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Thermoreversible gelation of mixed triblock and diblock copolymers in *n*-octane

José R. Quintana, Estíbaliz Hernáez, Issa Katime*

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

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Abstract

The thermoreversible gelation of blends of polystyrene-block-poly(ethylene/butylene)-block-polystyrene (SEBS) and polystyrene-block-poly(ethylene/propylene) (SEP) copolymers in *n*-octane was studied. The solvent is selective for the polyolefine blocks of the copolymers. The influence of the composition of the hybrid gels on the sol–gel transition and on the mechanical properties of the gels was analyzed. The sol–gel transition temperature increased with the concentration of both type of copolymers and did not depend on the hybrid gel composition for SEBS2 proportions higher than 50% at a total copolymer concentration higher than 6 wt%. The mechanical properties of the different gels were examined through oscillatory shear and compressive stress relaxation measurements. The elastic storage modulus increased with the triblock copolymer concentration but kept almost constant with the diblock copolymer concentration for SEBS concentrations higher than 5.0%. The stress relaxation rate was not dependent on the concentration of triblock and diblock copolymers, but the hybrid gels show lower stress relaxation rates than the pure SEBS2 gels. In the hybrid SEBS/SEP gels the SEP chains impart stability to the micelles or nodes of the network whereas the SEBS chains are responsible for the bridges that keep the gel as one-phase system.

Keywords: Gelation; Triblock and diblock copolymers; *n*-Octane

1. Introduction

This study is a part of our investigation on properties of block copolymer gels formed by triblock copolymers of styrene and ethylene/butylene. In previous papers we have described studies on the ability of these block copolymers to form thermoreversible gels [1] and the influence of the selective solvent [2,3] and of the copolymer molar mass [4,5]. We have also investigated the physical gelation of polystyrene-block-poly(ethylene/butylene)-block-polystyrene in presence of homopolystyrene [6]. In this paper, we report a more complicated case, the physical gelation of mixed block copolymers with different chain lengths and different structures: polystyrene-block-poly(ethylene/butylene)-block-polystyrene triblock copolymers, SEBS, and polystyrene-block-poly(ethylene/propylene) diblock copolymers, SEP.

The self-assemble behaviors of ABA triblock copolymers and AB diblock copolymers in selective solvents of B blocks are quite different. Whereas a AB diblock chain can only have the A block in the micellar core and the B block dangling in the corona, a ABA triblock chain can form either a loop, being both A blocks in the same micelle core, or a bridge, belonging each A block to different micelle core, or a chain where an A block belongs to a micelle core and the other A block dangles into the solution [7,8].

The ability of self-associated ABA triblock chains to bridge two insoluble regions is one main feature distinguishing them from self-associated AB diblock or BAB triblock chains. At low concentrations, solutions of AB and BAB block copolymers in selective solvents of B blocks show the existence of standard micelles [9,10] and only at high concentrations macrolattice structures are observed [11,12] as a consequence of extensive entanglements of the B blocks in the corona of the close-packed micelles. In a ABA triblock system, well defined micelles [13,14] or loose and polydisperse aggregates rather than standard micelles [15] can be found at low concentrations and a physical gelation could occur in semi-diluted solutions [16–21] by bridging of the micelles in addition to entanglements at high concentrations.

The purpose of this work has been to extend our investigation to the thermoreversible gelation of mixtures of polystyrene-block-poly(ethylene/butylene)-block-polystyrene

* Corresponding author. Tel.: +34-9-4601-5441; fax: +34-9-4464-8500.
E-mail address: qfpkaami@lg.ehu.es (I. Katime).

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Table 1
Characteristics of the block copolymer samples: mass average molar mass of the copolymer, M_w, of the polystyrene blocks, $M_{w,PS}$, and of the polyolefine block, $M_{w,Po}$, polystyrene weight percentage and polydispersity index, I

	M_w	$M_{w,PS}$	$M_{w,Po}$	PS (wt%)	I
SEBS2	87 300	$2 \times 14\,000$	59 400	32	1.11
SEP2	105 000	37 000	68 000	35	1.06
SEP3	145 000	38 000	107 000	26	1.08

and polystyrene-block-poly(ethylene/propylene) block copolymers in semi-diluted solutions of *n*-octane. *n*-Octane is a selective solvent of poly(ethylene/butylene) and poly (ethylene/propylene) blocks. We have studied the sol–gel transition and the mechanical properties of the hybrid-gels as a function of the gel composition and the molar mass of the copolymers.

2. Experimental

Materials and gel preparation. The polystyrene-b-poly (ethylene/butylene)-b-polystyrene triblock copolymer and polystyrene-b-poly(ethylene/propylene) diblock copolymer samples are commercial products kindly provided by Shell España, S.A. The samples have been previously characterized in detail [22,23]. They are homogeneous in chemical composition and their mass average molar masses, polydispersities and styrene contents are shown in Table 1. *n*-Octane was analytical purity grade and was used without further purification.

Sample gels were prepared by dissolving the copolymer samples in *n*-octane at 120 °C in sealed flasks. Once the solutions were clear they were allowed to cool in order to form the gels. In this study the concentrations are expressed in wt% and when no explanations are made, the values are with respect to the total copolymer content plus solvent. The total concentration ranges used were chosen in order to get a sufficient consistency of the gels and melting temperatures low enough to avoid the solvent evaporation.

Sol–gel transition. Two methods were used to determine the sol–gel transition. The gelation temperatures were determined by inverting a test tube containing the copolymer solutions. On cooling down the solution, the temperature at which the solution changes from a mobile to a immobile system was considered as the gelation temperature, T_{GL}. The melting temperatures were determined by measuring the elastic storage, G', and the lost modulii, 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. To measure the storage and loss modulii, dynamic viscoelastic measurements were performed on a TA instruments AR1000-N rheometer using the parallel-plate shear mode. The plate diameter was 40 mm. The amplitude of the oscillatory strain was 0.2. The temperature scan was 1.0 °C min^{-1}.

Dynamical mechanical experiments. Oscillatory shear measurements were performed in a Polymer Laboratories dynamical 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. The copolymer solutions were poured into the fluid cup at high temperature and then allowed to cool and to stabilize to the measuring temperature. The elastic storage, G', and loss modulii, G'', were measured as a function of frequency between 0.1 and 10 Hz at a maximum strain amplitude of 6.25 mrad. The temperature was controlled with a precision of 1 °C.

Relaxation experiments. Compression measurements were made in a Perkin Elmer dynamic mechanical analyzer DMA7. A cup and a plate with diameters of 18 and 10 mm, respectively, were used for all measurements. The gels were formed in the cell in the same way as described earlier, having a height of 3 mm. The stress relaxation measurements were performed measuring the load as a function of time, keeping both the gel deformation and the temperature constant. The temperature was controlled with a precision of 0.1 °C.

3. Results and discussion

The sol–gel transition temperatures were determined by tilting a test tube containing the copolymer solution. The temperature at which the solution no longer flowed was taken as the gelation temperature, T_{GL}. To confirm the goodness of the tilting method some sol–gel temperatures were also determined by oscillatory shear measurements. A plot of $\log G'$ and $\log G''$ as a function of temperature for a SEBS2 gel with a copolymer concentration of 11 wt% is shown in Fig. 1. A sharp drop of G' is observed when the gel melting takes place. 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. Gelation and melting temperatures are found to be very similar although two different experimental methods were used for SEBS2 gels (Fig. 5). The coincidence of both methods has been also found in other gel investigations [1,2,4,6].

The sol–gel transition for the blend SEBS2/SEP2 (50/50) was studied covering the concentration range of 6.6–23.0 wt%. The variation of T_{GL} with the total copolymer concentration is plotted in Fig. 2. The concentration dependence of the gelation temperature is linear over the concentration range studied. The gelation temperature increases as the total copolymer concentration increases, suggesting that the higher the copolymer concentration was, the minimum number of physical junctions necessary to form the gel can

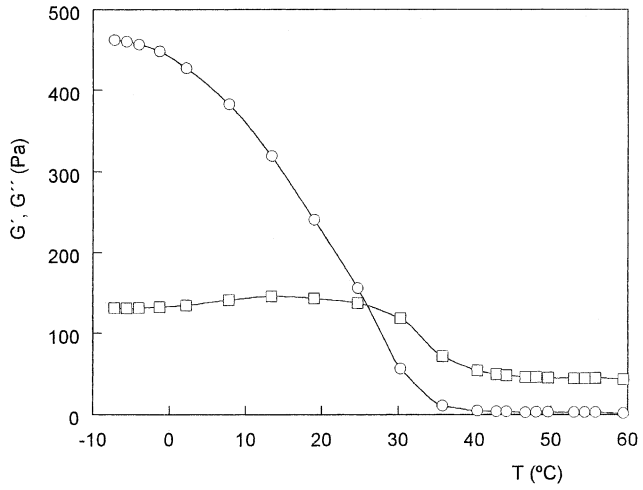

Fig. 1. Temperature dependence of G' (○) and G'' (□) for a SEBS2 gel (11 wt%) at 1 Hz. Heating rate: 1.0 °C min^{-1}.

be reached at higher temperatures. On comparing the concentration dependence of the gelation temperature for these hybrid gels with pure SEBS2 gels [5], two practically coincident straight lines are found, suggesting that in this case the substitution of a 50%, with respect to the total copolymer content, of SEBS2 by SEP2 has no influence in the sol–gel transition.

To study the influence of the gel composition on the sol–gel transition, gel formation temperatures for gels with different percentages of both copolymers with respect to the total copolymer content and at several total copolymer concentrations were determined. These temperatures are plotted in Fig. 3 against the SEBS2 percentage with respect to the total copolymer in the gel for several total copolymer concentrations. The replacement of SEBS2 chains by SEP2 ones keeps the thermal stability of the gel unchanged up to a determined composition. SEP2 chains can form part of the SEBS2 micelles rising up to hybrid micelles, however, SEP2 chains cannot form bridges between these hybrid micelles. This is the cause that on reaching a limit SEBS2

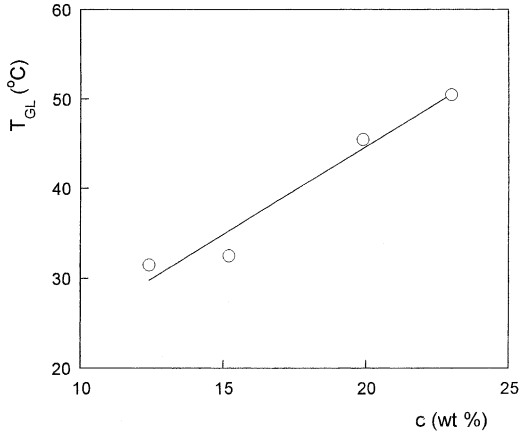

Fig. 2. Gel formation temperature as a function of total copolymer concentration for gels SEBS2/SEP2 (50/50) in *n*-octane.

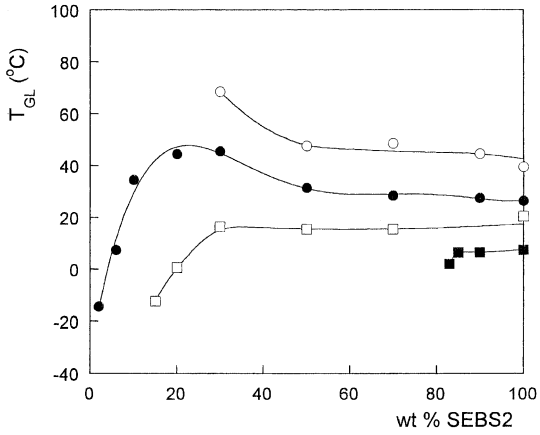

Fig. 3. Gel formation temperature versus gel copolymer composition for four total copolymer concentrations: 3.4 (■), 6.6 (□), 12.4 (●) and 19.9 wt% (○).

percentage, a decrease in the SEBS2 concentration causes a sharp decrease in the thermal stability of the gels due to a significant reduction in the number of gel bridges. For gels with a higher total copolymer concentration, an increase in the thermal stability of the gel is found for SEBS2 percentage lower than 50%. This increment can be caused by a higher thermal stability of the hybrid micelles due to the increment in the number of SEP2 chains in the micelles. It has been reported that SEP micelles in *n*-octane have higher critical micelle temperatures than SEBS micelles [24].

The influence of the SEP2 concentration on the sol–gel transition of the hybrid gels can be observed in Fig. 4 where the gelation temperatures are plotted against the SEP2 percentage for the SEBS2 percentages: 1.0, 5.0 and 10.0 wt%. For the three SEBS2 concentrations, the gelation temperature increases linearly with the SEP2 concentration. The addition of SEP2 chains increases the thermal stability of the gel because the critical micelle temperature of the hybrid micelles is higher and the number of these micelles also increases with the copolymer concentration.

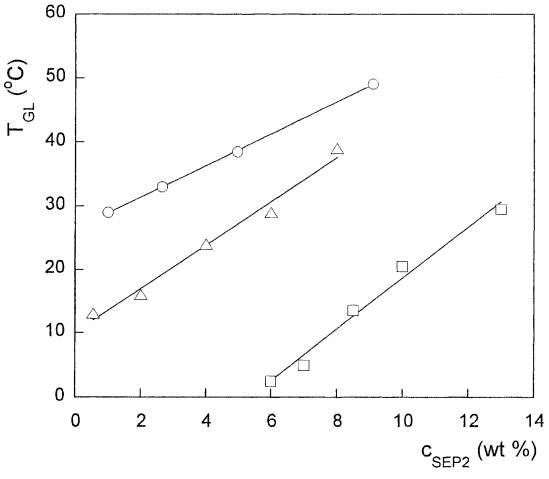

Fig. 4. Gelation temperature as a function of the SEP2 concentration for three SEBS2 percentages: 1.0 (□), 5.0 (△) and 10.0 wt% (○).

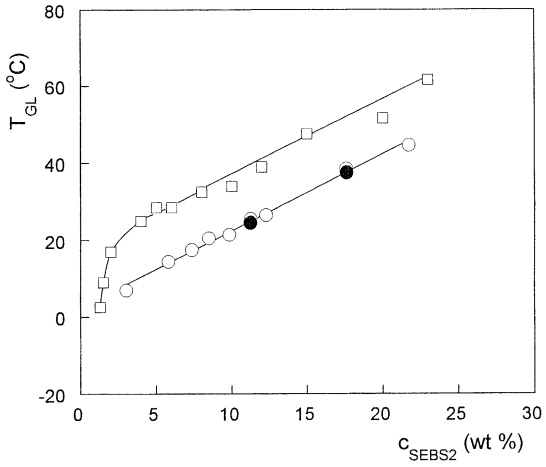

Fig. 5. Gelation temperature (unfilled symbols) and melting temperature (filled symbols) as a function of the SEBS2 concentration for pure SEBS2 gels (○) and hybrid SEBS2/SEP2 gels with a 5% of SEP2 (□).

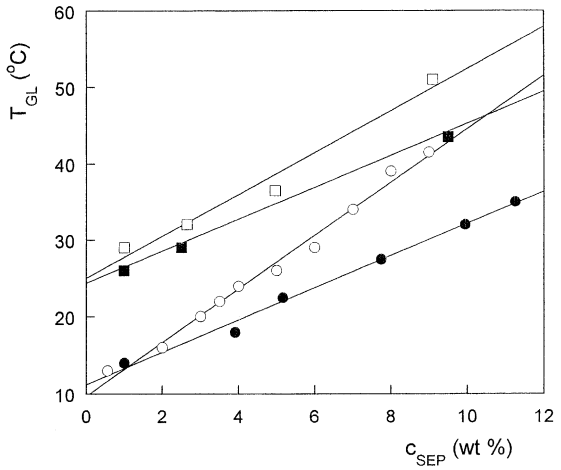

Fig. 6. Gel formation temperature as a function of the SEP concentration for SEBS2/SEP2 (unfilled symbols) and SEBS2/SEP3 (filled symbols) gels for two SEBS2 percentages: 5.0 (○) and 10.0 wt% (□).

In Fig. 5 we can compare the percentage dependences of the gelation temperatures for pure SEBS2 gels and hybrid SEBS2/SEP2 gels with a SEP2 percentage of 5.0 wt%. In both cases the T_{GL} dependences are linear, but for a given SEBS2 percentage, the hybrid gel has a higher T_{GL} than the SEBS2 gel. The SEP2 chains in the gels cause an increment in the number of micelles and in the thermal stability of these hybrid micelles. For SEBS2 concentrations lower than 3.0 wt%, the pure SEBS2 gels cannot exist as a one-phase gel. Hybrid gels with a SEP2 percentage of 5.0 wt% were observed up to SEBS2 percentages close to 1.0 wt%, but a sharp decrease in the gelation temperature can be seen for SEBS2 concentrations lower than 3.0 wt%. This means that though at these concentrations the capability to form micelles or network nodes is high enough due to the SEP2 chains existing in the solution, the capability to form bridges between the existing micelles decreases dramatically with the SEBS2 percentage since only the SEBS2 chains are able to join the existing micelles.

The influence of the diblock copolymer concentration in the gelation temperature for two copolymer blends (SEBS2/SEP2 and SEBS2/SEP3) and for two SEBS2 concentrations (5.0 and 10.0 wt%) is shown in Fig. 6. SEP2 and SEP3 diblock copolymers have similar polystyrene blocks, but SEP3 has a longer poly(ethylene/propylene) block. The SEP concentration dependence of the gelation temperature is linear in any studied system. However, for a given SEP concentration the SEBS/SEP2 gels have a higher gelation temperature. The lower thermal stability of the SEBS2/SEP3 gels could be due to the larger thickness of the hybrid micelle shells of the pair SEBS2/SEP3 that interfere with the bridge formation between micelles. According to reported data [23] the SEP3 micelles in *n*-octane have a shell thickness of 61 nm whereas the SEP2 micelles have a shell thickness of 42 nm.

Measurements of the real and imaginary parts, G' and G'', of the complex shear modulus were also made as a function of the frequency of a small oscillatory shear strain. Gels of pure SEBS2 and SEBS2/SEP2 and SEBS2/SEP3 blends at different concentrations and at −20 °C were analyzed. In any studied system the storage and loss moduli were practically independent of frequency over two orders of magnitude. G' exceeds also G'' over the entire range of frequency examined by one or two orders of magnitude. These features are consistent with the dynamic mechanical behavior of a physical gel [25].

The variations of the storage modulus with the total copolymer concentration for pure SEBS2 copolymer and SEBS2/SEP2 blends with a SEP2 concentration of 5.0 wt% are plotted in Fig. 7. In both cases the storage modulus increases with the SEBS2 concentration. At lower concentrations the pure SEBS2 gels show higher G' values than for the SEB2/SEP2 blends suggesting a larger number of bridges in the gel as a consequence of a larger number of SEBS2 chains.

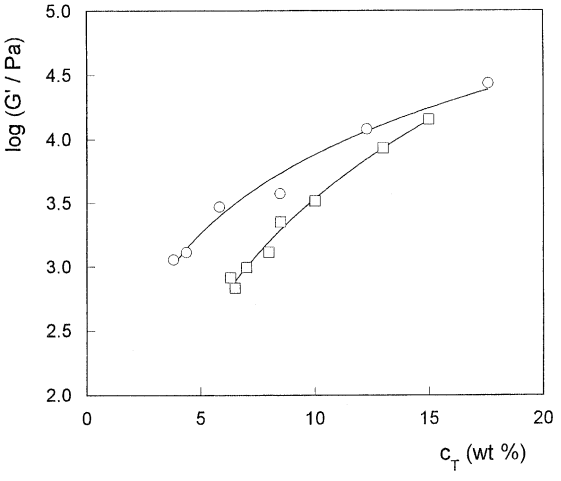

Fig. 7. Dynamic storage modulus, G', versus total copolymer concentration on a semilogarithmic scale for pure SEBS2 (○) and SEBS2/SEP2 blends with 5.0 wt% of SEP2 (□) at −20 °C.

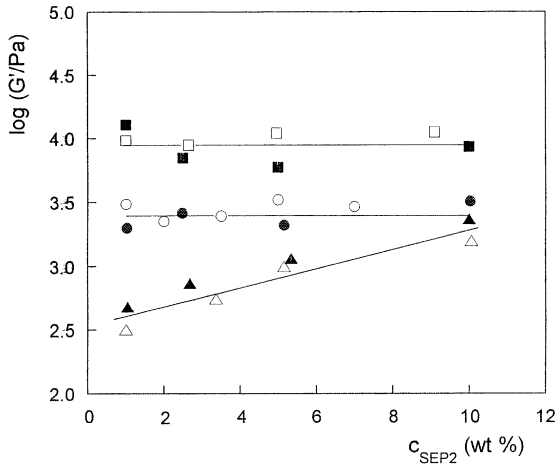

Fig. 8. Dynamic storage modulus, G', versus SEP concentration on a semi-logarithmic scale for SEBS2/SEP2 (unfilled symbols) and SEBS2/SEP3 blends (filled symbols) with 3.1 (△), 5.0 (○) and 10.0 wt% of SEBS2 (□) and at −20 °C.

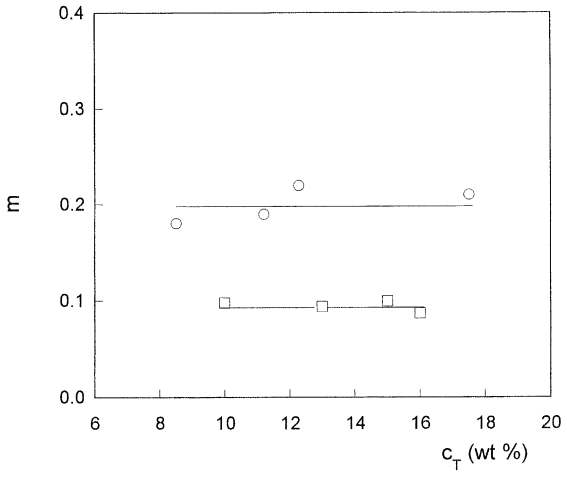

Fig. 9. Stress relaxation rates as a function of the total copolymer concentration for SEBS2 gels (○) and SEBS2/SEP2 gels (□) with 5.0 wt% of SEP2 at −20 °C.

However, as the SEBS2 percentage increases in the hybrid gels the difference in the G' values decreases because the excess of SEBS2 chains (5 wt%) in the pure SEBS2 gels is no longer significant and the hybrid gels have enough SEBS2 chains to form the possible bridges.

The variations of the dynamic storage modulus with the SEP concentration for SEBS2/SEP2 and SEBS2/SEP3 gels with different SEBS2 percentages are plotted in Fig. 8. At the SEBS2 concentrations of 5.0 and 10.0 wt% the storage modulus does not depend on the diblock concentration suggesting that for SEBS2 concentrations higher or equal to 5.0 wt% the increment in the number of hybrid micelles does not favor the formation of more bridges in the gel. The behavior for lower SEBS2 concentrations is quite different. For the hybrid gels with a SEBS2 concentration of 3.1 wt% the dynamic storage modulus increases with the SEP concentration. In this case, the increase in the number of SEP chains raises to an increment in the hybrid micelles in a way that more SEBS2 chains are able to form bridges, increasing the bridge density in the gel. This effect is not detected at higher SEBS2 concentrations because the pure SEBS2 gels have already the maximum bridge density that is possible. The type of polystyrene-*b*-poly(ethylene/propylene) copolymer influences in the gelation temperature, but does not have a clear influence in the dynamic storage modulus.

The stress relaxation responses to a compressive deformation were determined for SEBS2 gels and SEBS2/SEP2 gels with a 5.0 wt% of SEP2 at different concentrations and at −20 °C. At an early stage, the relationships between stress, σ, and time, t, were linear in a double logarithmic plot. The stress relaxation rates $m = -\mathrm{d}(\log \sigma)/\mathrm{d}(\log t)$ were relatively independent of the copolymer concentration in the experimental range studied and for deformations between $\lambda = 0.9$ and 0.7. The stress relaxation rates as a function of the total copolymer concentration are plotted in Fig. 9.

The relaxation rates would be related to the lifetime and weakness of the physical crosslinks. A higher relaxation rate suggests the existence of weak junctions or with a short lifetime compared to the measurement time. Values similar to those obtained have been reported for physical gels with an absence of crystalline order in the physical junctions [26,27] ($m = 0.08$–0.2).

The lower relaxation rate found for the hybrid gels suggests that the formation of hybrid micelles by the addition of SEP2 chains to the *n*-octane solution increases the lifetime of the physical junctions in the gel. This increment would be caused by a higher stability of the hybrid micelles due to the increment in the number of SEP2 chains in the micelles. This explanation would be supported by the higher capability of micellization of SEP2 compared to SEBS2 in *n*-octane solutions [24].

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