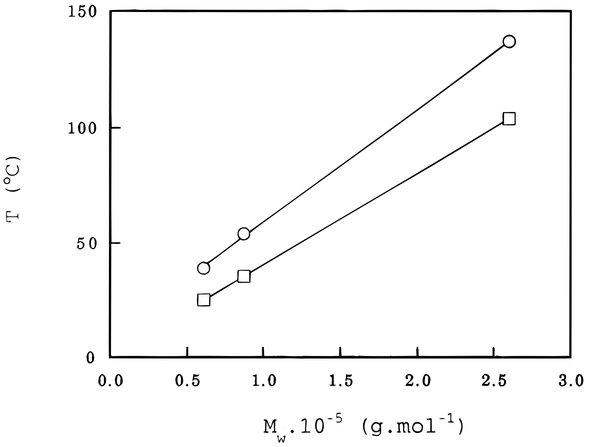

**Figure 2.** Dependence of the sol−gel transition temperature on the copolymer molar mass for two concentrations: 5 (☐) and 10 wt % (○).

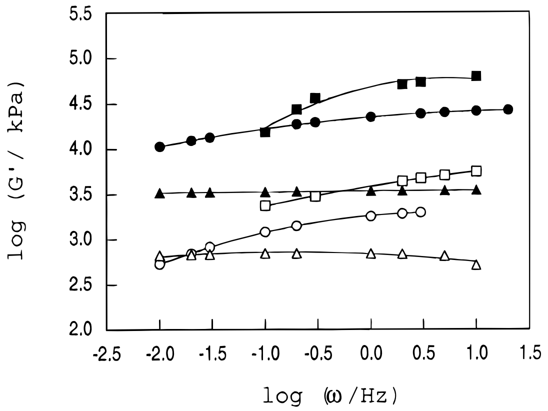

**Figure 3.** Dynamic mechanical spectrum of the elastic storage modulus, *G*′, for SEBS1, SEBS2, and SEBS3 gels at 25 °C. Copolymer concentrations: 15 (☐) and 30 wt % (■) for SEBS1, 6.0 (○) and 17 wt % (●) for SEBS2, and 2.5 (△) and 6.5 wt % (▲) for SEBS3.

above result implies that the chain length of this copolymer block determines the ease of gelation and consequently the stability of the gels formed in a given solvent. This behavior accords with the results found for different polystyrene-*b*-poly(ethylene/propylene) copolymers in 5-methyl-2-hexanone[25] and SEBS coploymers in 4-methyl-2-pentanone[20] where the stability of the micelles formed by these copolymers increased as the length of copolymer block which formed the micelle core increased. This behavior seems logical since the incompatibility with the solvent will increase as the molar mass of the copolymer block for which the solvent is precipitant increases.

The effect of the copolymer molar mass on the critical gel concentration, CGC, defined as the concentration at which a particular polymer is capable of forming a one-phase gel, was not very appreciable. For the three copolymer samples, the CGC ranged between 2 and 3 wt %, having the lowest value for SEBS3 and the highest for SEBS1.

Measurements of the real and imaginary parts, *G*′ and *G*″, of the complex shear modulus were also made as a function of the frequency, *ω*, of a small deformation oscillatory shear strain. Figure 3 shows the plots of log *G*′ against frequency for six gels of SEBS1, SEBS2, and SEBS3 at 25 °C and at two copolymer concentrations. In this figure, different behaviors can be observed. Whereas *G*′ is not dependent on oscillation frequency for SEBS3, for the other two copolymers *G*′ tends to a constant value at high frequency but decreases more sharply as the frequency becomes lower. This behavior suggests that the junctions are not strong enough and under a weak stress they will eventually split and, therefore, the long-time behavior of SEBS1 and SEBS2 gels will be liquidlike. We could speak of a weak gelation process where the junctions are not completely stable but are associated with a reaction (bonding ↔ nonbonding) that proceeds in both directions. The frequency dependence of *G*′ is more important for SEBS1 than for SEBS2. This reveals an increment in the lifetime of the junctions in the gel when the copolymer molar mass increases, the SEBS3 gels showing long-lived cross-links compared to the experiment time. These behaviors suggest that the junction life time at a given temperature could be related to the interval between this temperature and the sol−gel transition temperature because the larger this interval is, the lower the frequency dependence of *G*′ is. Similar results were found for an atactic polystyrene in carbon disulfide.[26]

There is no concentration dependence seen for the log *G*′ − log *ω* curves, however a weaker frequency dependence for the highest concentrations of the SEBS1 and SEBS2 gels can be observed. This behavior would be also explained by the difference between the experimental temperature and the sol−gel transition temperature since, for a given copolymer, the sol−gel transition temperature becomes higher as the concentration increases.

Figure 3 also shows how the value of *G*′ at high frequencies depends more on copolymer concentration than on the copolymer molar mass. As the concentration increases *G*′ shows higher values meaning that the number of long-lived junctions in the gel increases.

The variation of the elastic store modulus as a function of the copolymer concentration for each of the three copolymer samples, SEBS1, SEBS2, and SEBS3, at 25 °C is plotted in Figure 4. The copolymer concentrations range from 15 to 30 wt % for SEBS1, from 6 to 17 wt % for SEBS2, and from 2.5 to 6.5 wt % for SEBS3. At these concentration intervals the gels had enough consistency and the melting temperatures were not too high. For the three copolymer samples, the data are linear in a double-logarithmic scale and yield the following power relations (in these relations the copolymer concentration is expressed in g/g):

$$\text{SEBS1} \qquad G' \sim C^{2.2 \pm 0.2}\ \text{kPa}$$

$$\text{SEBS2} \qquad G' \sim C^{2.2 \pm 0.2}\ \text{kPa}$$

$$\text{SEBS3} \qquad G' \sim C^{1.9 \pm 0.2}\ \text{kPa}$$

Norpar 15 is a selective solvent for the poly(ethylene/butylene) block, PEB, therefore the gels should possess a fringed micellar structure characterized by knots formed by aggregated polystyrene blocks and linked by one well-solvated poly(ethylene/butylene) block when the connection is direct. The mesh size will be determined by the poly(ethylene/butylene) block length. Considering that one is dealing with gels flexible as those prepared chemically, the predicted value (2.25)[27] should be found.

Whereas the copolymers SEBS1 and SEBS2 have exponents with equal values close to those predicted for flexible gels, SEBS3 has an exponent with a lower value and therefore shows a different behavior. This differ-

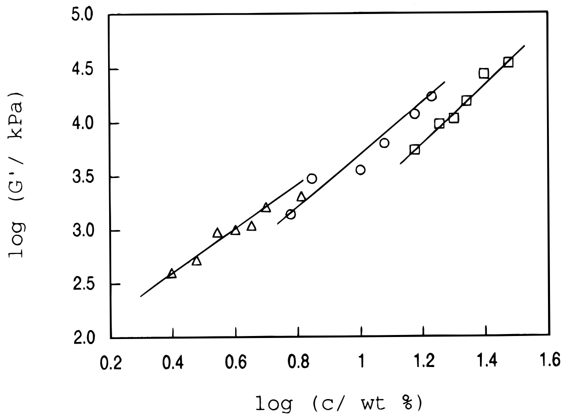

**Figure 4.** Elastic storage modulus $G'$ vs concentration on a logarithmic scale for SEBS1 (□), SEBS2 (○) and SEBS3 gels (△) at 25 °C.

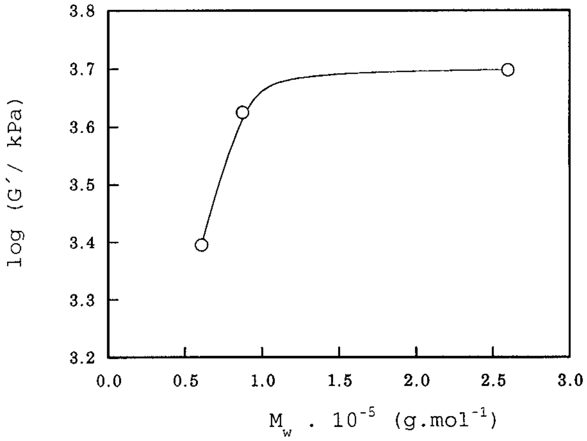

**Figure 5.** Dynamic storage modulus $G'$ as a function of the copolymer molar mass for SEBS gels at a concentration of 10 wt % at 25 °C.

ence has been also observed in diluted solutions of these copolymer samples in octane. The copolymers SEBS1 and SEBS2 are capable of forming proper micelles at concentrations higher than a critical micelle concentration.[28] However, the chains of the copolymer SEBS3 aggregate form clusters which can be seen even with the naked eye. This behavior was observed at very low concentrations.

In Figure 5, the dynamic storage moduli as a function of the copolymer molar mass are plotted for three copolymer gels with a concentration of 10 wt %. Whereas SEBS2 and SEBS3 show similar values of log $G'$, for the SEBS1 gel the dynamic storage modulus is lower. However these differences could be attributed to the curves $G' = f(\omega)$ for SEBS1 and SEBS2 since they have not reached the rubber plateau at a frequency of 1 Hz. Therefore the $G'$ corresponding to this plateau, $G_N$, will have a higher value. The results seem to suggest that the copolymer molar mass has little influence in the dynamic storage modulus. In consequence, one can assume that the gels of the three copolymer samples have a similar number of cross-links, although the lifetime of the junctions increases with the copolymer molar mass.

Figure 6 shows the stress relaxation responses to a compressive deformation $\lambda = 0.7$ for gels of the three copolymer samples. The gel concentrations are 30, 15, and 11 wt % for SEBS1, SEBS2, and SEBS3, respectively. At an early stage, the relation between the stress, $\sigma$, and the time, $t$, is, within experimental uncertainties, linear in a double logarithmic plot. The stress relaxation rates $m = d(\log \sigma)/d(\log t)$ are quite noticeable and are very dependent on the copolymer molar mass. At relaxation times $t < 3000$ s the following values were measured

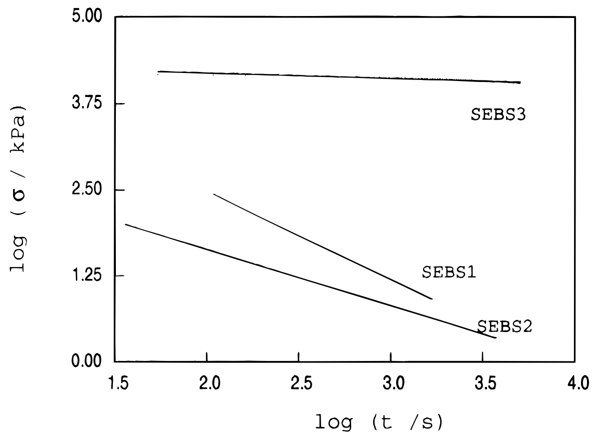

**Figure 6.** Compressive stress relaxation, log $\sigma$ vs log $t$, for SEBS gels at 25 °C. Deformation $\lambda = 0.7$. Copolymer concentrations: 30 (SEBS1), 15 (SEBS2), and 11 wt % (SEBS3).

$$\text{SEBS1} \qquad m = 0.9 \pm 0.2$$

$$\text{SEBS2} \qquad m = 0.7 \pm 0.2$$

$$\text{SEBS3} \qquad m = 0.07 \pm 0.04$$

The double logarithmic rates of relaxation are relatively independent of the copolymer concentration in the experimental range studied.

These high relaxation rates give a possible indication of how weak the physical junctions are. The higher the $m$ value is, the weaker the cross-links are. Values similar to those found for the SEBS3 gels have been reported for physical gels with an absence of crystalline order in the physical junctions.[29,30] In these systems the relaxation rate ranged between 0.08 and 0.2. The physical gels whose junctions are crystalline show even lower relaxation rates,[31,32] $m = 0.01-0.03$. These values are quite similar to those reported for chemical gels with permanent cross-links.[33]

The large relaxation rate values obtained for the SEBS gels suggest a high mobility in the network over the time of measurement and could be explained according to a classical network in which the junctions break and re-form. This fact would be confirmed by the dynamic equilibrium free chain/micelle that the block copolymers show in selective solvent solutions. The SEBS gels would be in a dynamic equilibrium state where some junctions are broken and new ones are formed continously. The higher $m$ values found for SEBS1 and SEBS2 would be then a consequence of the shorter life of their junctions compared to those of the SEBS3 gels. Longer PS blocks will increase its incompatibility with the solvent and cause stronger and more lasting gel junctions.

When SEBS gels were immersed into an excess of Norpar 15, they swelled up to reach an equilibrium swelling. Let us consider the swelling ratio $G$ as the ratio

$$G = P/P_0 \tag{2}$$

where $P_0$ is the sample weight after preparation but just before the immersion in a solvent excess and $P$ is the

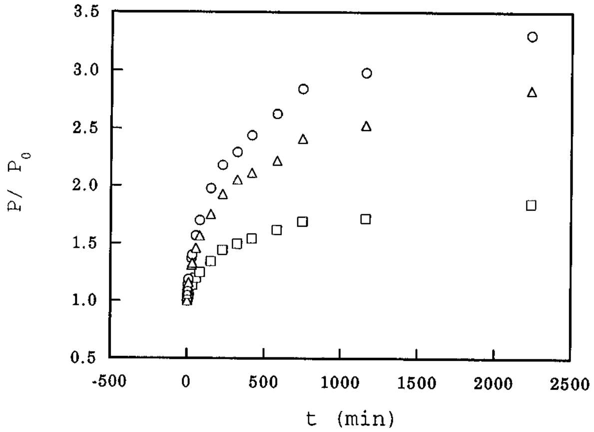

**Figure 7.** Evolution of the swelling ratio $P/P_0$ as a function of time for SEBS2 gels at 25 °C. Copolymer preparation concentrations: 7 (□), 12 (○), and 15 wt % (△).

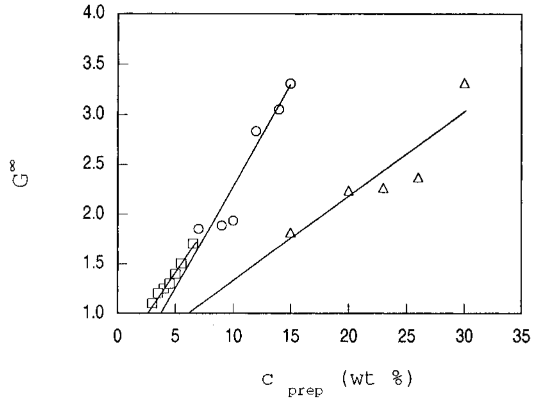

**Figure 8.** Equilibrium swelling ratio, $G^{\infty}$, vs preparation concentration, $c_{prep}$, for SEBS1 (□), SEBS2 (○), and SEBS3 gels (△) at 25 °C.

sample weight after a certain time from the inmersion. The swelling equilibrium ratio $G^{\infty}$ is then expressed as

$$G^{\infty} = (P/P_0)_{t\rightarrow\infty} \tag{3}$$

The swelling behaviors are similar for the three SEBS copolymers. As an example, the evolution of the swelling ratio as a function of time is plotted in Figure 7 for several SEBS2 gels at different copolymer concentrations. In the three systems a quasi-equilibrium was obtained after many days.

The degree of swelling as a function of copolymer concentration was investigated. The variations of $G^{\infty}$ vs the preparation concentration are plotted in Figure 8 for the three kinds of SEBS gels. Though the experimental errors can be considerable due to the lack of consistency of some gels after being immersed in excess solvent for a long time, one can conclude that the concentration dependences of the swelling equilibrium ratio are linear withim the preparation concentration range studied for each copolymer. It is remarkable that in no case is the ordinate of the linear plot close to unity as has been found for other physical gels.[30,31] Within the appreciable experimental error, SEBS2 and SEBS3 gels show a similar swelling behavior. However the swelling capability of the SEBS1 gels is markedly smaller.

## Conclusion

Polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene copolymers show thermally reversible gelation in semidiluted solutions of a paraffinic oil. This liquid is a selective solvent for the poly(ethylene/butylene) block. The sol–gel transition temperature increases with the copolymer concentration and molar mass. The concentration dependences of the elastic storage modulus are similar for the three SEBS copolymers with an exponent close to that expected for systems in good solvents (2.25) that possess a structure close to that of chemical networks. The relaxation rates observed are extremely high, suggesting a considerable mobility in the gel over the measurement time, and could be explained according to a classical network in which the junctions break and re-form. The relaxation rate increases as the copolymer molar mass decreases, suggesting a shorter life of the junctions of the gel for those copolymers with a lower molar mass. When SEBS gels were immersed into an excess of a paraffinic oil, they swelled up to reach an equilibrium swelling. The swelling capability of the SEBS1 gels (copolymer with the lower molar mass) is markedly smaller than those corresponding to SEBS2 and SEBS3 gels.

**Acknowledgment.** The authors thank the CICYT, the CYTED, Departamento de Educación, Universidades e Investigación del Gobierno Vasco, and Vicerrectorado de Investigación de la Universidad del País Vasco for their financial support.

## References and Notes

(1) Brown, W.; Schillén, K.; Almgren, M.; Hvidt, S. and Bahadur, P. *J. Phys. Chem.*, **1991**, *95*, 1850.
(2) Brown, W.; Schillén, S.; Hvidt, S. *J. Phys. Chem.* **1992**, *96*, 6038.
(3) Malmsten, M.; Lindman, B. *Macromolecules* **1993**, *26*, 1282.
(4) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145.
(5) Luo, Y.-Z.; Nicholas, C. V.; Attwood, D.; Collet, J. H.; Price, C.; Booth, C.; Chu, B.; Zhou, Z.-K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 539.
(6) Deng, Y.; Yu, G.-E.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1441.
(7) Nicholas, C. V.; Luo, Y.-Z.; Deng, N.-J.; Attwood, D.; Collett, J. H.; Price, C.; Booth, C. *Polymer* **1993**, *34*, 138.
(8) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Attwood, D.; Padget, J. C.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1243.
(9) Plestil, J.; Hlavatá, D.; Hrouz, J.; Tuzar, Z. *Polymer* **1990**, *31*, 2112.
(10) Tuzar, Z.; Koák, C.; Stepánek, P.; Plestil, J.; Kratochvíl, P.; Procházka, K. *Polymer* **1990**, *31*, 2118.
(11) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975.
(12) Rodrigues, K.; Mattice, W. L. *Polym. Bull.* **1991**, *25*, 239.
(13) Nguyen-Misra, M.; Mattice, W. L. *Macromolecules* **1995**, *28*, 1444.
(14) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J.-P. *Macromolecules* **1994**, *27*, 2956.
(15) Lairez, D.; Adam, M.; Raspaud, E.; Carton, J.-P.; Bouchard, J.-P. *Macromol. Symp.* **1995**, *90*, 203.
(16) Sato, T.; Watanabe, H.; Osaki, K. *Macromolecules* **1996**, *29*, 6231.
(17) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J.-P. *Macromolecules* **1996**, *29*, 1296.
(18) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R.; Blacher, S.; Brouers, F.; L'Homme, G. *Macromolecules* **1996**, *29*, 5384.
(19) Quintana, J. R.; Díaz, E.; Katime, I. *Macromol. Chem. Phys.* **1996**, *197*, 3017.
(20) Villacampa, M.; Quintana, J. R.; Salazar, R.; Katime, I. *Macromolecules* **1995**, *28*, 1025.
(21) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367.
(22) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
(23) Izuza, A.; Winter, H. H.; Hashimoto, T. *Macromolecules* **1992**, *25*, 2422.

(24) Tan, H. M.; Moet, A.; Hiltner A.; Baer, E. *Macromolecules* **1983**, *16*, 28.

(25) Quintana, J. R.; Villacampa, M.; Salazar, R.; Katime, I. *J. Chem. Soc., Faraday Trans.* **1992,** *88*, 2739.

(26) Lehsaini, W.; Weill, G.; François, J. *J. Macromol. Symp*. **1995**, *93*, 163.

(27) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter 5.

(28) Quintana, J. R.; Jáñez, M. D.; Katime, I. *Polymer*, submitted for publication.

(29) Guenet, J. M.; Mckenna, G. B. *J. Polym. Sci*: *Polym. Phys.* **1986**, *24*, 2499.

(30) Fazel, Z.; Fazel, N.; Guenet, J. M. *J. Phys. II Fr.* **1992**, *2*, 1745.

(31) He, X.; Herz, J.; Guenet, J. M. *Macromolecules* **1987**, *20*, 2003.

(32) Mutin, P. H.; Guenet J. M. *Macromolecules* **1989**, *22*, 843.

(33) Janacek, J.; Ferry J. D. *Macromolecules* **1969**, *2*, 397.

MA961597Z