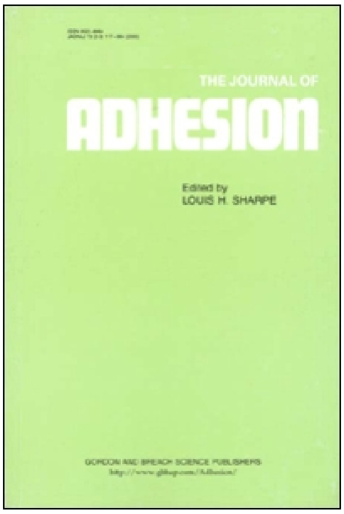

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Rheological Properties of Hot Melt Pressure Sensitive Adhesives (HMPSAs) Based on Styrene-Isoprene Copolymers, Part 3: Rheological Behavior of Different Block Copolymers With High Diblock Content

M. N. Cazenave[a]; C. Derail[a]; F. Leonardi[a]; G. Marin[a]; N. Kappes[b]
[a] Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067, Université de Pau et des Pays de l'Adour, Pau, France [b] ExxonMobil Chemical Europe Inc., Hermeslaan 2, Machelen, Belgium

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Rheological Properties of Hot Melt Pressure Sensitive Adhesives (HMPSAs) Based on Styrene–Isoprene Copolymers, Part 3: Rheological Behavior of Different Block Copolymers with High Diblock Content

M. N. Cazenave
C. Derail
F. Leonardi
G. Marin
Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067,
Université de Pau et des Pays de l'Adour, Pau, France

N. Kappes
ExxonMobil Chemical Europe Inc., Hermeslaan 2, Machelen, Belgium

The processing and application properties of hot-melt pressure-sensitive adhesives (HMPSA) are governed, to a large extent, by their rheological properties. Coating of the HMPSA is performed at high temperatures in the molten state. At room temperature, the adhesive satisfies the Dahlquist criterion and, consequently, has permanent tack. We have particularly studied the full formulations based on triblock and diblock copolymers, and also those based on newly designed molecules, such as tetrablock or radial copolymers. We have demonstrated in the previous articles of this series that, for these systems, the volume fraction of the free polyisoprene is the most important parameter that drives the tack performances by controlling the level of the secondary elastic plateau modulus observed in the low-frequency range. To improve the end-user properties, we have increased the diblock content in the blends. We describe here the dynamic mechanical properties, at room temperature, of the pure copolymer blends (i.e., without addition of a tackifying resin) and the full HMPSA formulations. We focus particularly in this article on blends that contain a high diblock content. The effect of the morphology of the diblock copolymer on the rheological behavior of the adhesive is discussed in detail. Finally, we propose a model, based on molecular dynamics concepts, which describes the rheological behavior in a very wide range of frequencies for all copolymers and full formulations of the study.

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Address correspondence to Christophe Derail, Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067, Université de Pau et des Pays de l'Adour, BP 1155, F-64013 Pau, France. E-mail: christophe.derail@univ-pau.fr

Keywords: Adhesion; Rheological properties; Hot-melt adhesives; Pressure-sensitive adhesives; Rheological model; Mechanical spectroscopy; Copolymers; Blends of block copolymers; Tackifying resin; Master curve; Morphology; Small-angle neutron scattering; Thermomechanical analysis

INTRODUCTION

For hot-melt pressure-sensitive adhesives (HMPSAs), especially those designed for label and tape applications, it is well established that the tack properties are linked to the level of the tensile elastic modulus at intermediate times/frequencies (at 1 Hz the modulus should be lower than 0.1 Mpa, following Ref. [1]). More recently, tack measurements performed on full formulations based on blends of diblock and triblock copolymers [2] show that the adherence performances of the adhesive formulations are strongly linked to the amount of diblock copolymer. We have already studied in detail the relations between the rheological properties and adherence properties of HMPSAs based on homopolymers [3, 4]. We have shown, in particular, that the fracture location is controlled by the viscoelastic properties of the full formulation, in a reasonable agreement with the "trumpet model" [5], which describes, from molecular dynamics concepts based on the reptation picture, the dissipation along the fracture in a viscoelastic solid. Moreover, the trumpet model predicts that the peeling force is linked to the ratio between the secondary elastic plateau modulus (exhibited at low frequencies or large times) and the rubbery modulus (exhibited at intermediate times/frequencies) of the viscoelastic solid adhesive, through an amplifying factor resulting from the large viscoelastic dissipation within the adhesive.

HMPSA formulations based on blends of diblock and triblock copolymers have already been studied in detail in the two first papers of this series [6, 7]. In the first paper, we described the rheological behavior of the pure copolymers and their blends. We showed, in particular, that these blends exhibit a solid-like behavior, with a "soft" secondary elastic plateau in the low-frequency domain. In the second paper, we described how we can replace the polymer base, made of diblock/triblock copolymer blends, by a single tetrablock molecule or by a blend synthesized *in situ*. This is a real breakthrough toward what may be called "dedicated molecular design" [7]. The HMPSA formulations based on these new molecules mimic the rheological behavior of the classical formulations at room temperature, but their processing and end-user properties are improved. In this third paper of this series, we focus on the search for solutions to decrease the secondary elastic plateau in the low frequency range, for all the block copolymers bases described previously [6–10]. One option, which has been explored here, consists of increasing the diblock content within the copolymer blend.

The morphology of the block copolymers [11] can be determined from their phase diagram. It depends on the molecular weight and ratio of the different sequences within the copolymers and on the product between the Flory interaction parameter (χ) and the degree of polymerization (N) [12]. For the diblock copolymers of this study, based on polystyrene and polyisoprene, the phase diagram that defines the copolymer morphology from the variations of the product χN as a function of polyisoprene content may be found in the literature [13, 14]. The different morphologies change the viscoelastic behavior of the copolymer significantly [15], particularly in the low-frequency range where, for the diblock copolymer, it is possible to observe a solid-like behavior for a cubic structure and a liquid-like behavior for the disordered state. Furthermore, the order–disorder temperature allows us to differentiate the copolymers. This particular feature is used in this paper where we have studied the rheological behavior at high diblock content of the copolymers described in the two previous papers [6, 7] by using mechanical spectroscopy and thermomechanical analysis.

After describing the samples and experimental techniques used in this work, we present an exhaustive rheological study of two pure diblock copolymers, mainly to characterize their morphology and understand its relationship with the viscoelastic properties. Then we describe the behavior, at high diblock copolymer (or equivalent) content, for the three families of copolymers: triblock–diblock [SIS-SI] blends, tetrablock [SISI] blends, and radial–diblock [$(SI)_n$-SI] blends. In the third part, we present a rheological model that describes the behavior of these blends (at high diblock content), which improves a model already detailed [6] by taking into account the morphology of the diblock part. As a concluding remark, we propose a concept of "dedicated virtual formulation" based on the molecular dynamic models presented in this series of papers.

EXPERIMENTAL

Samples

As described in our previous papers [6, 7] and patents [8–10], all the pure copolymers as well as the pure blends in copolymers in this paper are based on styrene and isoprene blocks ("pure" means "without addition of a tackifying resin"). All copolymers have about the same styrene content (15%). We have reported in Tables 1 through 4 the

TABLE 1 Characteristic Parameters of Pure Triblock [SIS] and Diblock [SI] Copolymers

Sample	%SI	M_w of SIS ($g{\cdot}mol^{-1}$)	%S in SIS	M_w of SI ($g{\cdot}mol^{-1}$)	%S in SI
Pure diblock copolymers [SI]					
Sample 1	100	—	—	75000	15
Sample 2	100	—	—	87000	16.1
Pure triblock copolymer [SIS]					
Sample 3	0	128000	16	—	—

TABLE 2 Characteristic Parameters of Triblock–Diblock Blends [SIS-SI]

Sample	%SI	M_w of SIS ($g{\cdot}mol^{-1}$)	%S in SIS	M_w of SI ($g{\cdot}mol^{-1}$)	%S in SI
Sample 4	71	128000	16	87000	16.1
Sample 5	76	128000	16	87000	16.1
Sample 6	81	128000	16	87000	16.1
Sample 7	86	128000	16	87000	16.1
Sample 8	75.7	128000	16	75000	15
Sample 9	81	128000	16	75000	15
Sample 10	85	128000	16	75000	15
Sample 11	80	128000	16	104000	16
Sample 12	85	128000	16	104000	16

main structural parameters for the pure diblock [SI] and triblock [SIS] copolymers (Table 1), the blends of diblock and triblock copolymers [SIS-SI] (Table 2), and radial copolymers [$(SI)_n$-SI] (Table 3). The data for tetrablock copolymers are reported in Table 4. All copolymers are noted as sample *n*.

The formulations presented are basically made of 31% of the pure copolymer blends detailed in this paper with two tackifying resins: 42% of solid resin (Escorez 1310, manufactured by ExxonMobil Chemical Co, Houston, TX, USA) and 27% of liquid resin (Wingtack

TABLE 3 Characteristic Parameters of Radial–Diblock Copolymers [$(SI)_n$-SI]

Sample	%SI	M_w of SI ($g{\cdot}mol^{-1}$)	%S
Sample 13	70	70400	17
Sample 14	71	86000	18
Sample 15	75	83000	17.3
Sample 16	88	75000	16.8

TABLE 4 Characteristic Parameters of Tetrablock Copolymers [SISI]

Sample	(equivalent) %SI	M_w of SISI ($g \cdot mol^{-1}$)	%S
Sample 17	71.4	147100	14.5
Sample 18	77.8	157700	16.4

10, manufactured by the Chemical Division of the Goodyear Tire and Rubber Company, Akron, OH, USA). All formulations are based on samples presented in Tables 2 to 4 and are noted HM *n* where *n* is the same number as the copolymer base (sample *n*).

Rheological Experiments

Mechanical Spectroscopy Experiments

The measurement of the complex shear modulus $G^*(\omega)$ (G' storage modulus and G'' loss modulus) as a function of circular frequency, ω, were performed in the frequency range from 10^{-2} to $100\,rad \cdot s^{-1}$, using a Rheometrics RDA II rotational rheometer (Rheometrics, New Castle, Delaware, USA) in parallel–plate geometry and in the linear viscoelastic domain. The time–temperature superposition principle can be used as a first approximation to build a master curve at room temperature reference ($T_{ref} = 20°C$ for all master curves of this article). We have previously demonstrated that the temperature range where the time–temperature superposition can be applied is limited in these systems [6].

The linear viscoelastic domain is defined by a strain sweep at fixed temperature. The strain value for the mechanical spectroscopy experiments is chosen in the domain where the stress presents a linear variation with the strain and the moduli do not depend on the strain value. The master curve exhibits the main relaxation domains and, particularly, the terminal region of relaxation where the diblock copolymer has a strong effect [6].

We recall here that the master curves of the diblock–triblock blends exhibit different relaxation domains, ranging from glassy domain at high frequencies (low temperatures) down to the terminal region at very low frequencies (high temperatures). We observe in the intermediate frequency domain the alpha relaxation (mechanical image of the glass transition), the rubbery domain, and, at last, the slow relaxation of the polyisoprene sequence of the diblock copolymer, which depends on its molecular weight. In the terminal region, we obtained for pure copolymers, as well as for blends and formulations, a secondary elastic plateau that characterizes the behavior of a viscoelastic solid.

In this paper, we focus on the level of the secondary plateau as a function of the diblock content in blends with a high diblock content.

Thermomechanical Analysis

To observe the transition between the different types of morphologies or the order–disorder transition for block copolymers, we have performed thermomechanical experiments ($2^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$), following the variation of G′ and G″ at a fixed circular frequency ($1\,\mathrm{rad} \cdot \mathrm{s}^{-1}$) in the temperature range from 50 to 200 or 260°C, according to the copolymers. The plateau diameter was varied from 5 mm to 20 mm, depending on the modulus level, to minimize instrument compliance and slip effects. These experiments were performed on the same apparatus and with the same geometry as the mechanical spectroscopy experiments previously described.

Small-Angle Neutron Scattering

SANS measurements were performed at the Léon Brillouin Laboratory (CEA-Saclay, France) on the PAXY spectrometer. We have selected a wavelength (denoted λ) of 1 nm (the resolution being about 10%) and a distance (denoted D) between the sample and the detector of 3 m. The sample is held between two quartz cells with a 2-mm path length. Data correction allowed for sample transmission and detector efficiency. Absolute intensities were obtained by reference to the attenuated direct beam; furthermore, the scattering intensity of the pure polyisoprene, considered as the continuous phase for the copolymers of the study, was subtracted from the signal.

For all samples presented in this paper, the scattering figures obtained were isotropic. The one-dimensional data set was generated by circular integration of the corresponding two-dimensional patterns.

EXPERIMENTAL RESULTS AND DISCUSSION

As previously described [6, 7], the polyisoprene part of the diblock copolymer in [SIS-SI] blends acts like a solvent for the entanglement network of the polyisoprene of the triblock copolymer. The variation of the secondary elastic plateau modulus (noted G_{s}) of the blend is well described by a power law:

$$G_{\mathrm{s}} = G_{\mathrm{SIS}}(\omega \to 0) \cdot C_{\mathrm{I/SIS}}^{2} \qquad (1)$$

where $C_{\mathrm{I/SIS}}$ is the volume fraction of polyisoprene phase in the [SIS-SI] blend, which is in the form of triblock copolymer and G_{SIS} is the plateau modulus of the pure triblock copolymer.

We have demonstrated that this law can be applied for volume fraction values of the diblock in the blend lower than 70%. As presented previously [7], the same power law, Equation (1), applies also to the newly designed copolymers: [SISI] (tetrablock copolymers) and [$(SI)_n$-SI] (radial–diblock copolymers). We concluded that the free polyisoprene sequence of the [SISI] tetrablock (the end one) plays the same role as the polyisoprene sequence of the diblock in the blends [SIS-SI] and [$(SI)_n$-SI].

In the present paper, as discussed in the Introduction, we have increased the diblock (or equivalent diblock) content. So, in the next sections, we present the behavior of the pure diblock copolymers of the study and then the behavior of the copolymer bases ([SIS-SI], [SISI], and [$(SI)_n$-SI]) with a high diblock content.

Diblock Copolymers

Rheological Behavior of Pure Diblock Copolymers

The diblock copolymers of the study (samples 1 and 2) are mainly differentiated by the molecular weight of the free polyisoprene sequence. The styrene content is about the same. Both copolymers exhibit a viscoelastic solid behavior as shown in Figure 1, with a secondary elastic plateau appearing at low frequencies. One can observe that the levels of the secondary plateau modulus differ slightly for the two copolymers. One can notice in Figure 1 the effect of the molecular weight of the diblock copolymer. Here, the molecular weight of sample 1 is lower than the molecular weight of sample 2. The styrene content is the same for both copolymers; the molecular weight of the free polyisoprene sequence of sample 1 is, consequently, lower than the molecular weight of the free polyisoprene sequence of sample 2. For sample 2, the terminal region (which can be generally defined from the crossover point between G' and G'') appears at a frequency lower than for the sample 1, because sample 2 has a higher molecular weight (see the shift in Figure 1). This point confirms that the terminal region may be attributed to the relaxation of the free polyisoprene sequence of the diblock [6].

The block copolymers present some microphase separation [11, 12]. At a fixed volume fraction of styrene in the diblock copolymer, one can observe various types of organization that can be characterized by SAXS (small-angle X-ray scattering), SANS (small-angle neutron scattering), or TEM (transmission electron microscopy) as a function of temperature. Another method [16–18] may consist of measuring the evolution of the complex shear modulus at a fixed frequency, as a function of temperature. We have reported in Figure 2 the data obtained

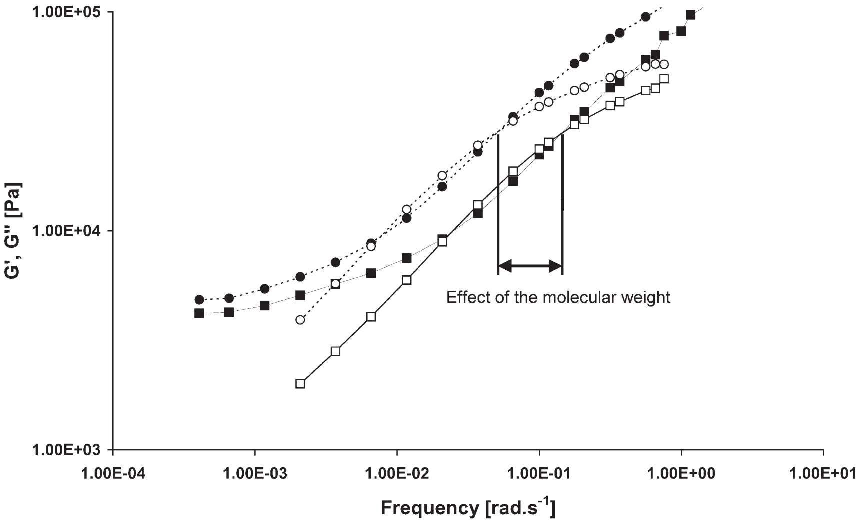

FIGURE 1 Storage and loss moduli *versus* frequency for samples 1 and 2: ■, G′ sample 1; □, G″ sample 1; ●, G′ sample 2; ○, G″ sample 2.

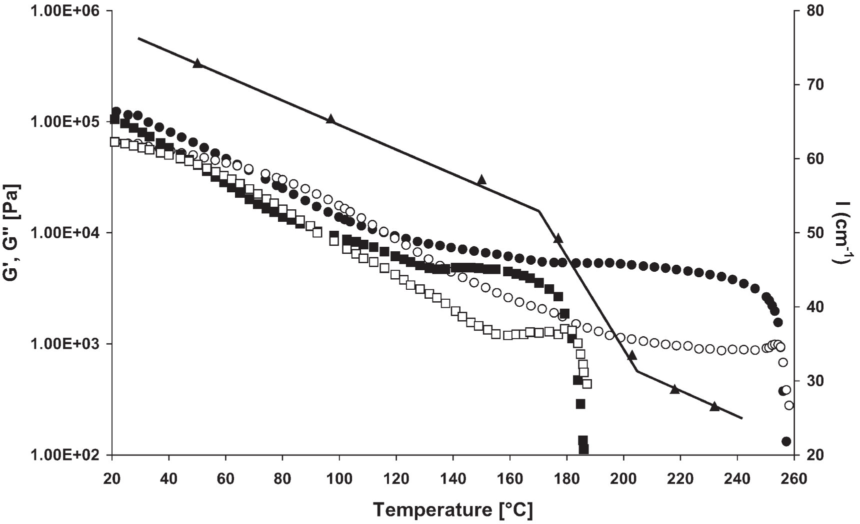

FIGURE 2 On the left scale: Storage and loss moduli *versus* temperature for samples 1 and 2. On the right scale: Imax (cm^{-1}) *versus* temperature for sample 1. ■, G′ sample 1; □, G″ sample 1; ●, G′ sample 2; ○, G″ sample 2; ▲, Imax sample 1.

on samples 1 and 2. We can observe on the thermomechanical analysis curves that both copolymers exhibit a similar behavior as a function of temperature. For sample 1, at $T = 133°C$, we observed that G' increases then drops sharply at a temperature of about $T = 175°C$, which corresponds to the order–disorder temperature, T_{ODT}. For sample 2, the curve presents the same type of variation, with a slight increase of G' at $T = 190°C$, which corresponds to an order–order transition; in the same way as for sample 1, G' decreases sharply at $T_{\text{ODT}} = 250°C$.

One can notice also that the glass transition temperature of the polystyrene part is not the same as for the two copolymers, as already related on similar block copolymers [2].

The large difference measured between the order–disorder temperatures allows us to differentiate between the two diblock copolymers; we see in the next section that this is a very important feature to discriminate between the behavior of the blends. We cannot define exactly the reason for the difference between the two copolymers. It may be due to the specific preparation mode of the two diblock copolymers, which we cannot detail for industrial property reasons.

It is interesting to notice that it has been recently demonstrated, from SAXS experiments, that the nanostructural organization of styrene–isoprene block copolymers may depend on the molecular weight of some free polyisoprene added to a diblock copolymer with a high styrene content [19]. In the next paper, we demonstrate that this point is very important and also that it is possible to correct the solid-like behavior of the diblock copolymer by adding some polyisoprene homopolymer to the blend.

Rheological Behavior of Pure Diblock Formulation

We have formulated sample 2 (pure diblock copolymer) with the same tackifying resins as for the blends. Figure 3 exhibits the rheological behavior of this formulation. One can notice that we obtain a viscoelastic solid behavior with a secondary plateau lower than the secondary plateau of the pure diblock according to the power law (exponent 2) describing the dilution effect of the resins [3]. This result shows that the morphology of the diblock copolymer is maintained in spite of the dilution effect of the tackifying resins. On the same graph, we notice the thermodynamic effect of the tackifying resins, which translates the master curve to a lower frequency range (*i.e.*, increases T_g) [6].

It is important to notice that the industrial formulations must present a secondary plateau that induces aggressive tack and no flow domain. According to the result described here, it should be possible to design a pure diblock copolymer, with a higher value of the secondary

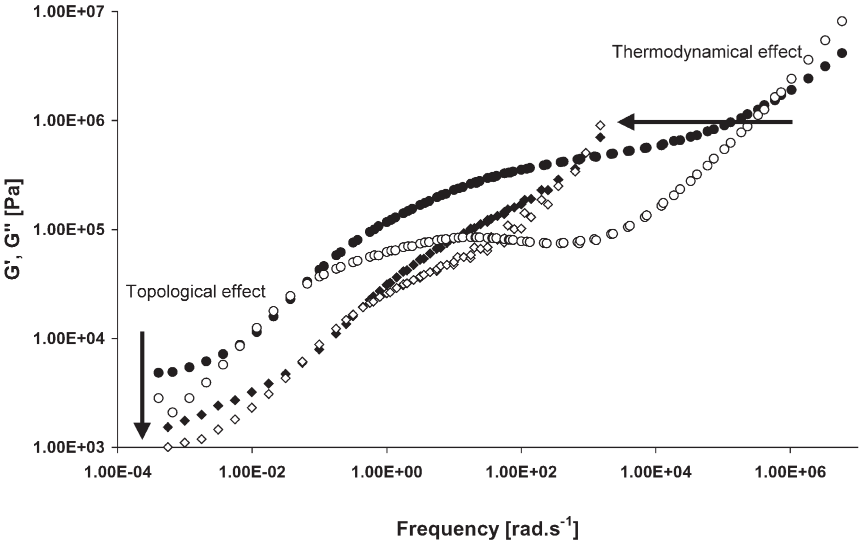

FIGURE 3 Storage and loss moduli *versus* frequency for HM 2 compared with sample 2: ●, G′ sample 2; ○, G″ sample 2; ◆, G′ HM 2; ◇, G″ HM 2.

plateau modulus, which may be a good candidate for industrial applications without added triblock copolymer.

SANS Experiments

According the theoretical phase diagram of a diblock copolymer [13] and the styrene content in the diblock copolymers of the study, one can expect that, for samples 1 and 2, the glassy styrene sequences are organized.

The two-dimensional diffraction diagram of sample 1 and the variation of the scattered intensity are given in Figure 4. Similar graphs describe the properties of sample 2. One can observe that the pattern is isotropic and the scattered intensity exhibits a maximum, which indicates that there is segregation between the styrene sequences (which are glassy at room temperature) and the isoprene parts, but it is not possible to detect the type of the organization.

In Figure 5, we show the effect of temperature on the scattering intensity for sample 1. One can observe that the intensity decreases when temperature increases. We have reported the evolution of the maximum of the scattering intensity on the same graph as the evolution of the shear complex modulus as a function of temperature (Figure 2). One can notice that we measured about the same T_{ODT} with the two experiments.

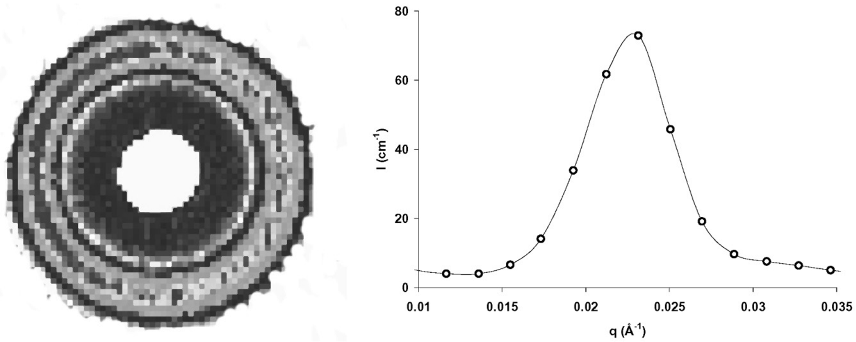

FIGURE 4 Two-dimensional diffraction diagram and scattered intensity of the sample 1 at T = 50°C.

We have also compared the scattering intensity for samples 1 and 2 and reported it in Figure 11. One can observe that the maximum of the scattering intensity for the two diblock copolymers is measured at different amplitudes of the scattering vector, *q*, which is linked to the lattice parameter [20]. So, it is possible to differentiate qualitatively between the two diblock copolymers by SANS.

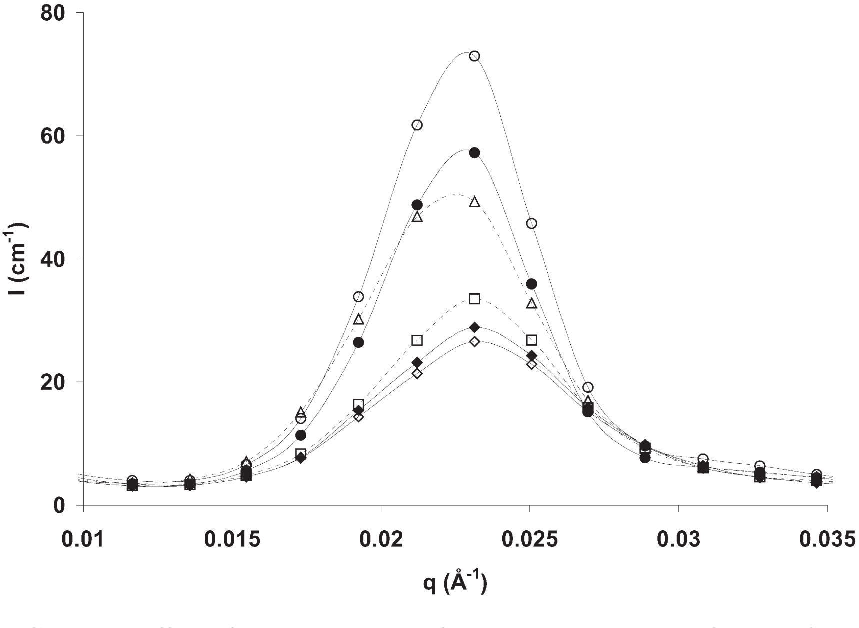

FIGURE 5 Effect of temperature on the scattering intensity for sample 1: ○, 50°C; ●, 150°C; △, 177°C; □, 203°C; ◆, 218°C; ◇, 232°C.

[SIS-SI] Blends

Rheological Behavior

We have increased the diblock copolymer content in the [SIS-SI] blends from 70% to about 90% and measured the rheological behavior of these blends. One can observe in Figure 6 (sample 8) that the rheological behavior of these blends is the same as the samples with a low diblock content; one retrieves the five rheological domains already described [6]:

1—a glassy domain for the higher frequency range,
2—the transition region from the glassy domain down to the rubbery domain at intermediate frequencies,
3—a rubbery plateau domain,
4—a decrease of the storage modulus corresponding to the relaxation of the isoprene sequences of the diblock copolymer, and
5—at lower frequencies, a terminal region corresponding to the secondary plateau modulus (noted G_s). In this work, the value of G_s is measured at a fixed frequency equal to $10^{-3}\,\mathrm{rad{\cdot}s^{-1}}$.

We have performed the rheological analysis on all the samples of the study. We have previously demonstrated [6, 7] that the variation of the secondary plateau level as a function of isoprene volume fraction

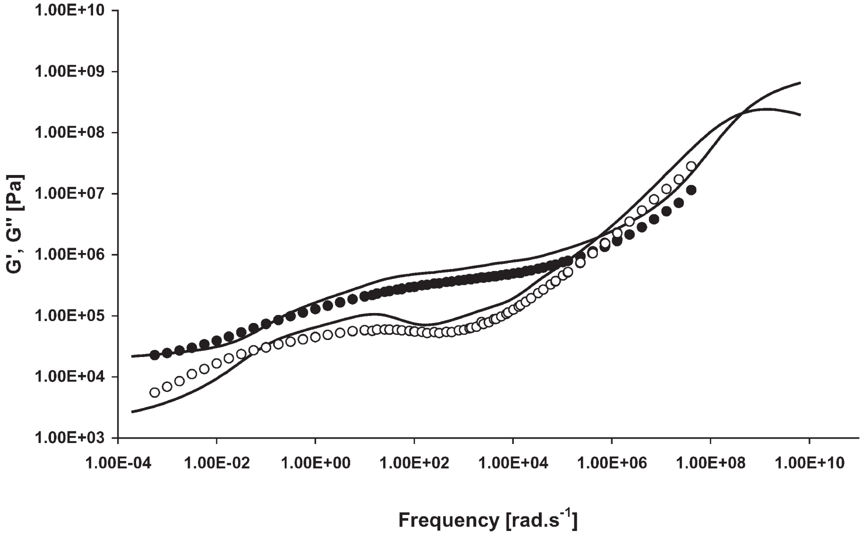

FIGURE 6 Storage and loss moduli *versus* frequency for sample 8. Full line, model: ●, G′ sample 8; ○, G″ sample 8.

in the SIS matrix allows the conclusion that the free isoprene of the diblock plays the same role as the tackifying resin, swelling the entanglement network of the polyisoprene sequence of the SIS triblock copolymer. For example (see Figure 7), samples 6 and 9 (81% of the two different diblock copolymers) exhibit a slight difference for the level of the secondary elastic plateau in the lower frequency range. This difference is about the same as for the level of the secondary elastic plateau of pure diblock copolymers (see Figure 2). Figure 8 exhibits the variations of the secondary elastic plateau modulus for all blends, within the whole range of diblock contents and for the two different diblock copolymers. One can observe that, for the [SIS-SI] blends, Equation (1), which describes the behavior for diblock content lower than 70%, cannot be applied to samples 4 to 7 (blends based on the diblock copolymer, noted sample 2), whereas, for samples 8 to 10 (blends based on the diblock copolymer, noted sample 1) the variation of G_s can be described by Equation (1). Moreover, we observed that, for the blends containing sample 2, the level of the secondary plateau at high diblock content tends toward a constant value of G_s, which is indeed the level of the secondary plateau of the pure diblock.

As described previously, the full formulations (*i.e.*, containing the tackifying resins) based on these pure blends exhibit a solid-like behavior with the appearance of a secondary plateau modulus. As for the pure

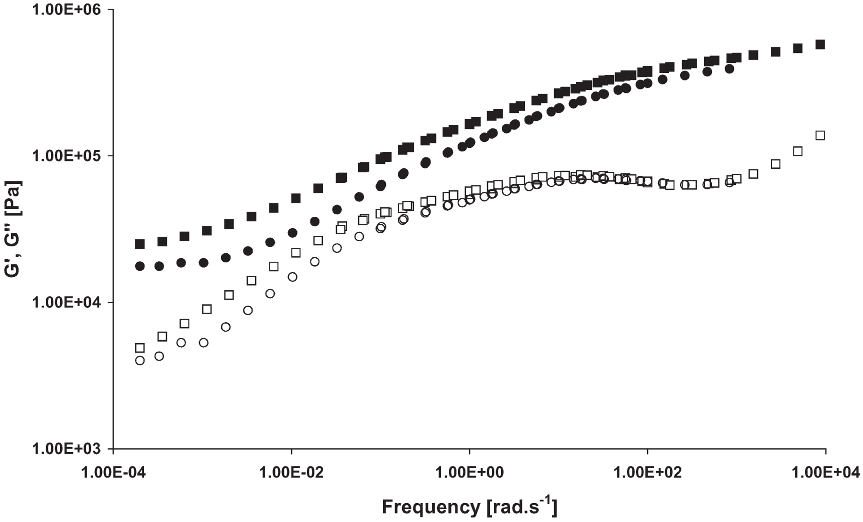

FIGURE 7 Storage and loss moduli *versus* frequency for sample 6 and sample 9: ■, G′ sample 6; □, G″ sample 6; ●, G′ sample 9; ○, G″ sample 9.

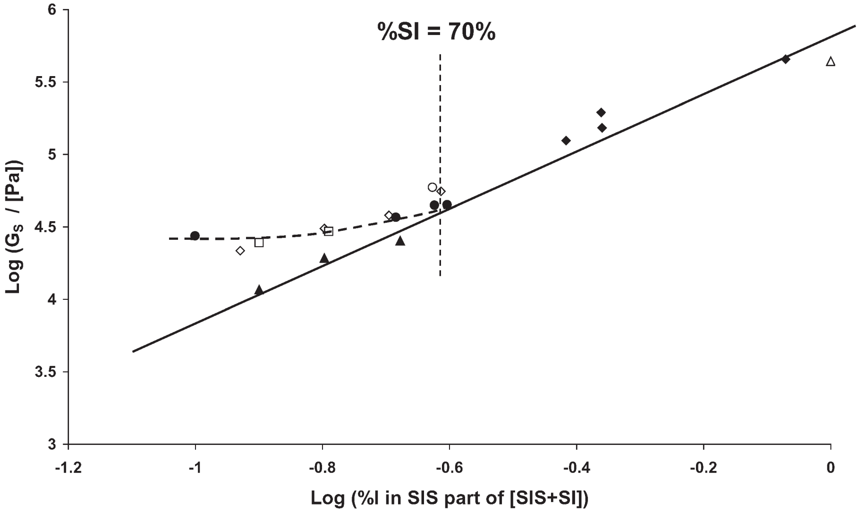

FIGURE 8 Secondary plateau modulus for samples 4 to 18 and from Refs. [1, 2] *versus* polyisoprene volume fraction in the SIS part in the pure [SIS-SI] blend: ◇, sample 4 to 7; ▲, sample 8 to 10; □, sample 11 and 12; ●, sample 13 to 16; ○, sample 17; ◆, samples from Refs. [1, 2]; △, pure polyisoprene.

blends, we can notice in Figure 9 that the variation of the level of the secondary plateau as a function of the polyisoprene fraction of the triblock part within the formulation is exactly the same as for the pure blends.

We observe that the value of G_s for sample HM 9 follows the same rule as for samples containing less than 70% of diblock. The other formulations (HM 5 to 7) present the same constant value of G_s as for the pure copolymers. We have reported in Figure 9 the limiting value of G_s obtained for the formulation based on the pure diblock (see Figure 3). The variation of the secondary plateau tends to this limit. This last point shows that the diblock content is a key parameter to control the rheological behavior of the [SIS-SI] blends.

Thermomechanical Analysis

We have reported in Figure 10 the variation of the complex shear modulus of samples 7 and 10, which are based on the two different diblock copolymers and with similar diblock contents (respectively, 86% of sample 2 and 85% of sample 1). On the same figure, we compare the thermomechanical behavior of these blends and the pure diblock copolymers.

One can confirm, as previously pointed out, that the T_{ODT} of each blend is approximately the same as the T_{ODT} of the pure diblock

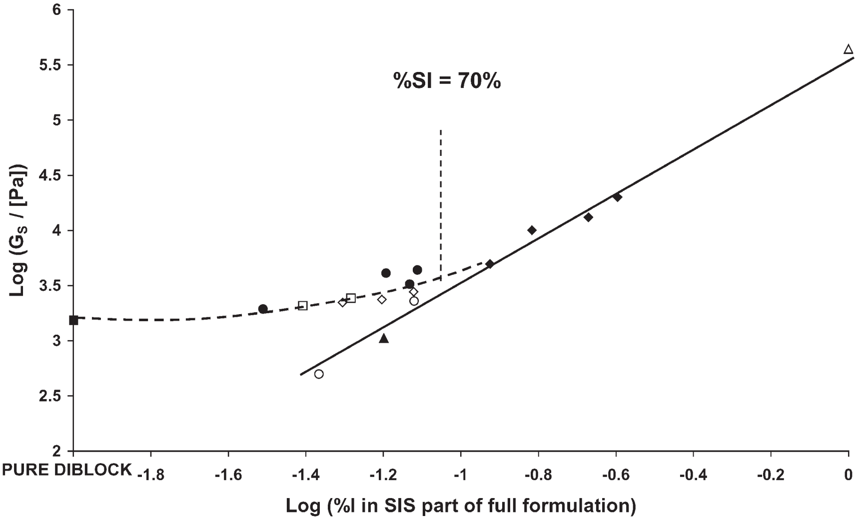

FIGURE 9 Secondary plateau modulus for samples 4 to 18 and from Refs. [1, 2] *versus* polyisoprene volume fraction in the SIS part in the formulation: ■, HM 2; ◇, HM 4 to 6; ▲, HM 8; □, HM 11 to 12; ●, HM 13 to 16; ○, HM 17 and 18; ◆, HM from [1, 2] ; △, pure polyisoprene.

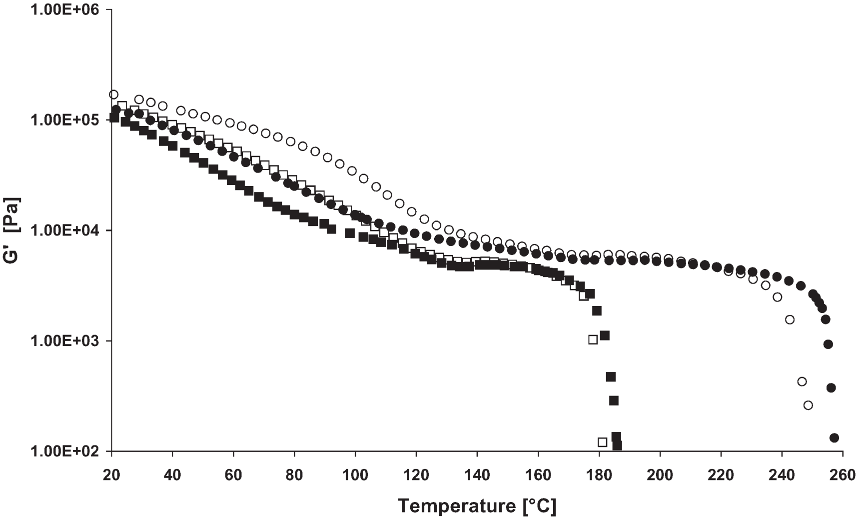

FIGURE 10 Storage modulus *versus* temperature for samples 1 and 2 (pure diblock) and the samples 7 and 10: ■, G′ sample 1; □, G″ sample 10; ●, G′ sample 2 ; ○, G′ sample 7.

copolymers contained in the blends. For samples 7 and 10, we have measured T_{ODT} values of 241°C and 177°C, respectively. We recall that for the pure diblock copolymers, we obtained, respectively, 250°C and 175°C.

SANS Measurements

We have compared the results obtained by SANS experiments on sample 7, sample 10, and the pure diblock contained in these [SIS-SI] blends, that is, respectively, samples 2 and 1. We have reported in Figure 11 the evolution of the normalized scattering intensity for the four samples. In both cases (samples 7 and 2, and samples 10 and 1), the curves are similar, with one peak indicating a segregation of the polystyrene phase within a polyisoprene matrix. We can notice that the values of *q* for the maximum intensity and the value of the maximum intensity are about the same for samples 7 and 2 and for samples 10 and 1.

As a conclusion of this section regarding the [SIS-SI] blends, the data indicate clearly that the diblock "imposes its behavior" on the [SIS-SI] blend at a high diblock content. It is possible to describe qualitatively

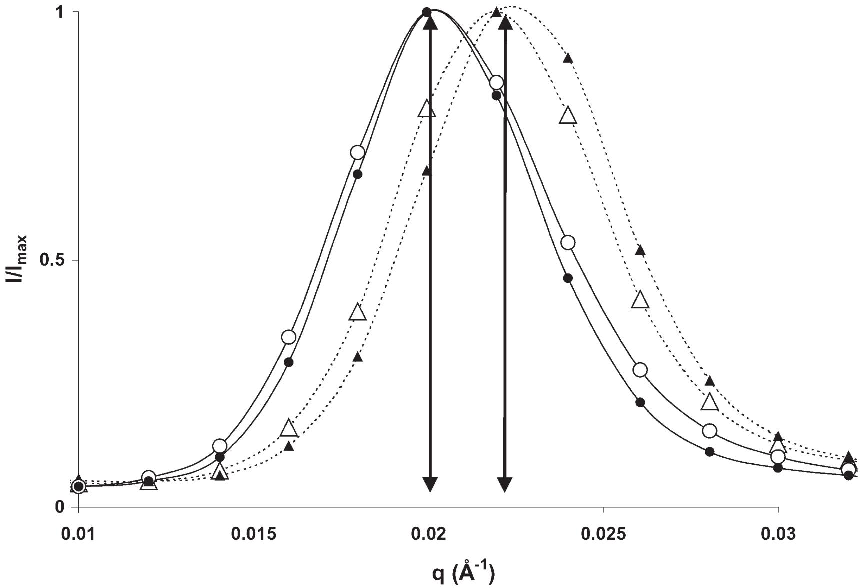

FIGURE 11 Scattering intensity (normalized by the maximum scattered intensity) of samples 1 and 2 and samples 7 and 10 at room temperature: ■, sample 1; △, sample 10; ●, sample 2; ○, sample 7.

the behavior of the [SIS-SI] blends containing sample 1 or sample 2 from the different parameters derived from this work, that is, q for the maximum scattering intensity for SANS experiments and T_{ODT} measured from SANS experiments or thermomechanical analysis.

Copolymers with a New Topology and Design: [SISI] and [(SI)$_n$-SI]

We have shown in our previous articles and patents [7–10] that it is possible to design new molecules that will exhibit a rheological behavior similar to [SIS-SI] blends at room temperature. Starting from our calculations based on the structure–properties relationship derived from molecular models, we have synthesized new molecules that are tetrablock [SISI] copolymers and [(SI)$_n$-SI] radial copolymers with a high diblock or equivalent diblock content.

We have reported in Figures 12 and 13, respectively, the rheological behavior of the HM 16 and HM 18 samples, which contain the highest diblock content copolymers (respectively, 88% and 77.8%) within the families of radial and the tetrablock. One can conclude that, as reported previously for low diblock content [6], the rheological behavior is the same as for [SIS-SI] blends with a similar diblock content. Particularly, in Figure 12 one can notice that the effects of the resins

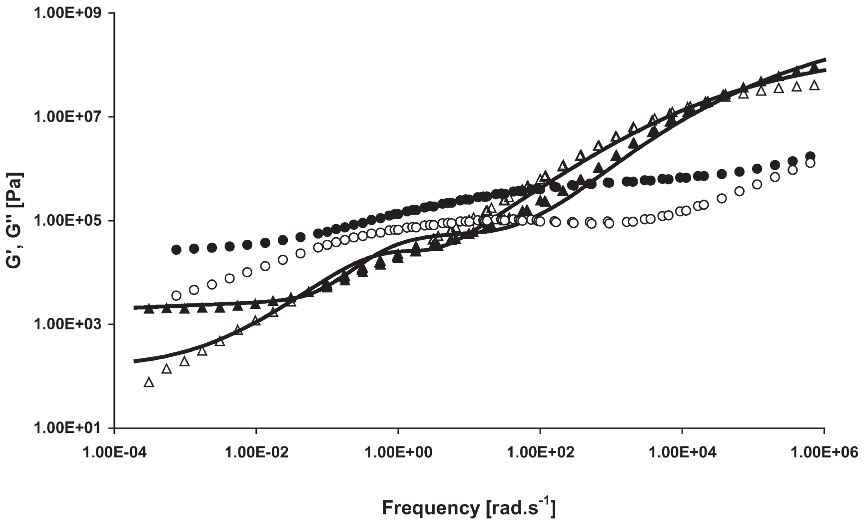

FIGURE 12 Storage and loss moduli *versus* frequency for sample 16 and HM 16. Full line, model: ●, G′ sample 16; ○, G″ sample 16; ▲, G′ HM 16; △, G″ HM 16.

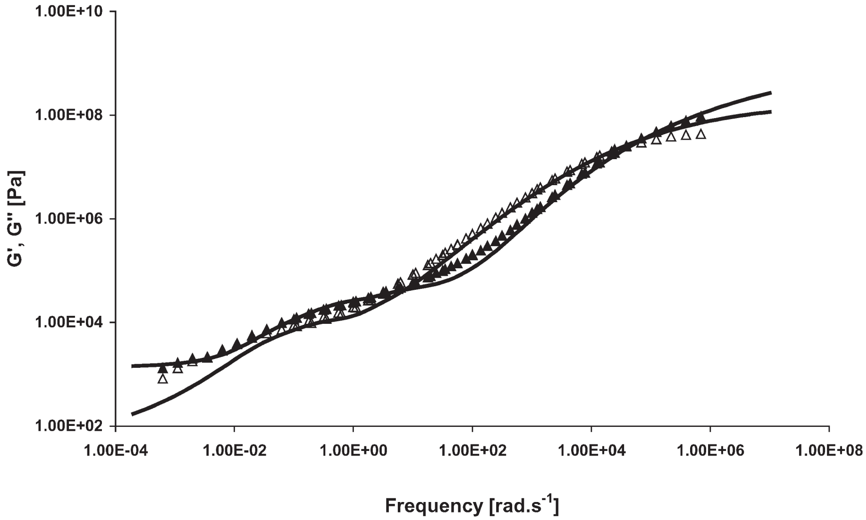

FIGURE 13 Storage and loss moduli *versus* frequency for HM 18. Full line, model: ▲, G′ HM 18; △, G″ HM 18.

described previously for the sample 2 and its formulation (see Figure 3) are similar for new design molecules (here $[(SI)_n\text{-}SI]$).

This feature is more clearly demonstrated in Figures 8 and 9 where one can see, for pure copolymers and full formulations, the variations of the secondary plateau modulus for the new designed copolymers compared with the data obtained for [SIS-SI] blends.

One can observe that all pure copolymers and their formulations have the same behavior; it is possible, however, as for [SIS-SI] blends, to distinguish two domains. The values of the secondary plateau of HM 17 and 18 (which correspond to the tetrablock copolymers without diblock copolymer added), exhibit the same variation as samples with a low diblock content. This variation can be described by Equation (1). The tetrablock copolymers exhibit an ideal behavior with the free polyisoprene end sequence, which swells the network of the trapped polyisoprene sequence as described in [7]. For the samples 13 to 16 and their formulations, which correspond to the radial copolymers, we obtain the same variation as [SIS-SI] samples prepared with sample 2 (pure diblock).

The same conclusions can be drawn for the full formulations.

MODEL FOR THE RHEOLOGICAL BEHAVIOR

We have built a model that describes the rheological behavior, at room temperature, of all copolymers and particularly the copolymers with a high diblock content. The model is based on an analytical approach previously developed [6, 7, 21].

Low Diblock Content

The initial model had been developed for formulations with a low diblock content. The rheological behavior of the diblock, at room temperature, is described as the sum of viscoelastic relaxations which are characteristic of a viscoelastic liquid:

$$G^*_{\mathrm{diblock}} = G^*_{\mathrm{HF}}(\omega) + \mathrm{f}(\Phi_{\mathrm{sty}})[G^*_{\mathrm{A}}(\omega) + G^*_{\mathrm{B}}(\omega) + G^*_{\mathrm{star}}(\omega)] \tag{2}$$

where the factor $\mathrm{f}(\Phi_{\mathrm{sty}})$ takes into account the filler effect of the glassy polystyrene phase and G^*_{i} is the complex shear modulus corresponding to the different domains of relaxation described in Ref. [6].

We have demonstrated [7] that this model can also be applied to the newly designed copolymers at diblock (or equivalent diblock) content lower than 70%, particularly with respect to the swelling effect of the free polyisoprene sequence.

High Diblock Content

When the diblock content increases, we have shown that we must take into account the organization of the diblock copolymer. A phenomenological approach has been proposed to describe the effect of the organization on the rheological behavior in the low frequency range:

$$G^*_{\mathrm{diblock}} = G^*_{\mathrm{HF}}(\omega) + \mathrm{f}(\Phi_{\mathrm{sty}})\left[G^*_{\mathrm{A}}(\omega) + G^*_{\mathrm{B}}(\omega) + G^*_{\mathrm{star}}(\omega) + \mathrm{K}(\mathrm{j}\omega)^{\mathrm{n}}\right] \tag{3}$$

where, in the additional last term, K is a constant and n is an exponent which can be varied with respect to the organization of the diblock. In our case, the value of n is kept constant for all copolymers and full formulations ($\mathrm{n} = 0.1$). This "critical gel" behavior describes reasonably well the terminal relaxation domain of a pure diblock or triblock copolymer.

The viscoelastic solid behavior brought by the organization of the copolymer is described as the behavior of a gel with defects leading to a slight slope for $G'(\omega)$ in the terminal region. It has been proposed in the literature that the value of n could be linked to the nature of the organization of the copolymer [15]. This point is not detailed in this work and we will consider n simply as a fitting parameter. We have determined the value of n by fitting the data obtained on the pure diblock copolymers; this value has been kept constant for pure blends and full formulations.

Comparison between Calculated and Experimental Values

We obtain a reasonable agreement between the calculated and experimental values as shown in Figure 6 for sample 8. For the tetrablock and the radial copolymers (Figures 12 and 13), there is also a good agreement, for the pure polymers as well as the full formulations, taking into account in that case the swelling and thermodynamic effects of the tackifying resins [6].

CONCLUSIONS

This series of papers allows one to describe the rheological behavior of full formulations based on [SIS-SI], [SISI], and [$(SI)_n$-SI] in a wide range of diblock content that corresponds to industrial formulations used for label and tape applications. We have detailed in this last paper the specific effect of a high content of diblock copolymer, which governs the secondary elastic plateau value. This feature explains the two different types of rheological behavior in the terminal region for full formulations based on (i) tetrablock copolymers (without diblock added) and (ii) triblock–diblock [SIS-SI] and radial–diblock [$(SI)_n$–SI] blends with a high diblock content. We have focused on the softening effect of the free polyisoprene sequence that is different according to the spatial organization of the diblock copolymer.

All the experimental results reported in this work demonstrate that the nature of the diblock is a key parameter that controls the rheological behavior of the blends.

The aim of this work is also to confirm that the rheological properties of the full formulations can be predicted from the main molecular parameters of the pure components. For formulations containing less than 70% of diblock, there is no solid-like effect of the diblock (or it is negligible) [6]. We have shown that for diblock content higher than 70%, the solid-like behavior at very low frequencies resulting from the diblock copolymer becomes a key parameter that controls the rheological behavior of the blends. The results obtained on the [SISI] tetrablock copolymers demonstrate that it is possible to "calculate" a copolymer that obeys an "ideal" behavior, whatever the equivalent diblock content.

We recall an important result derived from the trumpet concept, which predicts that the adherence properties of soft adhesives depend on the ratio between the values of the elastic moduli at low and intermediate frequencies. In our case, as the diblock copolymer presents a secondary plateau depending on the copolymer morphology, the adherence properties will be strongly affected accordingly. Using molecular dynamics concepts, we have proposed a molecular model that provides a reasonable description of the viscoelastic properties and gives an efficient "virtual formulation" tool for these systems.

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