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Linear Melt Rheology of Pom-Pom Polystyrenes with Unentangled Branches

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ABSTRACT: We measured the linear viscoelastic properties of a series of polystyrene melts with pom-pom architecture consisting of backbones ranging from marginally to well-entangled (of molecular weight M_b), end-grafted with q unentangled branches (M_{br}) per backbone end. In this case, the branches relax very fast and act primarily as solvents for the backbone. Using a time-marching tube-based model, we showed that, in such a case only, the pom-pom polymer is equivalent to a blend of long ($M_L \approx M_b + 2M_{br}$) and short ($M_S \approx M_{br}$) linear chains with respective proportion $(M_b + 2M_{br})/2(q - 1)M_{br}$.

1. Introduction

In recent years, significant progress has been made in the understanding of branched polymer dynamics; it has been triggered by the advances in the development of tube-model theories[1−5] and the availability of well-defined model branched polymers.[6−10] The latter are of prime importance, as the fundamental understanding of the dynamics of model polymers is the only hope for connecting the theoretical models to the performance of industrial products. This was recognized early on by Graessley,[11] and to date, complex polymers of different architectures have been successfully analyzed.[3]

Briefly, a breakthrough in the field has been the quantitative description of arm relaxation in star polymers, the simplest class of branched polymers, based on the combination of the tube model and the dynamic tube dilation.[12] This work opened the route for analyzing more complex topologies encompassing both reptation and fluctuation mechanisms, such as H-polymers[13,14] and comb polymers with linear backbones[15−17] or star-like backbones,[18] asymmetric star polymers,[14,19,20] more structured dendritically branched polymers,[21] and lately, more polymers of arbitrary architecture (branch-on-branch polymers).[22] The key concept here is that of hierarchical relaxations.[3,23] In other words, entanglements belonging to topologically different parts of the macromolecule (branches or backbone or different layers) relax in a certain sequence, obeying seniority rules according to which the outer parts of the molecule (those with free dangling ends) relax first and the inner ones last; only when the last relaxation has been completed the whole molecule has relaxed.

An architecture of particular importance is the so-called pom-pom polymer. This was recently proposed as an ideal model polymer that behaves in a very similar fashion to commercial polyolefins in strong shear and extensional flows.[24] The pom-pom constitutive equation represents the state-of-the-art molecular model for describing the processing behavior of polymers.[24] Despite this, however, little experimental evidence is available on the linear and nonlinear rheology of model pom-pom polymers, and it has focused on entangled backbones and entangled branches.[14,24−26] Very recently, a series of highly entangled polystyrenes with pom-pom architecture were synthesized anionically and their transient elongational viscosity was measured with the filament stretching apparatus.[27]

In this paper, we present a systematic study of the linear melt rheology of a series of model pom-pom polystyrenes with entangled backbones and *unentangled* branches. We analyze the data using a recently developed time-marching algorithm,[28] which proved quite successful in predicting the linear viscoelastic properties of mixtures of linear polymers, symmetric and asymmetric star polymers, as well H-polymers and pom-pom polymers.[5] It is based on the tube model predictions of the fluctuations and reptation processes, which proceed simultaneously but with different probabilities and without any imposed separation; the solvent effect due to relaxed segments is treated as a constraint release effect based on (i) the approach of Graessley, de Cloizeaux, and Tsenoglou[29,30] and (ii) the dynamic tube dilation concept.[31,32] More importantly, in the latter case, there is no need to invoke the p^2 parameter (as it is given a fixed value of 1).

The paper is organized as follows: We present the polymers used in Section 2, then the results are presented in Section 3, along with a quantitative interpretation based on the above-mentioned time-marching analysis. Finally, in Section 4, we conclude and discuss briefly possible perspectives from this work.

2. Experimental

Materials. A series of polystyrenes (PS) with "pom-pom" architecture were synthesized recently by convergent living anionic polymerization.[10] In this class of branched polymers, q linear chains are chemically grafted on each end of a linear chain (backbone). For $q = 2$, we have the limiting case of the H-polymer. The illustration below (Scheme 1) illustrates the molecular structure of a pom-pom polymer. The topology of these molecules suggests that the friction coming from the branches is concentrated at the ends of the backbone.

The samples investigated in this work consist of 4−5 short linear chains (of the same molecular weight) grafted on each side

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Scheme 1. Schematic of a Pom-Pom Molecule with 5 Branches (Red) Grafted at Each Backbone End.

of the backbone. While the branches are not entangled, the values of the backbone molecular weights vary from marginally to well-entangled (about 2−12 entanglements); even when the dilution effect of the branches is taken into account, this assessment for the backbone still holds (the respective number of backbone entanglements is 1−10). Table 1 presents the molecular characteristics of those samples.

The samples were press-molded under vacuum to obtain disks of diameter 8 mm, using a homemade vacuum press with temperature control. The protocol to generate the disks consisted of first heating the samples under vacuum to well above melting temperature (∼160−180 °C) and keeping them for 10−20 min (depending on the molecular weight) in order to melt the polystyrene and remove air bubbles, then the samples were pressed into disks and allowed to cool below glass temperature.

Rheology. The measurements were conducted on a Rheometrics Scientific strain-controlled rheometer ARES-2KFRTN1. Temperature control with accuracy of ±0.1 °C was achieved via an air/nitrogen convection oven. In the present study, the temperature varied from 115 to 180 °C under a nitrogen environment in order to reduce the risk of degradation (testing the reproducibility of the measurements served as an additional check, apart from the GPC measurements, of the sample condition). The sample was placed between two parallel plates of predetermined thermal expansion coefficient; the plate diameter was 8 mm and the sample height varied between 1 and 1.5 mm.

Dynamic frequency sweeps were carried out at different temperatures. Dynamic time sweep and strain sweep experiments (for the complete frequency range) were conducted in advance, at each temperature, to ensure thermal equilibrium of the samples and to determine the linear viscoelastic region for the frequency sweeps (small amplitude oscillatory shear measurements). To obtain the rheological master curves, we applied the time−temperature superposition principle (see for example, Figure 1 below). Vertical shift factors were determined directly from the change of sample density with temperature according to equation $b_T = \rho(T_{\mathrm{ref}})T_{\mathrm{ref}}/\rho(T)T$, using $\rho(T) = 1.2503 - 6.05 \times 10^{-4}T$ for PS.[33] Subsequently, the data were shifted along the frequency axis, and the horizontal shift factors for all samples were fitted with a single set of parameters of the WLF function,[34] $\log a_T = (-C_1(T - T_{\mathrm{ref}}))/(C_2 + T - T_{\mathrm{ref}})$, with $T_{\mathrm{ref}} = 443$ K, $C_1 = 5.6$ K, and $C_2 = 120$ K. These values are virtually identical to the values of the same chemistry for different architectures (for example, in Figure 2 we display the temperature dependence of the shift factors for the present pom-pom and some linear and comb polystyrenes) and, moreover, they are consistent with the relevant literature values when compared to the glass-transition temperature.[11,16,17] This result ensures the high quality and consistency of the measurements.

3. Results and Discussion

3.1. Experimental Data. Figure 1 depicts characteristic frequency sweeps for the various pom-pom polystyrenes investigated. The quality of the data is confirmed by the shift factors already discussed and depicted in Figure 2. All samples show one plateau followed by a single relaxation mode. The unentangled branches relax via Rouse modes. The entangled backbone is responsible for the plateau and the subsequent terminal relaxation. To rationalize the latter, the concept of dynamic tube dilation (DTD) can be invoked (see also Section 3.2).

Table 2 below lists some measured properties for all melt samples in this study, namely the glass-transition temperature (T_g), the zero shear rate viscosity (η_0), and the zero-shear recoverable compliance (J_e^0). The zero-shear viscosity was calculated by fitting with the Ellis model:[35] $\eta^*(\omega) = \eta_0/((1 + \omega/a)^{b-1})$, whereas the zero-shear recoverable compliance was determined from $J_e^0 = \lim_{\omega\to 0}(G'(\omega)/(G(\omega))^2)$.[34]

A sensitive way to present linear rheological data is the frequency dependence of the tangent of the phase angle ($\tan \delta = (G''(\omega)/G'(\omega))$), as this helps distinguishing various features of the relaxation processes. This is demonstrated in Figure 3a. As already noted, the branches are very short and exhibit Rouse-like relaxation. However, a careful inspection of the data in Figure 3a reveals the existence of a weak shoulder at a frequency of about 2×10^4 rad/s. This shoulder cannot be accounted for by a simple Rouse-like motion (e.g., as in the case of a linear homopolymer melt), suggesting that the shoulder should reflect the coupling of their relaxation with the branch point motion. Thus, the existence of even very short unentangled branches is sensitively reflected on the rheological data. Interestingly, qualitatively similar effects can be observed in long/short linear polymer mixtures only if the short chains are moderately to well-entangled;[36] for unentangled short chains, no shoulder is observed, as demonstrated in Figure 3b for a pom-pom and for the corresponding blends of linear chains (BB77-PS in Table 3).

3.2. Assessing the Dilution Effect of the Unentangled Branches. According to the dynamic tube dilution (DTD) picture, the parts of the branches that relax faster should not contribute to the stress and thus act as an effective solvent, diluting the unrelaxed parts. In the present situation, the branches, which are unentangled, relax very fast and so the backbones can be thought of as dispersed into their branches. In that case, the volume fraction of the backbone plays an important role in the determination of the terminal relaxation time of the polymer. This reflects the initial polymer fraction, which is entangled and which has to relax in order for the molecule to lose its orientation.

The concept of hierarchical motions suggests that the presence of entangled branches will effectively cause the backbone to remain frozen until they fully relax, thus imposing a delay on its relaxation. However, here the branches are so short that they should not really delay the branch point motion. They should act as a solvent for the backbone, speeding up its relaxation. Therefore, such a pom-pom macromolecule can be considered as a blend of two types of linear chains, long entangled (the backbone) and short unentangled (the branches); the long/short ratio is the same as the backbone/branches in the pom-pom. Indeed, in this specific case of long backbone with unentangled branches, friction due to the branches is negligible compared to the friction of the backbone itself. Therefore, the branches do not slow down the reptation process of the backbone, and its relaxation should be identical to one of the corresponding linear long chains in the presence of as many short linear chains as the branches, whose only contribution is a solvent effect.

We tested this hypothesis by preparing a blend of two linear polystyrenes, one entangled and one unentangled. We chose a blend with constituents of molecular weights and fractions analogous to a specific pom-pom sample. In particular, we measured the linear viscoelastic moduli of a blend of long linear PS ($M_L = 68$ kg/mol) and short linear PS ($M_S = 4.7$ kg/mol), sample BB68-PS of Table 3 below. This blend was chosen so that it could be compared with a pom-pom polymer, in particular, sample Tb-30-PS, which has a backbone with

Table 1. Molecular Characteristics of the Polystyrene Pom-Pom Molecules

samples	M_b (kg/mol) backbone	PDI (half pom-pom)[a]	M_{br} (kg/mol) branches	PDI branches	q (branches/branch point)	M_{tot} (kg/mol)
Tb030	69	1.1	4.4	1.07	5.2	115
Tb031	142	1.06	4.4	1.07	5.2	188
Tb032	182	1.04	4.4	1.07	5.2	228
Tb046	36	1.11	4.9	1.01	4.1	77
Tb047	58	1.07	4.9	1.01	4.1	99
Tb048	74	1.06	4.9	1.01	4.1	115

[a] With molecular weight $M_b/2 + qM_{br}$ (from ref 10). We expect the PDI of the whole pom-pom to be the same.

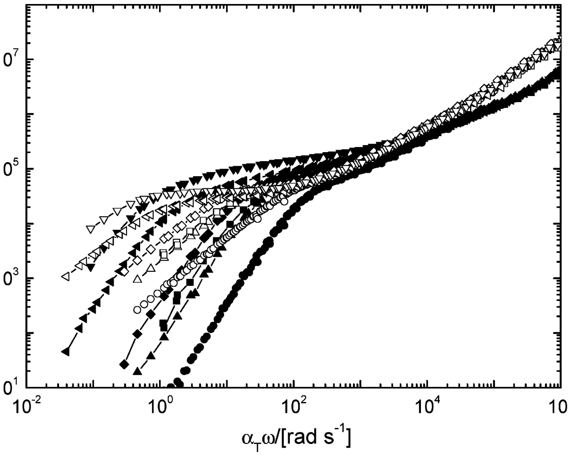

Figure 1. Master curves of storage modulus G' (closed symbols) and loss modulus G'' (open symbols) as functions of frequency for various pom-pom polystyrenes studied: (●, ○) Tb046, (▲, △) Tb047-PS, (■, □) Tb030-PS, (◆, ◇) Tb048-PS, (left-pointing solid triangle, left-pointing open triangle) Tb031-PS, (▼, ▽) Tb032-PS. The reference temperature is $T_{ref} = 170$ °C.

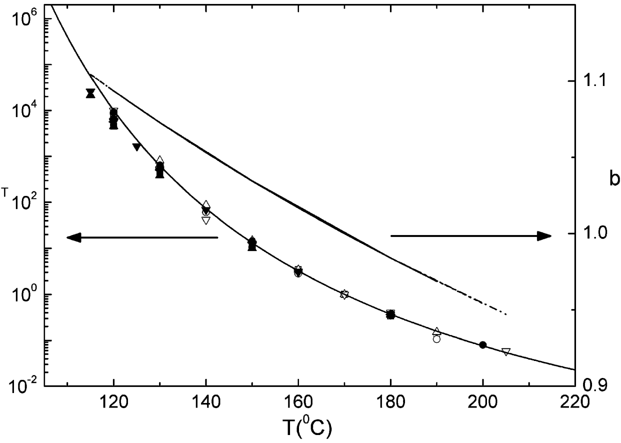

Figure 2. Temperature dependence of the horizontal (symbols, referring to the left axis, a_T) and vertical (nearly straight lines referring to the right axis, b_T) shift factors of polystyrenes with different architectures. The (□) linear PS and (○, △, ▽) linear combs data were taken from ref 16. The solid symbols are for the horizontal shift factors of the pom-pom molecules of this study: (■) Tb030-PS, (●) Tb031-PS, (▲) Tb032-PS, (▼) Tb046-PS, (◆) Tb047-PS, (left-pointing solid triangle) Tb048-PS. The solid line through the symbols represents the WLF fit of ref 16.

molecular weight nearly identical to that of the long linear chain ($M_L \approx M_b$) and branches, each having molecular weight nearly identical to that of the short linear chain ($M_S \approx M_{br}$); see also Table 1. The blend had a volume fraction of long chains identical to that of the pom-pom Tb-30-PS, $\phi_L = M_b/(M_b + 2qM_{br}) = 0.60$. As can be seen in Figure 4, the data indicate one relaxation process, that of the long chains (which is of course speeded up by the presence of the small unentangled ones). The same results were reported in the literature with

Table 2. Thermorheological Properties of the Pom-Pom Samples

sample	T_g (°C) (at 10 °C/min)	T_{ref} (°C)	J_e^0 (10^5Pa^{-1}) (at T_{ref})	η_0 (Pas) (at T_{ref})
Tb030-PS	102.8	170	2.3	8.299×10^2
Tb031-PS	104.4	170	4.0	1.059×10^4
Tb032-PS	104.6	170	3.3	1.285×10^4
Tb046-PS	102.3	170	0.3	2.089×10^2
Tb047-PS	103.7	170	1.4	7.870×10^2
Tb048-PS	104.4	170	1.6	1.279×10^3

similar long/short polybutadiene blends.[36] However, the comparison of these data with the respective pom-pom data (Tb030-PS) is rather discouraging; whereas the high-frequency data practically coincide (after a small horizontal shift, which is justified by the effect of short chains on the blend glass-transition temperature), as expected for local motions, the terminal relaxation of the pom-pom is clearly slower, indicating that the effect of the short chains is more than just dilution.

To resolve this issue, we followed the macromolecular coordinate system of ref 5 and considered another definition of the backbone of the pom-pom macromolecule: pom-pom molecules are rather seen as a kind of comb polymer, i.e., with an equivalent backbone with a molecular weight $M_w = M_b + 2M_{br}$ (see Figure 5), on each side of which $(q - 1)$ branches are grafted. According to this new definition of the macromolecular coordinate system, the long linear polymers of the equivalent binary linear blend are longer than the original pom-pom backbones ($M_L > M_b$). Moreover, the ratio of long to short chains is now different (compared to the case of blend BB68-PS above) and based on the consideration of $2(q - 1)$ branches. For the particular pom-pom polymers used in this work, this relative difference amounts to 10%, which certainly clearly affects the rheology of the blends. To test this idea, we compared the pom-pom sample Tb030-PS with a blend of linear polystyrenes having approximate molecular weights 69.2 kg/mol + 2 × 4.4 kg/mol = 78 kg/mol ($M_L \approx M_b + 2M_{br}$) and 4.7 kg/mol ($M_S \approx M_{br}$) for the long and short chains, respectively, based on the new molecular coordinate system of Figure 5. In fact, the measured blend had molecular weights of 77 kg/mol and 4.7 kg/mol for the long and short chain, respectively (sample BB77-PS in Table 3). The volume fraction of long chains in this blend was $\phi_L = (M_b + 2M_{br})/(M_b + 2qM_{br}) = 0.68$. The viscoelastic relaxation spectra are shown in Figure 4. We note that, in this case, the two curves superimpose perfectly. This justifies the suggestion that the backbone of such a complex macromolecule with short unentangled branches can be considered as the longest path from one end of chain to another one. Further support comes from the different response of the blend BB-68-PS (compared to the pom-pom Tb030-PS), as already discussed. This issue is further elaborated in the Discussion Section 3.3 below.

In the next Section, we use the tube-model-based time-marching approach that proved successful in predicting the linear rheology of polymers with different architectures (linear, star,

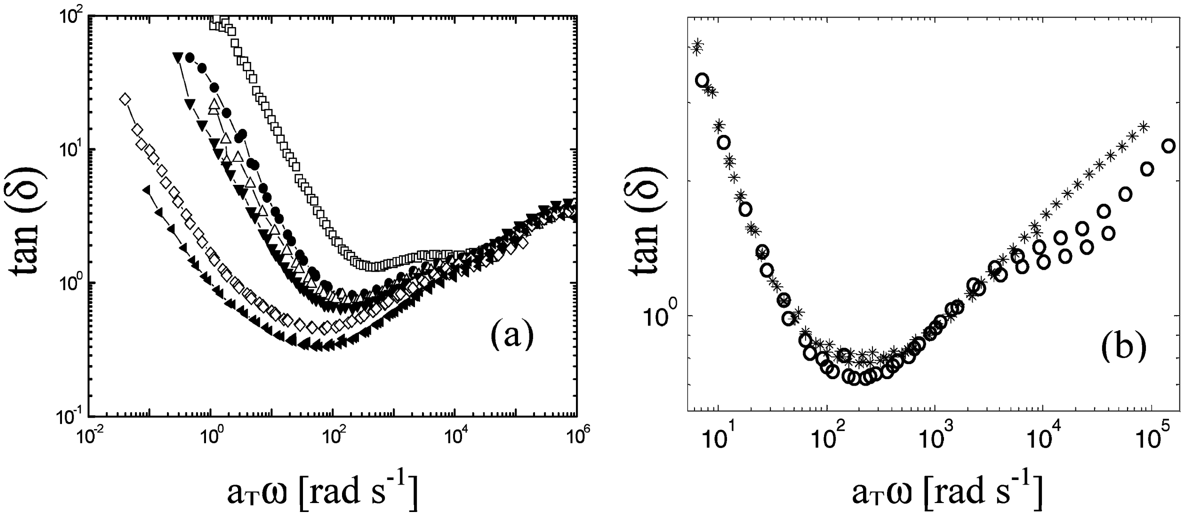

Figure 3. (a) Master curves of tangent of the loss angle against frequency for different pom-pom polystyrenes: (□) Tb046-PS, (●) Tb047-PS, (△) Tb030-PS, (▼) Tb048-PS, (◇) Tb031-PS, (left-pointing solid triangle) Tb032-PS. (b) Comparison of high-frequency behavior of the loss angle for the pom-pom Tb030-PS (○) and the blend of two linear polystyrenes BB77-PS (∗).

Table 3. Molecular Characteristics of the Polystyrene Blends[a]

samples	M_L (kg/mol)	M_S (kg/mol)	ϕ_L
BB68-PS	68.0	4.7	0.60
BB77-PS	77.0	4.7	0.68
BB177-PS	177	1.5	0.80

[a] Obtained from Polymer Source, Canada.

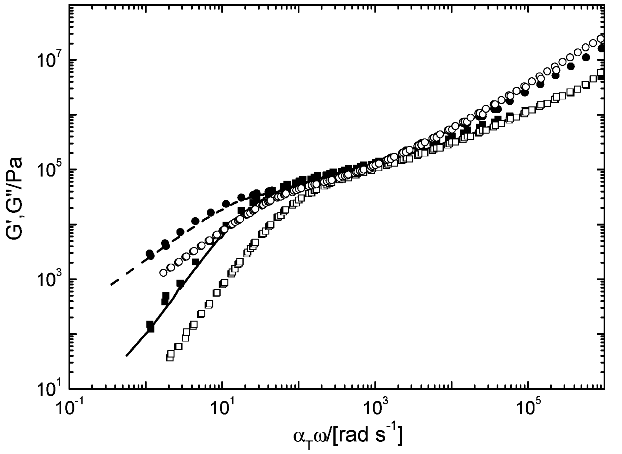

Figure 4. Comparison of the viscoelastic data of the pom-pom Tb030-PS (solid symbols) with the two blends of short and long linear chains: sample BB78-PS (lines) and sample BB68-PS (open symbols).

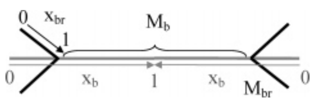

Figure 5. Macromolecular coordinate system for the modeling of the pom-pom macromolecules

H, and pom-pom) in order to analyze and interpret the experimental data.[5] In the present case, the peculiarity lies in the fact that the branches are unentangled, as already mentioned. Then, we compare the linear rheology of these pom-pom molecules with that of the corresponding blends of linear chains (according to the two definitions proposed to determine the backbone molecular weight). In particular, we study the sample Tb030-PS and its two corresponding blends of linear macromolecules and compare results obtained from modeling with experimental data.

3.3. Analysis and Interpretation. *Prediction of the Linear Viscoelastic Properties of the Pom-Pom Polymers.* The approach used here to predict the linear rheology of the pom-pom and linear molecules has been described in refs 5 and 28. The main idea is to use an algorithm that defines, for each time step, the survival probability of each initial molecular segment (rather the initial segmental orientation) and updates their total survival probability (from time $t = 0$) in order to determine the total unrelaxed fraction of the polymer melt at each time. Each molecular segment can relax by three different mechanisms: reptation, which includes additional friction coming from the branches of the pom-pom molecule, contour length fluctuations (CLF), and constraint release (CR). CLF are treated in such a way as to ensure to continuity from the branches of the polymer to the inner part of the backbone. In fact, as we already mentioned, we use a particular coordinate system for localizing a molecular segment of the backbone (coordinate x in Figure 5), moving from the end of a branch where $x = 0$ to the middle of the molecule where $x = 1$ (instead of setting $x = 0$ at the branching point, which is the conventional way). The CR mechanism is considered as a global effect, which increases the molecular weight of the segment between two effective entanglements, $M_e(t)$, yielding a modified "equilibrium state" of the polymer (defined by M_e, the tube diameter a, and the equilibrium length of the molecule L_{eq}). As a consequence, reptation, which is proportional to L_{eq}^2, and CLF, which depends on M_e, are accelerated, due to the DTD; note here that the full DTD picture is invoked (the p^2 parameter is fixed to 1). However, an additional condition for defining the value of the "polymer solvent" is needed in order to take into account the extended criteria of Struglinski and Graessley:[29] the polymer fraction relaxed at a fixed time, acts as a solvent for the relaxation (by both reptation and CLF) of the unrelaxed polymer fraction (that is still oriented) only if their respective relaxation times are well separated.[5] We used a dilution exponent[37] of 1, consistent with earlier works.[5,16−18]

Figure 6 compares the experimental data and the model predictions. It is evident that the model provides a very good description of the experimental data without adjustable parameters (all comparisons are at $T_{ref} = 443$ K). The only parameters used are the Rouse time of an entanglement ($\tau_e = 1.1 \times 10^{-3}$ s), the plateau modulus ($G_N^0 = 2.3 \times 10^5$ Pa), and the entanglement molecular weight ($M_e = 16\,000$ g/mol) of

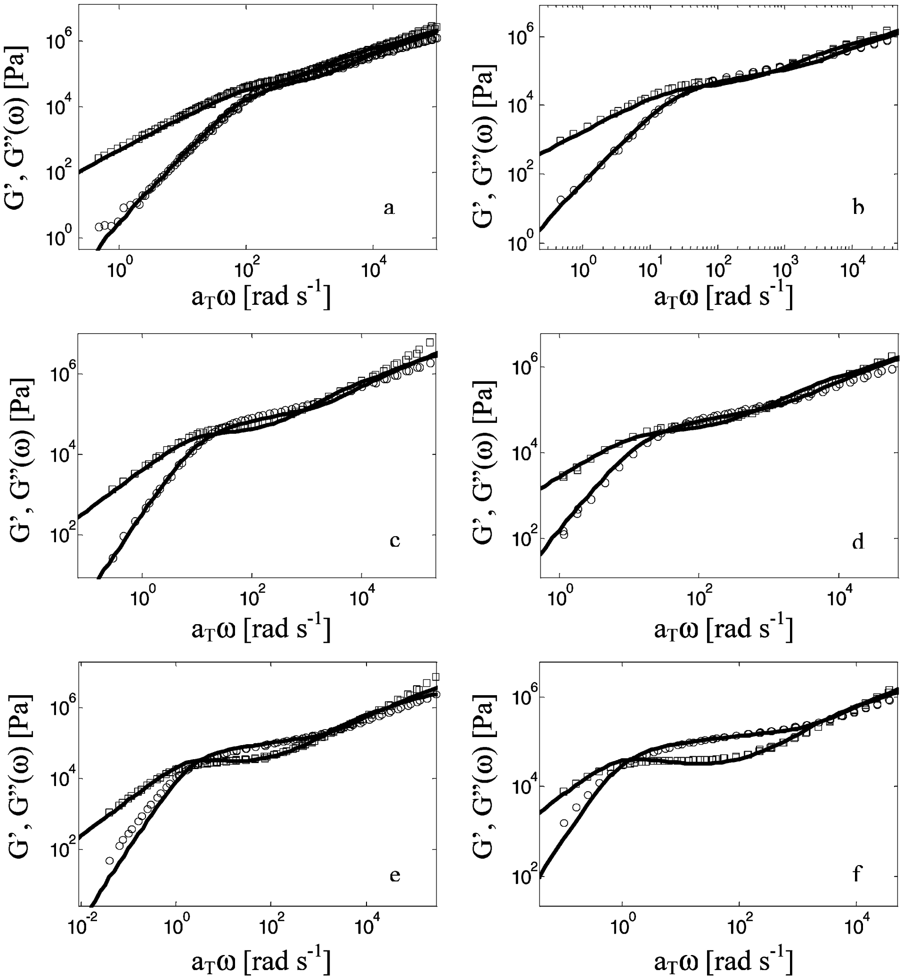

Figure 6. Comparison of experimental storage G' (○) and loss G'' (□) moduli with predictions (lines) for (a) Tb046-PS, (b) Tb047-PS, (c) Tb030-PS, (d) Tb048-PS, (e) Tb031-PS, (f) Tb032-PS at $T_{\mathrm{ref}} = 443$ K.

polystyrene; these values have been determined experimentally as discussed in ref 16. With this model, it is possible to assess the importance of the friction due to the branches. To do so, we looked at model predictions of the different contributions to the terminal time of the sample Tb030-PS (see Table 1): without including the dilution effect of the branches, this time is simply the backbone reptation, $\tau_{\mathrm{d}} = 0.38$ s. The contribution of the branches (due to their friction) is essentially their fluctuation time, $\tau_{\mathrm{br}} = 4.42 \times 10^{-3}$ s, whereas the respective contribution of the renormalized as per Figure 5 backbone (i.e., with molecular weight $M_{\mathrm{w}} = M_{\mathrm{b}} + 2M_{\mathrm{br}}$) is $\tau_{\mathrm{b}} = 0.377$ s. It is therefore clear that the contribution of the branches to the overall friction, and thus to the terminal relaxation, can be neglected for the present pom-pom macromolecules with unentangled branches. This is different from the case of the pom-pom polymers with long entangled branches, whose friction appears to dominate the terminal relaxation.[3,24,26]

Figure 7 depicts the experimental data and predictions in a loss angle ($\tan \delta = G''/G'$) representation. It also shows in a sensitive way the deviations of the model predictions from the experimental data in the low-frequency regime. They are attributed to the polydispersity of the pom-pom samples (Table 1). Indeed, as seen in Figure 7 for the case of Tb032-PS, in which one introduces polydispersity to the model (see also ref 5), the predictions come much closer to the experimental data. Note however that the high-frequency shoulder (Figure 3 and relevant discussion) is not captured by this model, which treats the branch relaxation as a simple Rouse motion. The comparison of model predictions with experiments focuses here in the plateau and terminal regions, i.e., those related to the backbone relaxation, which reflects the largest by far region of the viscoelastic response probed experimentally.

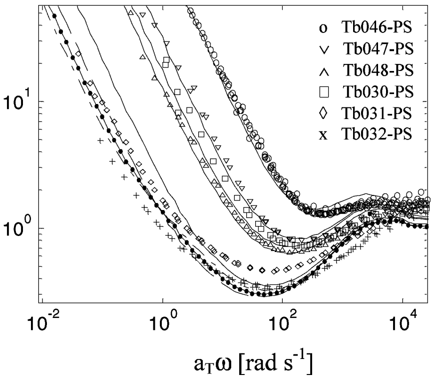

Figure 7. Loss angle spectra of the pom-pom polystyrenes at $T_{\mathrm{ref}} = 443$ K. The lines represent the model predictions (see text). For the Tb032-PS sample (×), there are three lines representing different polydispersities, respectively from right to left: PDI = 1, PDI = 1.1, and PDI = 1.15.

Approximation of a Pom-Pom Polymer by an Equivalent Blend of Two Linear Chains. The same model can be used to predict the rheology of long/short linear polymer blends. In Figure 8, predictions for two different binary blends of linear chains (BB-177-PS and BB-68-PS with volume fractions of long chains $\phi_{\mathrm{L}} = 0.80$ and $\phi_{\mathrm{L}} = 0.60$, respectively; see also Table 3) are compared against the respective experimental data; a very good agreement is found. Then, the equivalence in the response

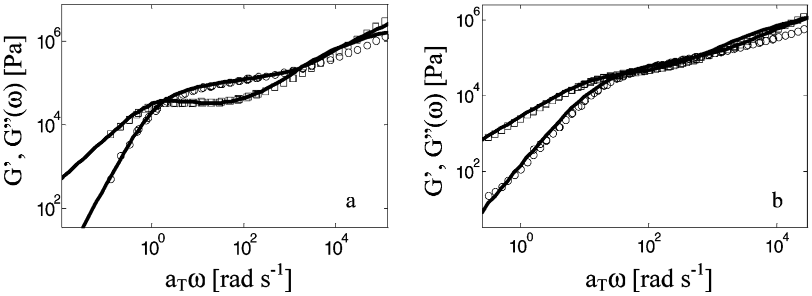

Figure 8. Comparison of experimental $G'(\omega)$ (○) and $G''(\omega)$ (□) with predictions (dashed lines) for blends of two linear macromolecules at $T_{\mathrm{ref}} = 443$ K: (a) sample BB177-PS, (b) sample BB68-PS.

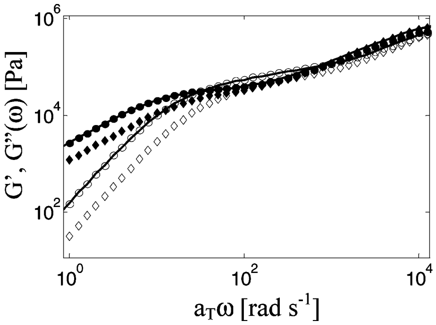

Figure 9. Model predictions of: (i) the storage G' (line through open circles) and loss G'' (line through closed circles) moduli of the Tb030-PS polystyrene, (ii) G' (◇) and G'' (◆) of a linear blend composed of long chains with $M_w = M_b = 69.2$ kg/mol and short chains with $M_w = 4.4$ kg/mol in proportion (61:39), and (iii) G' (○) and G'' (●) of a linear blend composed of long chains with $M_w = M_b + 2M_{\mathrm{br}} = 78$ kg/mol and short chains with $M_w = 4.4$ kg/mol in proportion (68/32). $T_{\mathrm{ref}} = 443$ K.

between a pom-pom with short unentangled branches and a binary linear blend with long and short chains virtually identical to the pom-pom's backbone and branches, respectively, is confirmed by modeling the experimental systems discussed in Section 3.2. Figure 9 depicts predictions for the pom-pom sample Tb030-PS and a blend of long and very short linear macromolecules, with short chains having a molecular weight $M_S = M_{\mathrm{br}}$ and long chains having (i) $M_L = M_b$ or (ii) $M_L = M_b + 2M_{\mathrm{br}}$. It turns out that, as already suggested by the experimental data of Figure 4, this equivalence works only if we consider the latter case (ii). For the former case (i), the model predicts a faster relaxation compared to the data. This result fully supports the experimental findings (see Section 3.2). Naturally, this observation is directly linked to the coordinate system used in this approach to describe a molecular segment of the backbone (Figure 5). To demonstrate the importance of the macromolecular coordinate system, we considered for the same sample Tb030-PS the value $x = 0$ at the branching point. In that case (not shown here), the predictions were in harmony with the respective blend having long linear chains of molecular weight $M_L = M_b$, but in clear disagreement with the experimental Tb030-PS data. The main difference between the predictions obtained with the two different coordinate systems lies in the CLF contribution. In short, by considering the original backbone of the pom-pom macromolecule (without the outer branches), the branching points are treated as ends of chain; therefore, segments of the inner backbone localized around will relax very fast, even faster than some molecular segment of the branches, contributing additional "polymer solvent effect" at very short times, which accelerates the relaxation of the deeper segments of the backbone. Even if the branches are very short (negligible friction) and they act as a solvent for the relaxation of the backbone, they are still important in the fluctuations process of the backbone.[5] Therefore, comparing for example a pom-pom with 5 unentangled branches of $M_{\mathrm{br}} = 4.5$ kg/mol with another one having 15 branches of $M_{\mathrm{br}} = 1.5$ kg/mol (and the same original inner backbone), their terminal relaxation times are expected to be different despite the negligible friction due to the short branches and the same proportion of branches.

4. Conclusions

The investigation of the present series of polystyrene pom-pom melts having backbones ranging from marginally to well-entangled (of molecular weight M_b) and 4−5 *unentangled* branches (M_{br}) revealed that their linear rheology is dominated by the reptation-like motion of the backbone. Still, the fast-relaxing branches (considered as an effective solvent, as their contribution to the overall friction is very small) have an effect that is clearly observed. To this end, we showed that in such a case, the pom-pom polymer with unentangled branches is equivalent to a blend of long ($M_L \approx M_b + 2M_{\mathrm{br}}$) and short ($M_S \approx M_{\mathrm{br}}$) linear chains with respective proportion $(M_b + 2M_{\mathrm{br}})/2(q - 1)M_{\mathrm{br}}$. Naturally, this equivalence does not hold for longer branches. There are important remaining issues, such as the extent of validity of the DTD picture in asymmetric binary linear polymer blends[38] such as the ones considered here, which need to be addressed in the future. Nevertheless, this simple approach is robust and captures systematically the observed features of this interesting class of branched macromolecules.

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