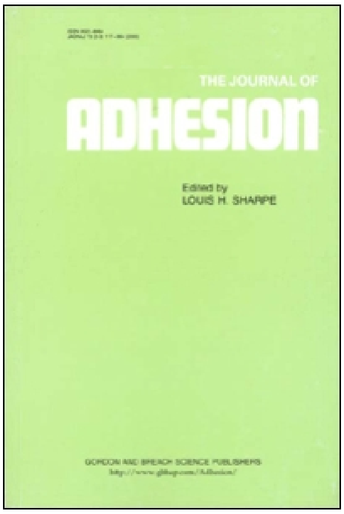

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RHEOLOGICAL PROPERTIES OF HOT-MELT PRESSURE-SENSITIVE ADHESIVE (HMPSAs) BASED ON STYRENE-ISOPRENE COPOLYMERS. PART 2: INNOVATIVE MOLECULAR DESIGN FROM PREDICTIVE FORMUlATION

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RHEOLOGICAL PROPERTIES OF HOT-MELT PRESSURE-SENSITIVE ADHESIVES (HMPSAs) BASED ON STYRENE–ISOPRENE COPOLYMERS. PART 2: INNOVATIVE MOLECULAR DESIGN FROM PREDICTIVE FORMULATION

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This article is the second in a series that deals with the viscoelastic properties of Hot-melt pressure-sensitive adhesives (HMPSAs) based on formulations of block copolymers and tackifying resins. The viscoelastic properties of HMPSAs govern, to a large extent, their adhesion, processing, and end-use properties.

In the first part of this article, we present a brief description of the rheological behavior of styrene isoprene styrene–styrene isoprene [SIS–SI] copolymer blends at room temperature. We then present an original approach that may lead to the design of new block copolymers (tetrablock and radial copolymers) that mimic the rheological behavior at room temperature of optimized SIS–SI blends used in adhesive formulations. We describe the concept and calculations that lead to the design of the characteristics of these new molecules. In the third part of this article, we discuss in detail the rheological behavior of these new block copolymers compared with the observed behavior of equivalent SIS–SI. In the last part we also demonstrate how the molecular model of the rheological behavior developed in the first article of this series can be applied to these new molecules. We propose,

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in particular, to apply the blending law (presented in the first article) on the complex shear modulus instead of the relaxation modulus, which simplifies calculations and even leads to a better agreement with experimental data. As a conclusion, we show how this original approach can bring really innovative solutions for the formulation of adhesives with specific properties by using molecular concepts of viscoelasticity.

Keywords: Adhesion; Rheological properties; Hot-melt pressure-sensitive adhesives; Rheological model; Mechanical spectroscopy; Copolymers; Blends of block copolymers; Tackifying resin; Master curve; Morphology; Molecular design

INTRODUCTION

Hot-melt pressure-sensitive adhesives (HMPSAs) classically used for labels and tapes are basically made of two components: a polymer base that brings the cohesion to the adhesive and a tackifying resin that generally shifts the glass transition and gives tack properties to the formulation [1–5].

The rheological properties of Triblock–Diblock copolymer blends have been studied in detail in the first article of this series [6]. In particular, we have described the effect of Diblock content in the low frequency range (*i.e.*, long times). In this article we have also presented a molecular model of the viscoelastic properties of these blends that is based on molecular dynamics concepts and that allows us to describe the observed behavior as a function of the molecular parameters of the components. We have shown, in particular, that the free polyisoprene sequences of the Diblock copolymer act, at low frequencies, like a solvent for the rubber-like network made by the polyisoprene sequences of the triblock copolymer. On the basis of this observed behavior, we have built a molecular model that presents good agreement with experimental results.

To improve both the processing properties at high temperature (*i.e.*, above the order–disorder transition) and the adherence properties at room temperature of such adhesives, we have designed new molecules from calculations using our molecular model. These new molecules should also bring some additional improvements, such as decrease in the number of components in the formulation and hence an optimization of the process. Thus, we have designed new copolymers that mimic the rheological and adherence properties at room temperature of styrene isoprene styrene–styrene isoprene [SIS–SI]-based formulations. All master curves presented in this article are reported at $T_{ref} = 20°C$, which is the typical end-user temperature of the HMPSA described in this study (labels and tapes applications).

The relationships between the rheological properties and the adherence properties have been described in previous papers [1–5, 7]. Furthermore, the adhesive properties of similar [SIS–SI—resin] blends using a probe tack test are described in Roos [8], where the effect of the Diblock content ($< 55\%$) is studied in particular.

In the first part of the present article we recall the main features expected from a "good adhesive" and the rheological behavior of pure copolymer blends [SIS–SI] as well as full [SIS–SI–resin] formulations. In this part, we describe how we have used our predictive approach to "calculate" the characteristics of new molecules, and we present the molecular characteristics of these new molecules, which have then been synthesized by Dexco (Houston, TX, USA), a partnership of ExxonMobil Chemical Co. (Houston, TX, USA) and Dow Chemical Co. (Midland, MI, USA). In the second part, we propose to compare the rheological properties of [SIS–SI] copolymer blends with the analogous behavior of the new molecules at room temperature. The same comparison is also presented for the full formulations. We compare, in particular, the variations of the secondary rubbery plateau as a function of polyisoprene content. In the last part we also propose to adapt our molecular model to the newly designed molecules.

As a conclusion, we will comment on the way to improve the rheological properties (which govern the adherence and die-cutting properties within the same family of adhesives) by using some newly designed molecules together with a high diblock content.

EXPERIMENTAL AND RESULTS

What is an "Optimized Rheological Behavior" For HMPSA applications?

HMPSAs are generally used at room temperature. These blends of block copolymers and tackifying resins are coated in the melt state at high temperature and must exhibit high tack properties at room temperature. In Figure 1 we present the schematics of a production line of labels with die cutting. The adhesive is coated on a substrate and the assembly is later cut according to the final shape of the labels. For this label application, one substrate is typically poorly adhesive (the release) while the other one is classically paper.

To obtain good tack properties (which can be evaluated by using the Dahlquist criterion [9] as a first approximation) and no (creep) flow at long times, the formulation must exhibit a solid-like viscoelastic behavior upon cooling, which is obtained either by cross-linking,

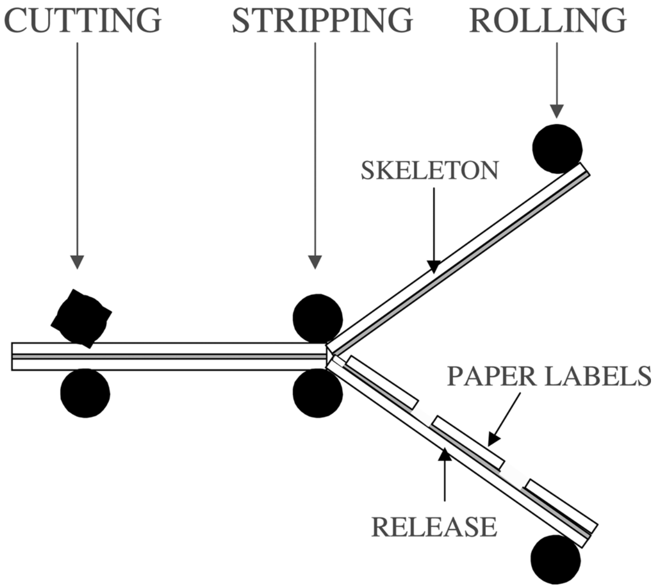

FIGURE 1 Schematic of the die-cutting process for labels and tapes applications. The adhesive is coated in the melt state, cut at intermediate temperatures, and used at room temperature.

crystallization, or by obtaining ordered morphologies in the case of block copolymers [3–5].

Diblock–Triblock Blends: Samples and Rheological Properties

The work presented in this article deals with blends of SI diblock copolymers with SIS triblock copolymers, "pure blends" denoted [SIS–SI] (named sample_n in Table 1), which can be formulated with tackifying resins to obtain a HMPSAs "formulation" denoted [SIS–SI—resin] (named HM_n in Table 1). In this work, all formulations contain: 31% copolymer base, which is detailed in this article; 42% solid resin (Escorez®1310, manufactured by ExxonMobil Chemical Co., Houston, TX, USA) and 27% of liquid resin (Wingtack®10, manufactured by the Chemical Division of the Goodyear Tire and Rubber Company, Akron, OH, USA). An example of the overall rheological behavior of a typical [SIS–SI—resin] is given on Figure 2 for HM_1 (Table 1). This master curve has been obtained by using time–temperature equivalence. We recall on this figure the various rheological domains and their relevant rheological parameters.

TABLE 1 Characteristic Parameters of Pure Triblock (SIS) and Diblock (SI) Copolymers, [SIS–SI] Blends and Full Formulations Based on [SIS–SI]

	% SI	SIS M_w (g . mol^{-1})	% S in SIS	SI M_w (g . mol^{-1})	% S in SI
Pure copolymer					
Sample_1	100	—	—	73000	16
Sample_2 [9]	100	—	—	50200	38
Sample_3	54.3	176000	16	86000	16
Sample_4	0	118000	18.2	—	—
Sample_5	0	154000	15.1	—	—
Sample_6	50	143000	13	65000	28.4
Sample_7	50	234000	12.7	68000	12.6
Full formulation					
HM_1	70	129000	17	102000	12
HM_2	54.3	176000	16	86000	16
HM_3	0	118000	18.2	—	—
HM_4	42	156000	15.1	72000	15
HM_5	19	154000	15.1	72000	15
HM_6	71	130000	17	89000	16.1

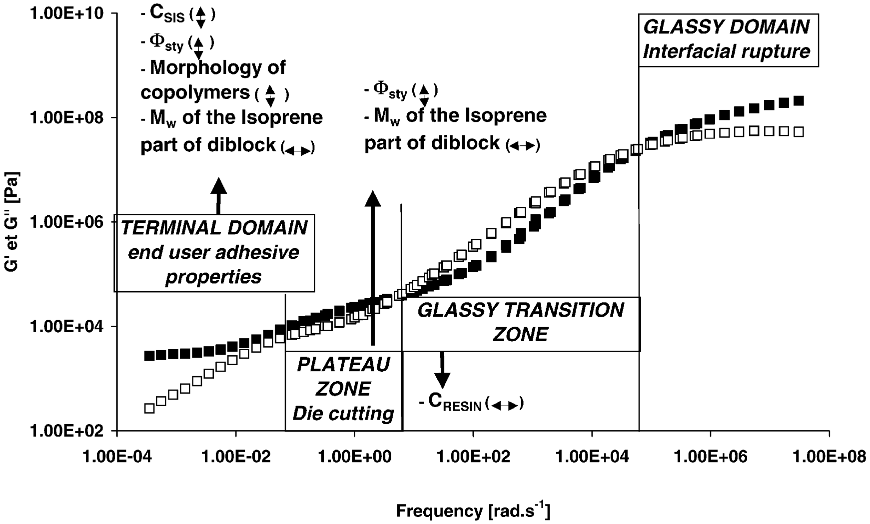

FIGURE 2 Storage and loss moduli *versus* frequency for a [SIS–SI] formulation (HM_1). Summary of the main parameters governing the modulus level (↕) and/or frequency range (↔) in each domain. ■, G′; □, G″.

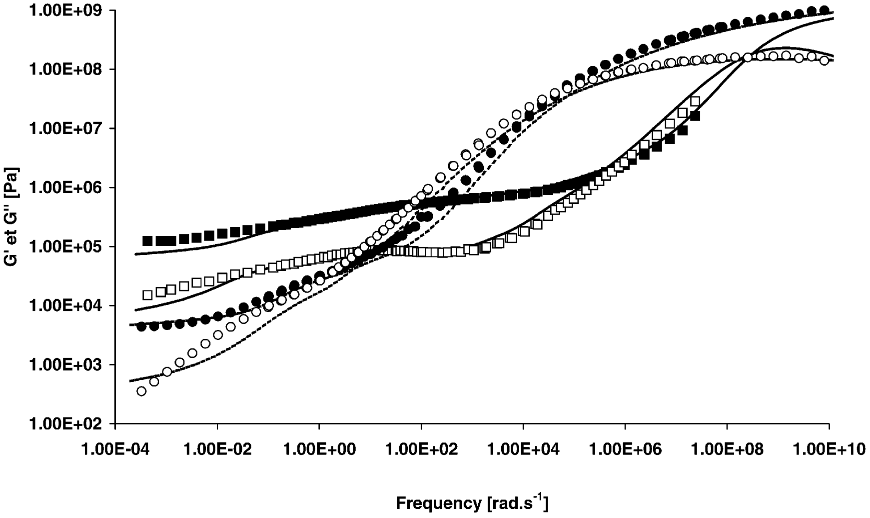

FIGURE 3 Storage and loss moduli *versus* frequency for a pure [SIS−SI] (sample_3) and formulation (HM_2). Comparison with model calculation (line). ■, G′; □, G″; experimental results for sample_3—results from calculation, —; ●, G′; ○, G″; experimental results for HM_2—results from calculation, - - -.

This behavior was described in detail in Gilbent *et al* [6], and it was well described by a model based on molecular dynamics concepts, which will be discussed in the last section of this article. Figure 3 demonstrates the good agreement one can obtain between experimental values and the results of the calculation in the whole frequency range, for a typical pure copolymer blend and its corresponding formulation (sample_3 and HM_2, Table 1). In this model, all parameters depend only on the structural characteristics of the pure copolymers and are not adjustable.

Below we describe an original approach for designing new block copolymers by using this theoretical description. We wish, in fact, to design new molecules that will simplify the composition of the blend and also improve the end-user properties (rheological and adherence) of full formulations as well as the processing of these adhesives (avoid one blending step, pelletizing, *etc.*).

Tetrablock and Radial Copolymers: Samples and Rheological Properties

In order to improve the end-user properties of adhesives based on formulations of copolymer blends with tackifying resins, we will start from the rheological properties of the copolymer base. The tackifying resin has a thermodynamic effect, which generally shifts the glass transition temperature to temperatures closer to the end-user temperature, and a topological effect, which lowers the elastic modulus and brings tack properties to the copolymer base (see Figure 3).

As previously described, the copolymer base is typically a blend of two copolymers synthetized separately. One may then think of designing new copolymers that will present the same rheological behavior at room temperature but will be prepared in only one step. We can imagine two possibilities:

- A single copolymer instead of a blend
- A blend prepared in batch (*i.e.*, without a mechanical blending step).

These methods allow one to simplify the processing operations.

We need a solid-like behavior at room temperature, hence, we need a secondary elastic plateau in the low frequency domain. The level of this secondary elastic plateau is adjusted by adding resin and/or by the free polyisoprene added by the SI part in the [SIS–SI] blend. In our case, the free polyisoprene of the SI Diblock acts like a solvent for the polyisoprene network of the SIS Triblock. Hence, we can reasonably assume that if we have a molecule simultaneously, presenting a free polyisoprene end sequence and another polyisoprene sequence trapped between two parts of polystyrene, we will get the same kind of configuration as for [SIS–SI].

Tetrablock Copolymers

The previously described configuration can be obtained with 4 sequences (Figure 4), polystyrene–polyisoprene–polystyrene–polyisoprene, which can be synthesized with controlled characteristics for each sequence. To obtain a rheological behavior close to the previously defined "optimized" formulations based on copolymer blends and according to the molecular description, we have to calculate the value corresponding to the molecular weight of each block. We will describe the tetrablock copolymers presented here as S_1-I_1-S_2-I_2. The different hypotheses for the calculation of the characteristics of this new molecule are as follows:

The polyisoprene content must respond to two constraints:

- The molecular weight of the free polyisoprene sequence I_2 should be the same as the free polyisoprene sequence of the SI Diblock of the

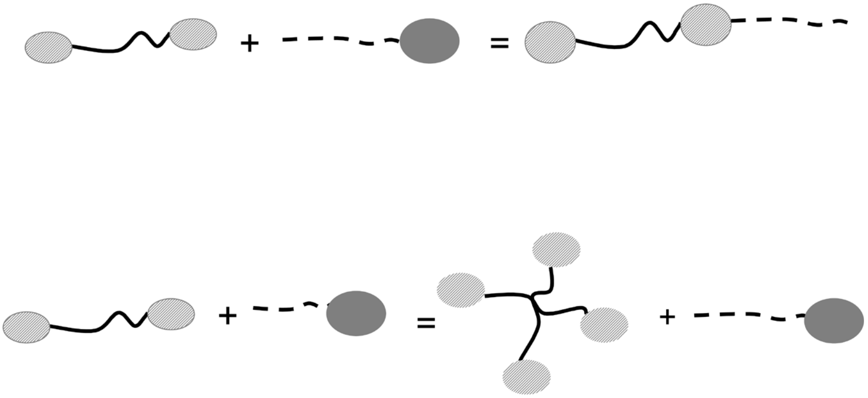

FIGURE 4 Schematic of equivalence between [SIS–SI], [SISI] and [$(SI)_4$–SI]. Black dotted line, free polyisoprene chains of Diblock or Tetrablock copolymers; black full line, polyisoprene chains of Triblock or Radial or Tetrablock copolymers trapped between polystyrene domains. Dark grey ovals, polystyrene domains of the Diblock copolymer. Light grey ovals, polystyrene domains of the Triblock or Radial or Tetrablock copolymers.

[SIS–SI] blend. The frequency range of the secondary plateau is indeed linked to the molecular weight of I_2.

- The molecular weight of the polyisoprene I_1 sequence trapped between the two polystyrene sequences must correspond to the same ratio between SIS and SI as in the blend. We have already demonstrated that the polyisoprene content in the SIS copolymer governs the level of the secondary plateau [6].

The polystyrene content must be the same as the overall styrene content in [SIS–SI], as we have shown that polystyrene acts like a filler of the polyisoprene network. The level of the storage modulus is governed to a large extent by this effect. It is important to recall at this point some important features related to the SIS part:

- The rheological behavior of [SIS–SI] blends does not depend on the overall molecular weight of the SIS copolymer [6]. Thus, the molecular weight of the S_1-I_1-S_2 part is not, as a first approximation, important.
- The polyisoprene of the SIS part in [SIS–SI] has to be entangled. Thus, the molecular weight of the polyisoprene part must be higher than the critical molecular weight for entanglements of polyisoprene.

It is possible to mimic sample_3 (which is a [SIS−SI] blend; Table 1) by designing the equivalent SISI copolymer. We define three variables according to the hypotheses previously described:

- M_{WS} is the molecular weight of the polystyrene block in the equivalent SIS of the new molecule: S_1-I_1-S_2 part in S_1-I_1-S_2-I_2 tetrablock. In this article, the molecular weights of the polystyrene parts are the same in all SISI tetrablocks.
- M_{WI1} is the molecular weight of the I_1 polyisoprene block in the equivalent SIS of the new S_1-I_1-S_2-I_2 tetrablock.
- M_{WI2} is the molecular weight of the terminal I_2 polyisoprene block in the equivalent SI of the new S_1-I_1-S_2-I_2 tetrablock.

According to the characteristics of the [SIS−SI] blend to mimic, one can calculate these new values for the SISI copolymer. Three equations must be written to calculate the three unknown parameters (M_{WS}, M_{WI1}, M_{WI2}):

$$2.M_{WS} = \Phi_{sty}.(2.M_{WS} + M_{WI1} + M_{WI2}), \tag{1}$$

$$M_{WI2} = \Phi_{SI}.(M_{WI1} + M_{WI2}), \tag{2}$$

$$M_{WI2} = M_{WSI}\cdot(1 - \Phi_{sty}), \tag{3}$$

where: Φ_{SI} is the volume fraction of Diblock in the [SIS−SI] blend, Φ_{Sty} is the volume fraction of polystyrene in the [SIS−SI] blend, and M_{WSI} is the molecular weight of the Diblock sequence.

Starting from the values corresponding to the [SIS−SI] blend, we have calculated the characteristics of its equivalent SISI copolymer; this tetrablock copolymer has then been synthesized by Dexco. The corresponding values are reported in the Table 2, sample_8.

The calculation is the same for all other newly designed molecules.We have reported on Figure 5 the rheological master curve corresponding to sample_3 (Table 1), which is a [SIS−SI] blend, while sample_8 (Table 2) is the [SISI] equivalent to sample_3. The calculations of the structural parameters of this tetrablock correspond to the above description. One can verify that we indeed obtain a very good agreement between the two pure copolymers at room temperature. This very encouraging result drove us to synthesize another [SISI] tetrablock copolymer with different characteristics (Table 2).

All of the tetrablock copolymers synthesized and the full formulations are reported in Table 2.

TABLE 2 Characteristic Parameters of Pure Tetrablock Copolymers [SISI] and Full Formulations Based on [SISI]

	SISI M_w ($g.mol^{-1}$)	I_2 M_w ($g.mol^{-1}$)	I_1 M_w ($g.mol^{-1}$)	S M_w ($g.mol^{-1}$)	% S
Pure copolymer					
Sample_8	154800	70000	60000	12400	16
Sample_9	147100	94300	31400	10700	14.5
Full formulation					
HM_7	139200	71000	47400	10400	15
HM_8	135500	45600	68300	10800	16
HM_9	163600	64600	72800	13100	16
HM_10	152700	60300	68000	12200	16
HM_11	147100	31400	94300	10700	14.5

Radial Copolymers

Another imaginable design is to attach four SI Diblock copolymers like a four-branch star, the polystyrene sequences being outside (Figure 4). If some excess Diblock copolymer remains in the reactor after polymerization of the radial polymer, we will get, in one step,

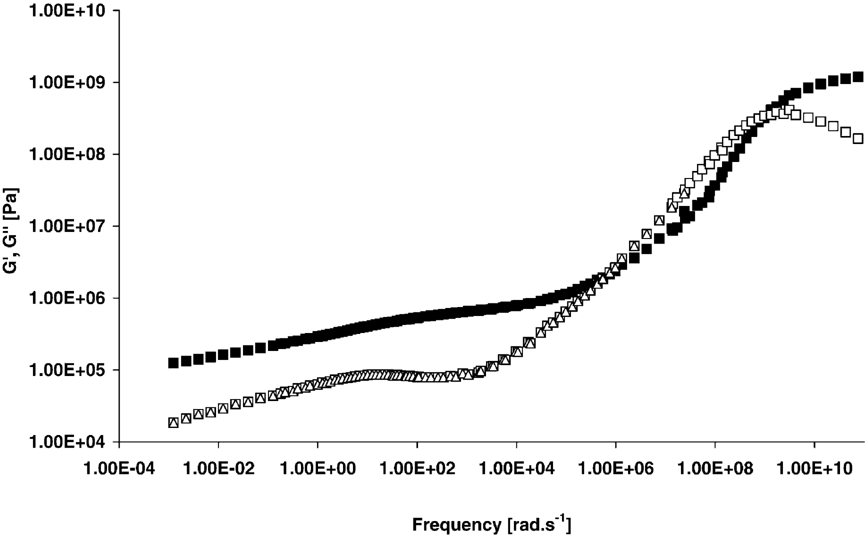

FIGURE 5 Storage and loss moduli versus frequency for [SIS–SI] sample_3 compared with SISI sample_8: ■, G′; □, G″, sample_3; ▲, G′; △, G″, sample_8.

a blend of Radial + Diblock copolymers noted [$(SI)_4$–SI]. The hypothesis for calculation of characteristics of each part of the radial copolymer are the same as previously described for tetrablock SISI.

We have performed the same calculation for a blend of a Radial and Diblock copolymers that was synthesized in batch. We have reported in Figure 6 the rheological master curve of sample_10 (Table 3).

All radial copolymers synthesized and the full formulations are reported in the Table 3.

As a first conclusion, one can say that, according to the molecular models we developed, molecules with a free polyisoprene end and a polyisoprene sequence trapped between polystyrene blocks would be good candidates to mimic the behavior of a regular [SIS–SI] blend. In order to test our concept, in the next part we will discuss the rheological behavior of these new copolymers.

Full Formulations

The main objective of this work is not rheology but, indeed, adhesive formulation. The rheological properties aimed for always correspond to optimized processing and/or adherence properties [3, 8, 13]. We have formulated these copolymers with a tackifying resin and

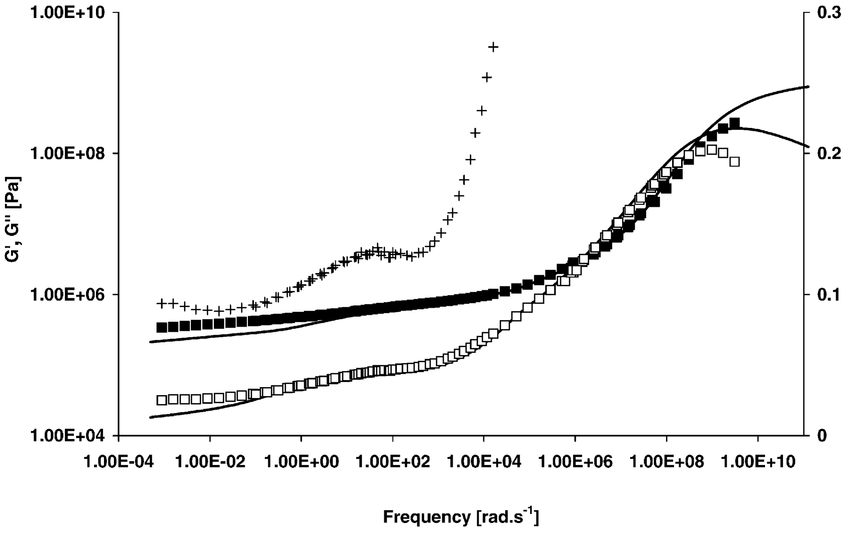

FIGURE 6 Storage and loss moduli *versus* frequency for [$(SI)_4$–SI] sample_10. Right scale refers to tan δ. ■, G′; □, G″; +, tan δ; full line, model.

TABLE 3 Characteristic Parameters of Pure Radial Copolymers [$(SIS)_4$−SI] and Full Formulations Based on [$(SIS)_4$−SI]

	[$(SI)_4$-SI] M_w (g.mol^{-1})	$(SI)_4$ M_w (g.mol^{-1})	SI M_w (g.mol^{-1})	% S	% SI
Pure copolymer					
Sample_10	335000	268000	67000	20.6	31
Sample_11	430000	344000	86000	18	71
Sample_12	352400	282000	70400	17	70
Full formulation					
HM_12	375000	300000	75000	18.3	50
HM_13	352400	282000	70400	17	70
HM_14	375000	300000	75000	18	69
HM_15	410000	328000	82000	18	70
HM_16	430000	344000	86000	18	71
HM_17	350000	280000	70000	17.3	50
HM_18	375000	300000	75000	18.3	50
HM_19	398000	318400	79600	17	60

measured their rheological behavior. Figure 7 shows the rheological master curves of sample HM_12 (Table 3) obtained from an [$(SI)_4$−SI] SI] base. The observed behavior is equivalent to that of the regular [SIS−SI]-based formulation reported on Figure 2.

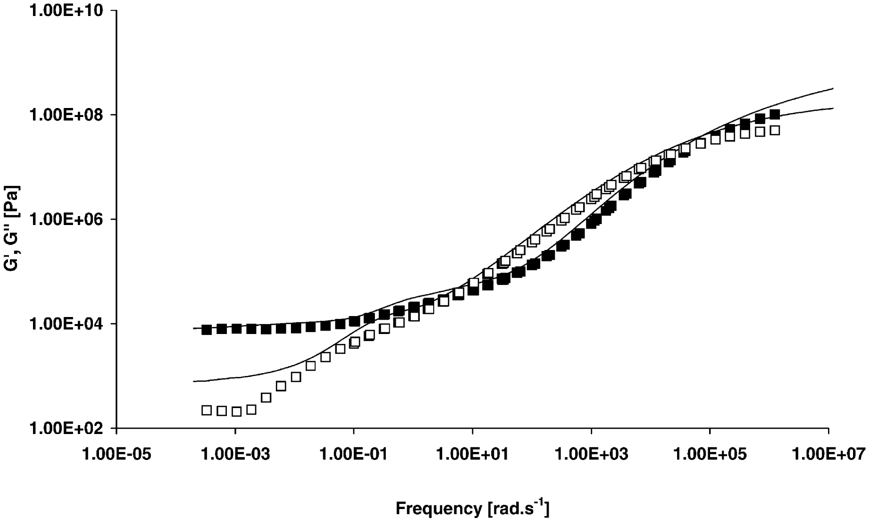

FIGURE 7 Storage and loss moduli *versus* frequency for a [$(SI)_4$−SI] formulation (HM_12, Table 3). Comparison with model calculation (full line). ■, G′; □, G″.

DISCUSSION

Different copolymers [SISI] and [$(SI)_4$–SI] have been synthesized in order to establish whether the rheological behavior at room temperature was close to its equivalent [SIS–SI] counterpart. We have performed the same experimental study as described in detail in the first article [6] of this series.

Rheological Properties of the Newly Designed Copolymers

As previously described (see Figures 5 and 6), we retrieve for these new samples the same relaxation domains as for [SIS–SI] blends (starting from high frequencies):

1. A glassy domain at higher frequencies;
2. A 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 polyisoprene sequence of the Diblock copolymer, which can be observed on the variations of tan δ; and
5. A terminal zone corresponding to the secondary plateau modulus (G_s) of the Triblock part, which is swollen by the polyisoprene sequence of the Diblock. This domain yields a specific viscoelastic solid behavior to the blend. In this domain, the value of the secondary plateau depends on the Diblock or equivalent Diblock content.

These two last figures show that, at room temperature, the rheological behavior of copolymers can really be predicted by using the molecular dynamics concepts developed in Gibert *et al.* [6].

Some Comments on the "Secondary Plateau"

As already pointed out, the level of the secondary plateau depends on the volume fraction of the Diblock (or equivalent Diblock) in the copolymer blend or in the tetrablock. In this article, we deal with Diblock volume fractions (or equivalent volume fractions) from 0–70%.

For [SIS–SI] copolymers, a secondary elastic plateau appears on the storage modulus, G', at very low frequencies. This is the rheological signature of the morphology of these block copolymers. We have demonstrated previously [6] that the level of this secondary plateau ($G_{SIS/SI}$) is linked to the Triblock (SIS) content following a power law,

$$G_S = G_{SIS/SI}(\omega \to 0) = G_{SIS}(\omega \to 0) \cdot C^2_{I/SIS}, \tag{4}$$

where $C_{I/SIS}$ is the volume fraction of polyisoprene within the SIS triblock in the [SIS−SI] blend and G_{SIS} is the plateau modulus of the pure Triblock copolymer. According to Equation (4), which agrees with the molecular dynamics concepts developed by de Gennes [14], the free polyisoprene sequence of a (SI) Diblock copolymer acts like a solvent for the polyisoprene entanglement network of the polyisoprene sequences of the Triblock copolymer, the polyisoprene sequences being trapped by glassy nodules of polystyrene. Furthermore, the glassy polystyrene acts like a filler of a polyisoprene matrix. In Figure 8 we show a scheme of this concept.

Besides the thermodynamic effect that increases the T_α (hence the Tg) of the formulation, the tackifying resin also has a topological effect by swelling the polyisoprene network, which decreases the level of the secondary plateau (softening/tackifying effect). This effect can be described as a power law of the volume of polymer in the formulation, in the same way as the SI effect, with a slightly higher exponent, still close to the theoretical value of 2.3 [2, 6, 15]:

$$G^0_{n,HM} = G^0_{n,SIS-SI} \cdot \Phi^{2.48}_{SIS-SI}, \tag{5}$$

where Φ_{SIS-SI} is the volume fraction of polymer in the formulation.

The specific morphologies observed for block copolymers explain the secondary elastic plateau [12] observed at low frequencies: we indeed

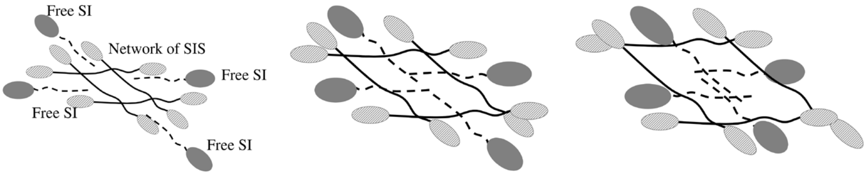

FIGURE 8 Schematic of the role of the free polyisoprene part of a Diblock copolymer in a network of Triblock copolymer. Polyisoprene acts like a solvent of the elastomeric entanglement network trapped by glassy domains of Polystyrene. Black dotted line, free polyisoprene chains of Diblock or Tetrablock copolymers; black full line, polyisoprene chains of Triblock or Radial or Tetrablock copolymers trapped between polystyrene domains; dark grey ovals, polystyrene domains of the Diblock copolymer; light grey ovals, polystyrene domains of the Triblock or Radial or Tetrablock copolymers.

observe this secondary plateau for pure Diblock copolymers, although the polyisoprene part is (partially) free. The detailed characterization of the morphology of our systems is clearly beyond the scope of the present article. This is presently under study and will be presented in a future article.

The rheological behavior of a Diblock copolymer synthesized by Dexco (Houston, TX, USA) is reported in Figure 9. In the literature [16] we found the rheological data at high temperature of a similar Diblock copolymer. In both cases we observe at low frequencies the onset of a secondary plateau due to the morphology, which leads to a solid-like behavior. The literature shows that copolymers exhibit a specific regular arrangement of glassy nodules at temperatures below the order–disorder transition, using transmission electron microscopy [17–20], small angle neutron scattering, or small angle X-ray scattering [20–22]. The work presented here deals precisely with the rheological behavior at room temperature, *i.e.*, below the glass transition of polystyrene. The secondary plateau is a signature of the viscoelastic solid behavior brought by this morphology, and we have considered that this effect can be described, at room temperature and in the low frequency domain, alternately as a purely elastic behavior (G = ct) or as the behavior of a gel with defects (power law with a small exponent).

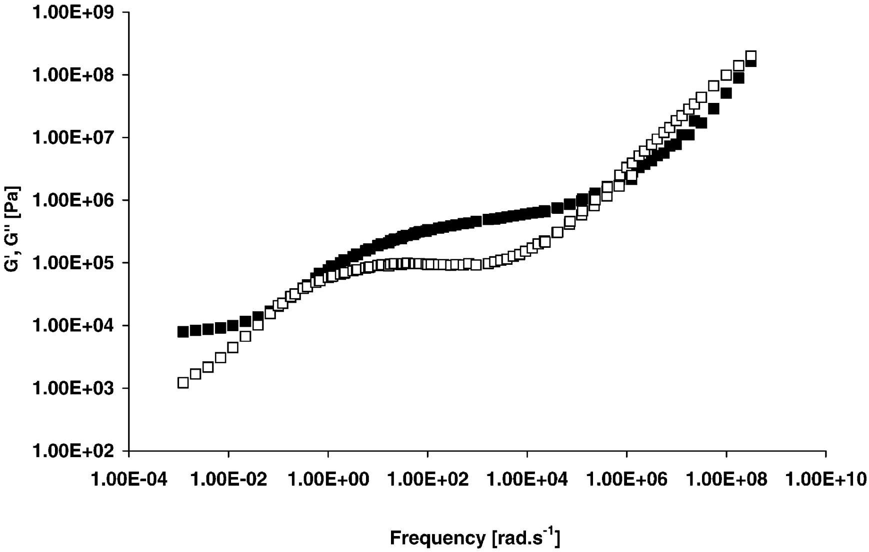

FIGURE 9 Storage and loss moduli *versus* frequency for pure SI Diblock sample_1. ■, G′; □, G″, sample_1.

There is no flow occurring in the temperature range corresponding to the end-use properties of these formulations. This is a key property to point out when one comes to mimic that type of rheological behavior with newly designed molecules. Besides, the high-frequency domain corresponds, as a first approximation, to the glass transition of pure polyisoprene, while the intermediate-frequency range corresponds to the plateau zone due to the polyisoprene network of SIS, as previously described [6, 23].

Pure Copolymers

In Figure 10 we have plotted the variations of the logarithm of the secondary plateau (for all pure copolymers reported in Tables 1, 2, and 3) as a function of the logarithm of the polyisoprene volume fraction (in the SIS part of [SIS$-$SI] blend, in the SI_1S part of [SISI], and in the $(SI)_4$ part for radials). We can observe that all points for the various families of copolymers lie along the same line with the same level of secondary plateau for a given polyisoprene volume fraction. The power law exhibits the same exponent as the [SIS$-$SI] blends, as a first approximation. This important point shows that, for all samples, the free polyisoprene sequence of the Diblock (or equivalent) part acts like a solvent for the polyisoprene network of the SIS (or equivalent) part.

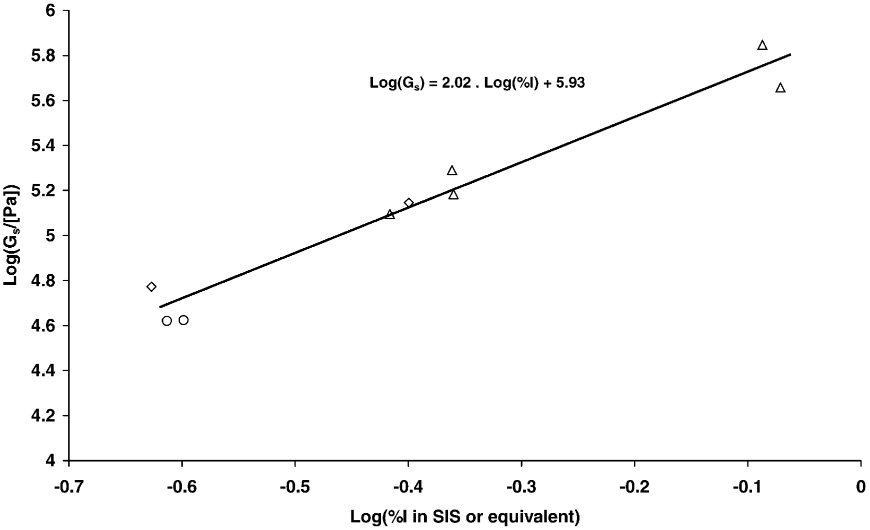

FIGURE 10 Double logarithm plot of the secondary plateau modulus of all samples (3, 4, 5, 8, 9, 10, 11, 12 (Tables 1, 2 and 3)) *versus* the polyisoprene volume fraction. △, [SIS$-$SI]; □, [SISI]; ○, [$(SI)_4$$-$SI].

In the same way, the filler effect of polystyrene seems to be basically the same as for [SIS−SI] blends because the level of the plateau modulus is the same at equivalent polystyrene volume fraction.

It is possible to describe the level of the secondary plateau (G_S) for all [SIS−SI] blends, as well as [SISI] and [$(SI)_4$−SI], as a function of Triblock (or equivalent) content by a power law:

$$G_S = G_{\mathrm{SIS\ or\ equivalent/SI}}(\omega \to 0).C^2_{\mathrm{I/SIS\ or\ equivalent}}, \tag{6}$$

where $C_{\mathrm{I/SIS\ or\ equivalent}}$ is the volume fraction of SIS (or equivalent) in the blend [SIS−SI] (or [SISI] or [$(SI)_4$−SI]) and $G_{\mathrm{SIS\ or\ equivalent}}$ is the plateau modulus of the pure copolymer. Equation (6) is, in fact, the same as Equation (4).

Full Formulations

As for pure copolymers, Figure 11 in we report the variations of the logarithm of the secondary plateau for all formulations (Tables 1, 2, and 3) as a function of the logarithm of the polyisoprene volume fraction in the SIS (or equivalent) part. The exponent is close to two, which demonstrates that the tackifying resin as well as the polyisoprene of the Diblock (or equivalent) part acts like a good solvent for

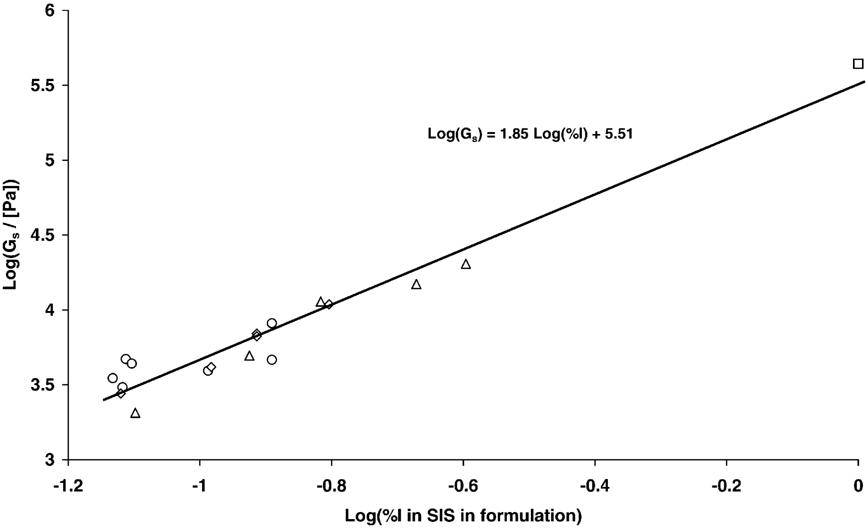

FIGURE 11 Double logarithm of the secondary plateau modulus of all HM (Tables 1, 2, and 3) versus the polyisoprene volume fraction. △, [SIS−SI]; ◇, [SISI]; ○, [$(SI)_4$−SI]; □, pure polyisoprene.

the polyisoprene network of the SIS (or equivalent) part. The line follows the same power law as Equation (6).

Figures 10 and 11 exhibit the same variations of the secondary plateau as a function of polyisoprene content in the SIS (or equivalent) part. All copolymers and formulations prepared on the basis of the hypothesis described in the previous section present a similar rheological behavior and exhibit, in particular, the same power law, describing the solvent effect of the free polyisoprene. This similar behavior can be modeled using the same approach as for [SIS−SI] blends.

A RHEOLOGICAL MODEL FOR THE NEW COPOLYMERS: TETRABLOCKS AND RADIALS

Blending Law

We recall the two principal equations that describe the viscoelastic behavior of Diblock and Triblock copolymers:

$$\mathrm{G}^*_{\mathrm{tribloc}}(\omega) = \mathrm{G}^*_{\mathrm{HF}}(\omega) + \mathrm{f}(\Phi_{\mathrm{sty}}).\Big(\mathrm{G}^*_{\mathrm{A}}(\omega) + \mathrm{G}^*_{\mathrm{gel}}(\omega)\Big), \tag{7}$$

$$\mathrm{G}^*_{\mathrm{dibloc}}(\omega) = \mathrm{G}^*_{\mathrm{HF}}(\omega) + \mathrm{f}(\Phi_{\mathrm{sty}}).\big(\mathrm{G}^*_{\mathrm{A}}(\omega) + \mathrm{G}^*_{\mathrm{B}}(\omega) + \mathrm{G}^*_{\mathrm{star}}(\omega)\big), \tag{8}$$

where each term corresponds to a relaxation domain described by an appropriate equation well detailed in Gibert *et al.* [6] and Gibert [23]. In this model, we have proposed a quadratic blending law of the "double reptation" type to express the viscoelastic behavior of [Diblock + Triblock] blends. This law was written for the relaxation modulus G(t) as

$$\mathrm{G}^{0.5}_{[\mathrm{SIS-SI}]}(\mathrm{t}) = \mathrm{C}_{\mathrm{triblock}}\mathrm{G}^{0.5}_{\mathrm{triblock}}(\mathrm{t}) + (1 - \mathrm{C}_{\mathrm{triblock}}).\mathrm{G}^{0.5}_{\mathrm{diblock.}} \tag{9}$$

It is also possible to write the same blending law on the complex shear modulus:

$$\mathrm{G}^{*0.5}_{[\mathrm{SIS-SI}]}(\omega) = \mathrm{C}_{\mathrm{triblock}}\mathrm{G}^{*0.5}_{\mathrm{triblock}}(\omega) + (1 - \mathrm{C}_{\mathrm{triblock}}).\mathrm{G}^{*0.5}_{\mathrm{diblock}}(\omega). \tag{10}$$

The results obtained from the two calculations are quite close. In Figure 12 we present the results of the calculation from both equations for a full formulation based on a SISI tetrablock (HM_7, Table 2).

The double reptation law applied to the complex shear moduli increases the coupling between the relaxation processes and "smooths" the intermediary domains, leading to a better agreement with experimental data. The other advantage of Equation (10) is a simplification of the calculation, avoiding the calculation of Fourier transforms from the time domain to the frequency domain.

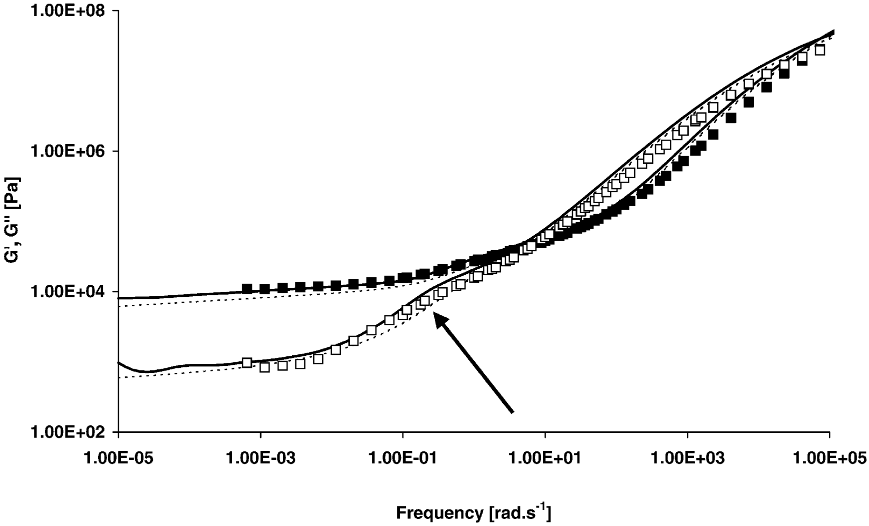

FIGURE 12 Storage and loss moduli *versus* frequency for a SISI formulation (HM_7, Table 2). Comparison with the two model calculations. ■, G′; □, G″, experimental value; - - -, blending law (Equation (10)); —, blending law (Equation (9)).

Comparison Between Experimental and Calculated Values

We have used the same approach to build a predictive rheological model for all copolymers presented in this article. One can observe in Figure 6 the good agreement between experimental values and results of the calculation for a pure Radial copolymer (sample_10, Table 3).

In the same way, we can observe on Figure 7 the good agreement between experimental values and calculation for a Radial copolymer-based full formulation (HM_12, Table 3).

CONCLUSIONS

The viscoelastic properties of HMPSAs based on blends of [Triblock + Diblock] copolymers and equivalent Tetrablock or Radial copolymers were studied over a wide range of frequencies using time–temperature equivalence. We introduced an original approach to design new molecules in order to improve both adhesive and processing properties. This approach is based on the molecular description of the behavior of the blends using molecular dynamics concepts. We demonstrated how to design copolymers with new architectures or new copolymer blends with expected rheological behavior at room temperature. We have shown that our model, based on molecular concepts, also presented a good description of viscoelastic properties for all new molecules in the range of the Diblock content explored (from 0–70%). We also revisited the double reptation blending law, which has been applied here to the complex shear modulus. This new calculation is simpler and gives a better agreement with experimental data, particularly in "smoothing" the intermediary domains.

In order to improve the adhesive properties and to optimize the process we have also studied the behavior of copolymer blends with a high Diblock content (> 70%); in a future article we will present the effects of the morphology of the Diblock part on the rheological behavior at low frequencies, and we will present how it is possible to take into account this morphology in the molecular model.

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