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Physical gelation of polystyrene-b-poly(ethylene/butylene)-b-polystyrene in several paraffinic oils†

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The thermoreversible gelation of a triblock copolymer polystyrene-b-poly(ethylene/butylene)-b-polystyrene in three paraffinic oils was studied. The paraffinic oils used (Norpar 12, Norpar 13 and Norpar 15) are selective solvents for the middle PEB block of the copolymer. The three oils are chemically similar and they only differ in the average carbon number. Thus the solvent influence on the sol–gel transition and on the mechanical properties of the gels was analysed. The sol–gel transition temperature increased with the copolymer concentration and the average carbon number of the paraffinic oil. 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 similar for the three paraffinic oils with exponents close to those expected for systems in good solvents (2.25) that possess a structure close to that of chemical networks. The relaxation rates observed were extremely high suggesting a considerable mobility in the gel over the measurement time. The relaxation rate increased as the oil carbon number decreased. The swelling behavior was also examined. All gels swelled significantly. The swelling equilibrium ratios varied linearly with the copolymer preparation concentration. The gels formed in Norpar 13 and Norpar 15 show a similar swelling behavior whereas the gels formed in Norpar 12 show a swelling capability markedly lower. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The aggregation phenomenon of triblock copolymers in solutions of midblock selective solvents has received growing attention in recent years[1–19]. Thermally reversible gelation of semidiluted solutions of triblock copolymers in selective solvents of the middle block has been reported by several authors[6–9,15–19].

The association complexity in these systems may be understood taking into account that, to bring the two end blocks into the micelle core, the middle block, which forms the micelle shell, must form a loop. This implies an additional entropic penalty to molecular aggregation. If this penalty in large enough, some of the copolymer chains in the micelle might elect to have one end block extending into solution. At concentrations large enough, this end block could form part of another micelle core or interact with another end block which stays in the same conditions. Micelle aggregates would be formed in this way [7]. Another possible mechanism for circumventing the entropy penalty is through the formation of a branched structure, consisting of droplets of the poorly solvated blocks that are joined by strands of the well solvated middle blocks[11,16].

In our laboratory, we have undertaken a series of studies on the polystyrene-b-poly(ethylene/butylene)-b-polystyrene copolymers, SEBS, in selective solvents of the poly(ethylene/butylene) block[20–23]. These studies have focused on the analysis of the micelles formed in dilute solutions of n-octane[21,23] and the physical gel found in semidiluted solutions of a paraffinic oil[20,22]. Viscoelastic and thermoreversible SEBS gels of sufficient consistency were found at concentrations higher than 2 wt%[20].

In the present paper we have analysed the paraffinic oil influence on the physical gels. For this purpose we chose three paraffinic oils of similar chemical composition and whose average molecule had a carbon number of 12, 13 and 15. Paraffinic oils (n-alkane mixtures) are selective solvents of the poly(ethylene/butylene) block[21,23,29]. We have studied the swelling behaviour, the sol–gel transition and the mechanical properties of the gels formed by a SEBS copolymer (molar mass: 87 300 g mol^{-1}, chemical composition: 32 wt% Ps) in different solutions of these three paraffinic oils. Oscillatory shear and compression measurements were carried out over concentration ranges at which the gels had sufficient consistency. The gels studied were thermally reversible and gel formation was reproducible.

EXPERIMENTAL

Materials and gel preparation

The copolymer sample of polystyrene-b-poly(ethylene/butylene)-b-polystyrene, SEBS2, was a commercial product (Kraton) kindly provided by Shell España. The sample has been previously characterised in detail[24]. It is homogeneous in chemical composition and its weight average molar mass, polydispersity and styrene content are 87 300 g.mol^{-1}, 1.11 and 32 wt%, respectively. The paraffinic oil samples,

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Norpar 12, Norpar 13 and Norpar 15 are Exxon products consisting of n-alkane mixtures with an average carbon number of 12, 13 and 15 and a distillation range of 188–217, 228–243 and 252–272°C, respectively. Sample gels were prepared by dissolving the copolymer in the oils at 120°C in sealed flasks. Once the solutions were clear they were allowed to cool to room temperature in order to form the gels. In this paper, the concentrations are expressed in wt%, i.e. per 100 g of solution.

Gel swelling

Samples used for the swelling experiments were obtained in cylindrical shapes with a diameter of 10 mm and a length of 5 mm. The gel samples were immersed in an excess of paraffinic oil to achieve equilibrium swelling. The swelling kinetics were followed by measuring the sample weight until equilibrium was reached. The equilibrium swelling ratio, G^{∞}, is defined as the ratio of the final weight to the initial weight of the sample.

Swollen gels were removed from the oil bath at regular intervals, dried superficially with Whatman No.1 filter paper, weighed and placed in the same bath.

Sol–gel transition

Two methods were used to determine the sol–gel transition. The gelation temperatures were determined by tilting a test tube containing the copolymer solution. On lowering the temperature, the temperature at which the solution no longer flowed was considered as the gelation temperature, T_{GL}. The melting temperatures were determined measuring the elastic storage, G', and the loss moduli, 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 solid-like state to a viscoelastic liquid-like state. However, it should be noted that the melting temperature so defined is frequency-dependent. A heating rate of 0.5°C min^{-1} was found to be slow enough to keep the gels in an equilibrium state and, therefore, not dependent on gel history[20].

Oscillatory experiments

Oscillatory shear measurements were performed in a Polymer Laboratories dynamic mechanical thermal analysis system. The mechanical mode used was the torsion one with a fluid cup and a torsion plate whose diameters were 44 and 38 mm, respectively. Gel bits were introduced into the cup prior to increasing the chamber temperature to 100–120°C in order to melt the gel. Once a homogeneous solution was obtained the sample was quickly cooled to 25°C. The elastic storage, G' and loss moduli, G'', were measured as a function of frequency between 0.01 and 20 Hz at a maximum strain amplitude of 6.25 mrad. Measurements of G' and G'' were also performed as a function of temperature at a frequency of 1 Hz and a heating rate of 0.5°C min^{-1}. The temperature was controlled with a precision of 0.1°C.

Relaxation experiments

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

RESULTS AND DISCUSSION

Swelling behaviour

When SEBS2 gels were immersed in an excess of paraffinic oil they swelled up to reach an equilibrium swelling after several days. Considering the swelling ratio G as the ratio

$$G = \frac{P}{P_0}$$

where P_0 is the sample weight after preparation but just before the immersion in a solvent excess and P the sample weight a certain time after the immersion. The swelling equilibrium ratio G^{∞} is then expressed as

$$G^{\infty} = \left(\frac{P}{P_0}\right) \quad t \rightarrow \infty$$

The swelling behaviour was similar for the three paraffinic oils. The evolution of the swelling ratio as a function of time is plotted in *Figure 1* for several SEBS2 gels in

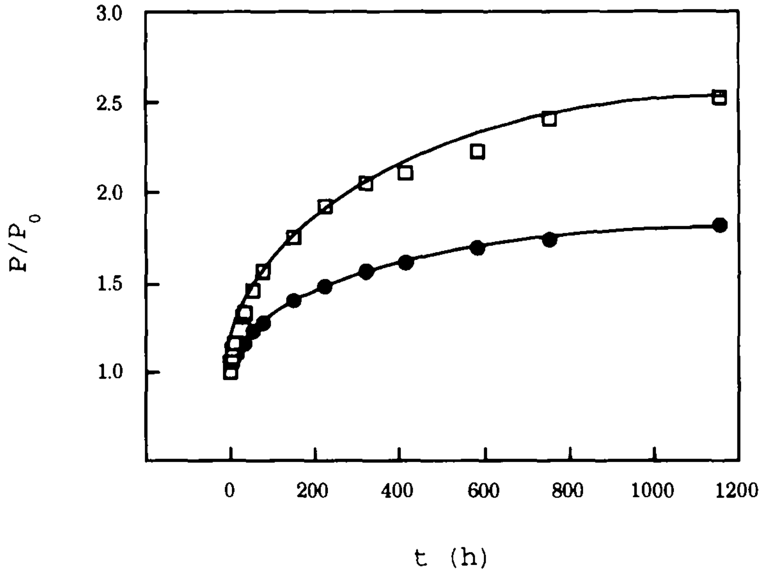

Figure 1 Evolution of the swelling ratio P/P_0 as a function of time for Norpar 15 gels at 25°C. SEBS2 preparation concentrations: 10 (●) and 12 (□) wt%

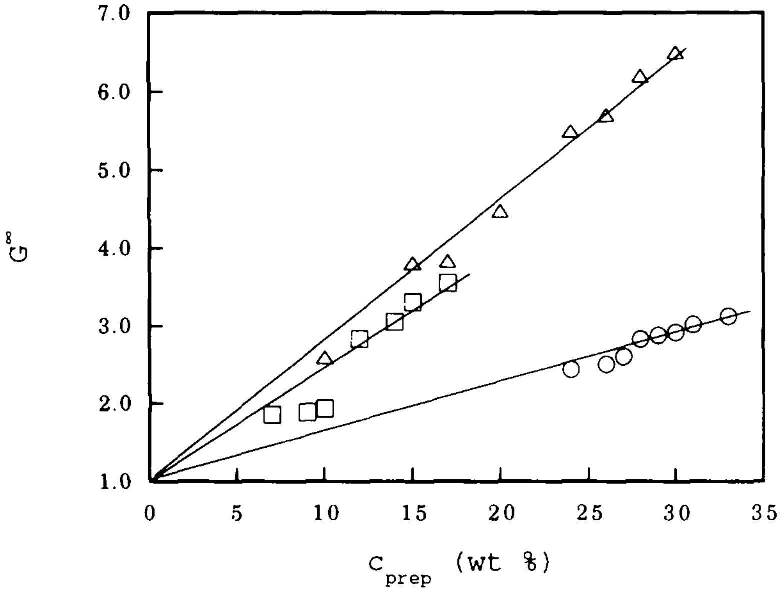

Figure 2 Equilibrium swelling ratio, G^∞, as a function of the preparation concentration, C_{prep}, for Norpar 12 (○), Norpar 13 (△) and Norpar 15 gels (□) at 25°C

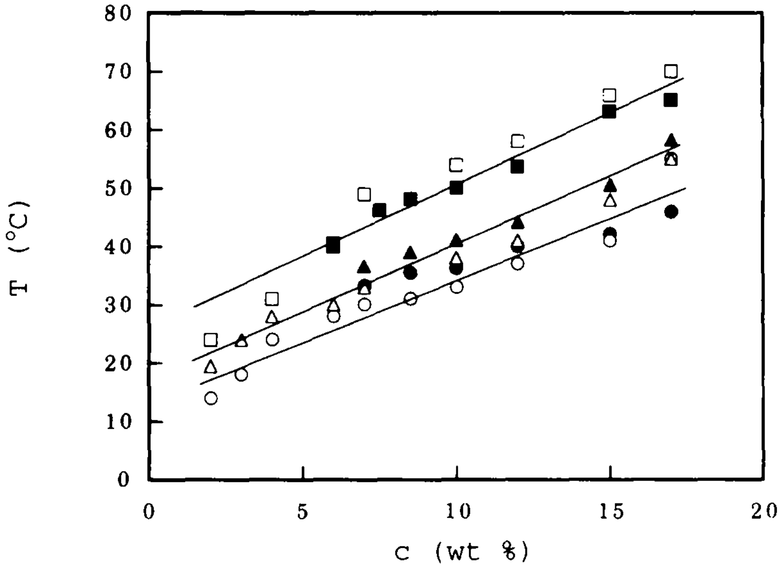

Figure 3 Sol–gel transition temperature against copolymer concentration for Norpar 12 (○), Norpar 13 (△) and Norpar 15 gels (□). Gel formation temperature determined by tilting method (unfilled symbols) and melting temperature determined by oscillatory shear measurements (filled symbols)

Norpar 13 at different copolymer concentrations. The swelling rate, d*G*/d*t*, is very rapid at the early stage but after 2 days, the swelling becomes slower to attain equilibrium after 10 days.

The variations of the swelling equilibrium ratio as a function of the preparation concentration are plotted in *Figure 2* for the SEBS2 gels in the three paraffinic oils. In spite of the considerable experimental errors found for the SEBS2 gels in Norpar 12 due to the lack of consistency of the gels, one can conclude that the swelling equilibrium ratio varies linearly with the preparation concentration at least within the preparation concentration range studied for each paraffinic oil. The SEBS2 gels formed in Norpar 13 and Norpar 15 have a very similar swelling behaviour. However the swelling capability of the SEBS2 gels formed in Norpar 12 is markedly lower.

This behaviour is very different to that found for covalent gels where the swelling increases with solvent ability and decreases with the degree of crosslinking. As will be shown later, the SEBS2 gels formed in Norpar 12 are the least consistent gels suggesting that the swelling capability of a copolymer gel is related to the number and strength of the gel junctions.

Sol–gel transition

For the gels studied, a large uncertainty was found in determining the temperature at which G' and G'' follow the known scaling relation [25–27]

$$G'(\omega) \sim G''(\omega) \sim \omega^n$$

The frequency dependence of the storage, G', and loss moduli, G'', was slightly curved at every temperature studied and near the gel melting temperature, both G' and G'' curves crossed with a crossover frequency that increased as the temperature increased. Therefore, we chose that temperature at which the crossover frequency becomes equal to

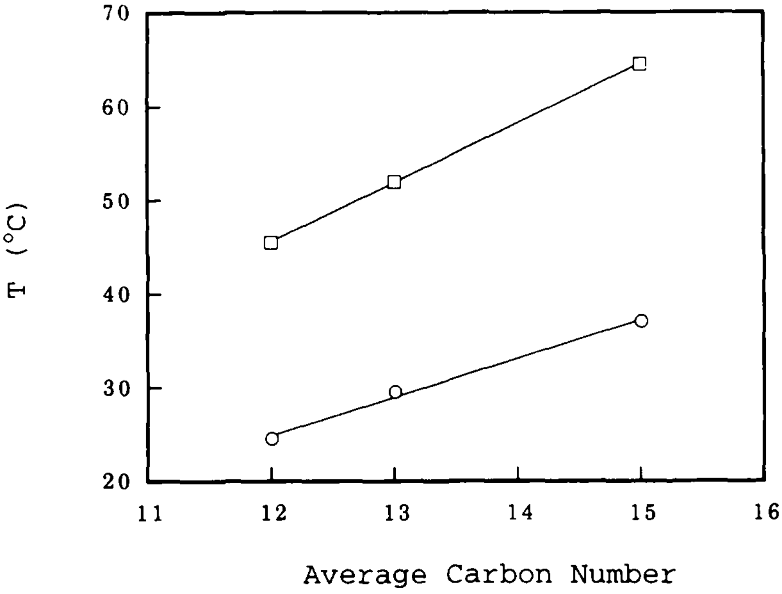

Figure 4 Sol–gel transition temperature as a function of the average carbon number of the paraffinic oils for two concentrations: 5 (○) and 15 wt% (□)

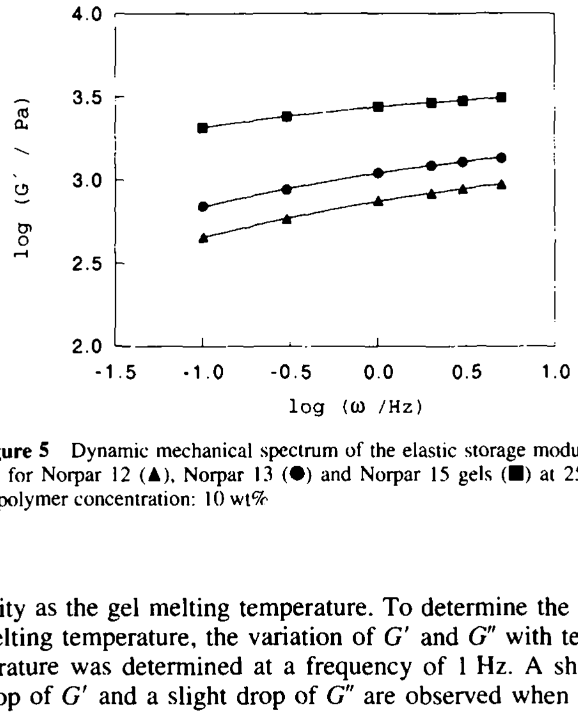

Figure 5 Dynamic mechanical spectrum of the elastic storage modulus, G', for Norpar 12 (▲), Norpar 13 (●) and Norpar 15 gels (■) at 25°C. Copolymer concentration: 10 wt%

unity as the gel melting temperature. To determine the gel melting temperature, the variation of G' and G'' with temperature was determined at a frequency of 1 Hz. A sharp drop of G' and a slight drop of G'' are observed when gel melting takes place. As mentioned above, the temperature at which $G' = G''$ was considered as the melting temperature, T_m, since it marks the transition from a solid-like state to a viscoelastic liquid-like state.

The influence of the copolymer concentration on the sol–gel transition is shown in *Figure 3* where the gel melting temperature, T_m, and the gelation temperature, T_{GL}, are plotted as a function of concentration for the three paraffinic oils. An appreciable difference between the gelation and melting temperatures is not observed for the three kinds of gel in spite of the different methods used. This behaviour agrees with others found for amorphous polymer gels and is contrary to the thermoreversible gelation of crystallisable polymers[28]. The concentration dependences of the sol–gel transition temperatures are linear over the concentration range studied for each paraffinic oil. It should be noted that for the lowest concentrations, the determination of the gelation temperatures suffers a large error due to the subjectivity of the experimental method. It is more difficult to determine the precise temperature at which the gel flows.

The concentration dependence increases slightly with the average carbon number of the paraffinic oil. To compare the sol–gel transition temperature of the gels formed in the different oils, two concentrations were chosen (5 and 15 wt%). These temperatures are plotted in *Figure 4* against the average carbon number of the paraffinic oil. The sol–gel transition temperatures vary linearly with the carbon number, being higher as the carbon number increases. Taking into account that the paraffinic oil is a selective solvent of the poly(ethylene/butylene) block, the polystyrene blocks are solely responsible for the gel junctions and therefore the above result implies that the ability of the solvent with respect to the polystyrene blocks determines the ease of gelation and consequently the stability of the gels formed in a given paraffinic oil. This behaviour agrees with the results found for a polystyrene-b-poly(ethylene/propylene) copolymer in different n-alkanes [29] where the micelles formed in these systems have higher critical micelle temperatures as the carbon number of the n-alkane increased. This behaviour seems logical since the incompatibility of the polystyrene blocks will increase as the carbon number of the alkane increases.

The effect of the paraffinic oil was not appreciable on the critical gel concentration, CGC, defined as the concentration at which a particular polymer is capable of forming an one-phase gel. For the three paraffinic oils, the CGC was close to 2 wt%. This result suggests that this concentration depends on the copolymer structure rather than on the solvent quality.

Measurements of the storage and loss moduli were also carried out as a function of the frequency of a small deformation oscillatory shear strain. *Figure 5* shows the plots of log G' *versus* frequency for three SEBS2 gels formed in the three solvents at 25°C and at a concentration of 10 wt%. The storage modulus tends to a constant value at high frequencies but decreases more sharply as the frequency decreases. This behaviour suggests that the junctions are not strong enough and under a weak stress they will eventually split. The frequency dependence of G'

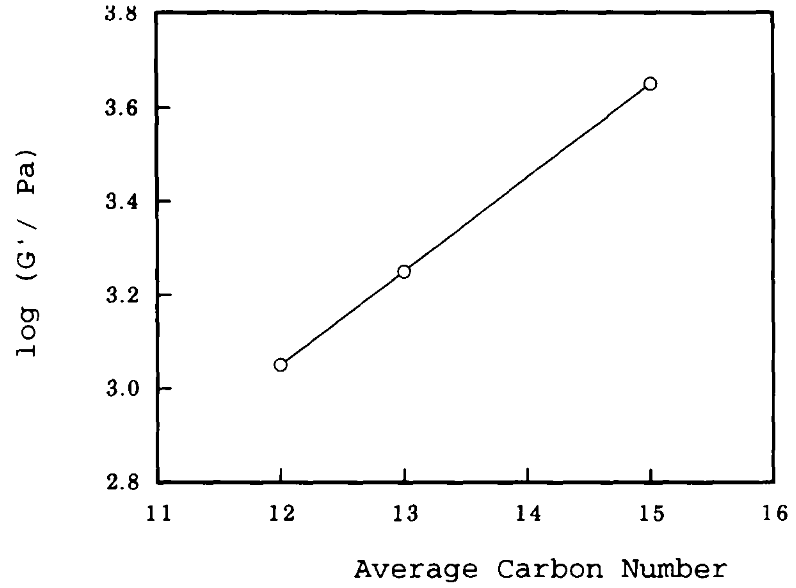

Figure 6 Dynamic storage modulus, G', versus average carbon number of the paraffinic oils at a concentration of 10 wt% and at 25°C

is also involved as the average carbon number of the paraffinic oil decreases. This reveals an increment in the strength of the crosslinks in the gel when the chain of the paraffinic oil is larger.

The concentration dependences of the elastic store modulus for the three paraffinic oils: Norpar 12, Norpar 13 and Norpar 15 were determined at 25°C. The copolymer concentrations ranged from 6 to 17 wt% and the measurements were carried out at a frequency of 1 Hz. At these concentrations the gels had sufficient consistency and the melting temperatures were not too high. For the three paraffinic oils the dependence is linear in a double-logarithmic scale and yield the following power relations:

Norpar 12: $G' \sim C^{2.23 \pm 0.1}$;
Norpar 13: $G' \sim C^{2.29 \pm 0.1}$;
Norpar 15: $G' \sim C^{2.26 \pm 0.1}$.

The results agree very well with the value expected for systems in good solvents[30] (≈ 2.25) that possess a structure close to that of covalent networks. Paraffinic oils are selective solvents of the poly(ethylene/butylene) block, PEB, therefore the gels should possess a fringed micellar structure characterised by knots formed by aggregated PS blocks and linked by one well solvated PEB block when the connection is direct.

The dynamic storage moduli as a function of the average carbon number of the oils are plotted in *Figure 6* for those gels with a concentration of 10 wt%. The experimental dependence is linear with the storage modulus increasing with the average carbon number of the oil. Taking into account that the solvent quality decreases with the carbon number, this behaviour could be explained by an increment in the number of crosslinks and a greater rigidity of the linking PEB blocks due to a lower solvation.

The stress relaxation responses to a compressive deformation were determined for gels of the three oils. At an early stage, the time dependence of the stress, σ, was linear in a double logarithmic plot. The stress relaxation rates, $m = \mathrm{d} \log \sigma / \mathrm{d} \log t$, were quite important and very dependent on the paraffinic oil. At relaxation times $t < 3000$ s, the following values were found:

Norpar 12: $m = 5 \pm 1.5$;
Norpar 13: $m = 3 \pm 0.9$;
Norpar 15: $m = 0.7 \pm 0.2$.

These high relaxation rates constitute a possible indication of how the physical junctions are weak. The higher the m value is, the weaker the junctions are. The values found were greater than those reported for physical gels with absence of crystalline order in the physical crosslinks [31,32] ($m = 0.08$–0.2).

The higher m values found for Norpar 12 gels would then be a consequence of the weakness of their junctions. A larger oil average carbon number will increase the PS block incompatibility with the paraffinic oil and will cause stronger and more permanent gel junctions.

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