Synthesis and Viscoelastic Properties of Model Dumbbell Copolymers Consisting of a Polystyrene Connector and Two 32-Arm Star Polybutadienes

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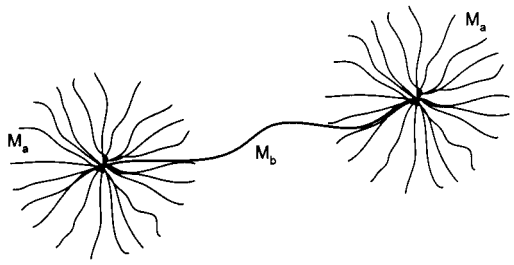
ABSTRACT: A series of well-defined dumbbell copolymers of $(PBd)_{32}PS(PBd)_{32}$ type, with the same polystyrene (PS) connector (10 600 g/mol) and 32 polybutadiene (PBd) branches of varying molecular weight (1200, 5000, 15 000, 43 000 g/mol) on each end, were synthesized, and their viscoelastic properties were investigated. For the three larger branches (above the entanglement molecular weight), their relaxation controls the dynamics of the macromolecular dumbbells, which exhibit starlike behavior. For the shorter branch, the backbone fraction (and thus its relaxation) is nonnegligible, and it should be considered in the assessment of the dynamics. A general map of the relaxation of such complex model branched polymers is proposed, where the dumbbell dynamics depend on the branch size for large branches (as in the star case) or on the total molecular size for short branches.

I. Introduction

The dynamics of branched polymers is a topic of scientific and technological importance, and as such it has received a great deal of attention in the past decade. Developments in this field will have important implications to the structural and processing control of commercial polyolefins, most of which are polymers with long chain branching,[1] as well as to the rational design of novel materials, which is based on the interplay of macromolecular architecture and macroscopic properties.[2] Recent advances in both directions rely on the opportunities offered by macromolecular chemistry and in particular the synthesis of well-defined new structures which provide the framework for exploring the effects of topology on the dynamics of complex macromolecules.[2,3] Typical examples represent the star,[4] comb,[5] and H-polymers[6] as well as the pom-pom polymers[7−11] which were motivated by theoretical advances[12] aimed at understanding the rheology of commercial branched polymers.

A great deal of work was devoted to the study of multiarm star polymers.[13,14] These polymers were found to exhibit a nonuniform monomer density distribution because of their topology,[14,15] which yielded a core−shell type of structure, resembling an ultrasoft grafted colloidal particle.[16] In nondilute solutions or in the melt, these systems [encompassing both polymeric (shell) and colloidal (core) features] exhibited a liquidlike order and an accompanying complex viscoelastic relaxation, thus serving as models for tuning the behavior of such hydrid systems at will.[13,17] Two multiarm star polymers connected with a linear chain comprise a macromolecular dumbbell (see Scheme 1). In such a situation the relative size ratio of star arm to the connecting chain is expected to play a crucial role in the ordering and dynamics of this macromolecular object. In this respect dumbbell macromolecules offer an additional molecular parameter for controlling material properties, and consequently they may be very important in the design of new materials.

Scheme 1. Schematic Representation of a Dumbbell Macromolecule[a]



[a] It consists of a main (connector) chain with molecular weight M_b and with each of its two ends attached to star polymers with the same high functionality, each having arm molecular weight M_a.

In this paper we present the synthesis and characterization of model dumbbell copolymers of styrene and butadiene. Essentially, they are nonlinear block copolymers, consisting of a polystyrene (PS) main chain (connector) with each of its two ends connected to a multiarm star (in our case 32-arm star) of 1,4-polybutadiene (PBd). We study a series consisting of dumbbells with constant PS molecular weight and PBd star functionality and varying PBd arm molecular weight. The linear viscoelastic properties of these samples are reported in view of existing data on star polymers with the same functionality and the PS−PBd interactions.

II. Experimental Part

A. Synthesis of Dumbbell Copolymers of the $(PBd)_{32}PS(PBd)_{32}$ Type. Styrene (99%), butadiene (99%), *n*-butyllithium (1.6 M) in hexane, benzene (99%), THF (99%), dichloromethylsilane (99%), dichlorodimethylsilane (99%), trimethylchlorosilane (99%), and dipiperidinoethane (99%) were purchased from Aldrich. Purification of monomers and solvents to the standards required for anionic polymerization has been described in detail elsewhere.[18] *sec*-Butyllithium (*s*-BuLi) was

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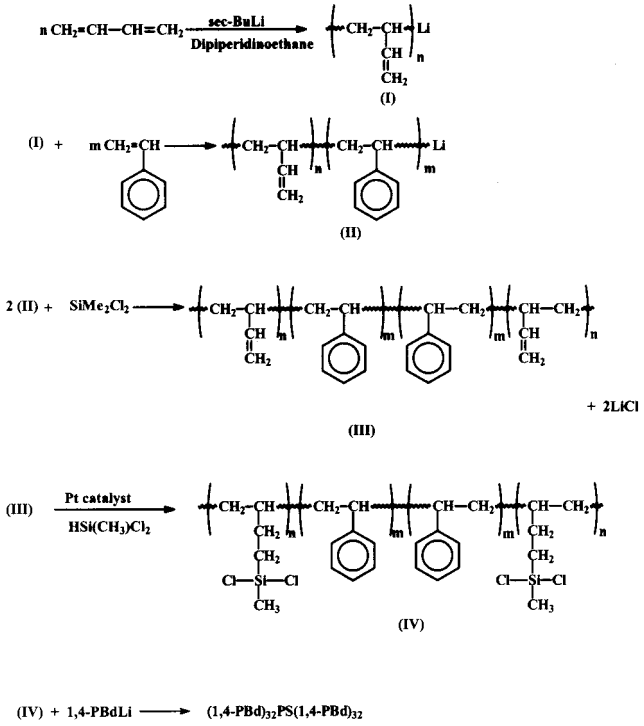
Scheme 2. Key Reactions for the Synthesis of the Dumbbell Copolymers $(PBd)_{32}PS(PBd)_{32}$



prepared in vacuo from *sec*-butyl chloride and lithium dispersion. All polymers were synthesized by using high-vacuum anionic polymerization. The basic reactions used for the synthesis of the dumbbell copolymers are shown in Scheme 2.

The synthesis of the common precursor (1,2-PBd)-*b*-PS-*b*-(1,2-PBd) with polystyrene (PS) molecular weight 1.3×10^4 and each PBd-1,2 molecular weight $1,2 \times 10^3$ was performed as follows: In a reactor, washed with a solution of *n*-BuLi and rinsed with benzene, 2.7 g of butadiene-1,3 was added along with 100 mL of benzene, 2.25×10^{-3} mol of *s*-BuLi, and 1×10^{-2} mol of dipiperidinoethane (DIPIP) (C−Li/DIPIP $\sim$ 1/4). After 24 h, 37 mL was removed in a side flask, neutralized with degassed methanol, and used for characterization. Subsequently, 9 g of styrene was added to the remained solution of living polybutadiene, and after 24 h 5.4 mL was removed and terminated with degassed methanol for characterization. Finally, 5.7×10^{-4} mol of dichlorodimethylsilane was added and allowed to react for 1 week. The excess of living chains was quenched with degassed methanol. The triblock copolymer was separated from the diblock copolymer by fractionation, using toluene/methanol as solvent/nonsolvent system.

An amount of 5 g of the triblock copolymer was dissolved in 50 mL of dry THF, and two drops of the divinyltetramethyldisiloxane complex in xylene (hydrosilylation catalyst) along with 0.27 mol of trimethylchlorosilane (drying agent) were added and stirred overnight. Then, 1.35×10^{-2} mol of dichlorodimethylsilane was added into the mixture, and the temperature was slowly raised to the boiling point of THF (67 °C). The hydrosilylation was allowed to proceed for 1 day at 67 °C. Me_3SiCl along with unreacted $MeSiCl_2H$ and THF was removed on the vacuum line by pumping for about 5 days. The hydrosilylated triblock copolymer was redissolved in benzene and subdivided into ampules, equipped with break-seals. More details concerning the hydrosilylation reaction are given elsewhere.[19]

The hydrosilylated triblock copolymer was allowed to react with the living PBd-1,4 chains exhibiting different molecular weight. The produced dumbbell copolymers were separated from the side products and excess arm by fractionation, using the toluene/methanol system.

B. Characterization of the Dumbbell Copolymers. SEC experiments were carried out at 25 °C using a Waters 610 pump, a Waters model 410 differential refractometer, a 996 diode-array UV detector, and six columns with a continuous porosity range from 10^2 to 10^6 Å. THF was the carrier solvent. The number-average molecular weight M_n was determined by using a Jupiter model 231 recording membrane osmometer at 37 °C, using toluene distilled over CaH_2 , as the solvent. When the molecular weight was lower than 1.0×10^4, the number-average molecular weight was obtained by using a Jupiter model 833 vapor pressure osmometer, at 50 °C, in toluene. The weight number-average molecular weights M_w were measured using a Chromatix KMX-6 low-angle laser light scattering photometer operating at 633 nm and at 25 °C. The solvent was THF, distilled over Na. The d*n*/d*c* values of the final products were measured with a Chromatix KMX-16 refractometer, operating at 633 nm and calibrated with aqueous NaCl solutions. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 300 MHz instrument with $CDCl_3$ as the solvent, at 25 °C, and were used for the determination of the composition and the microstructure of PBd.

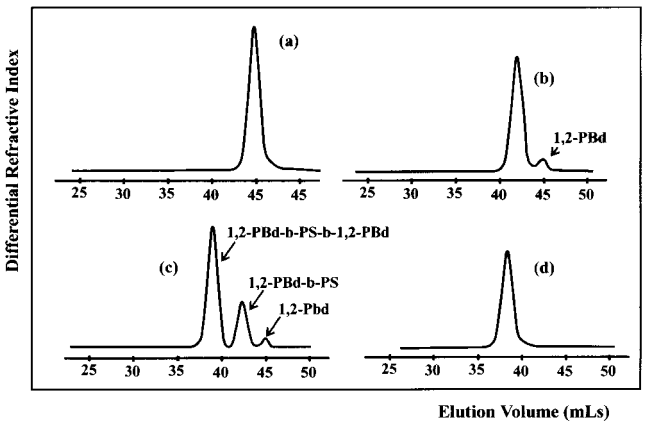


Figure 1. Monitoring the synthesis of the common backbone of the dumbbell copolymer by size exclusion chromatography: 1,2 PBd block (a), 1,2 PBd-*b*-PS diblock copolymer (b), the raw product after the coupling reaction (c), and the fractionated triblock copolymer 1,2 PBd-*b*-PS-*b*-1,2 PBd (d).

C. Viscoelastic Measurements. A Rheometric Scientific ARES strain rheometer was utilized with a dual range force rebalance transducer 2KFRTN1 in the parallel plate geometry (diameter 8 mm, sample gap about 1.5 mm). Temperature control with accuracy ±0.1 °C was achieved in the range −95 to 100 °C via an air/nitrogen oven coupled with a liquid nitrogen vessel. Measurements included dynamic time and strain sweeps to ensure steady state and linear viscoelastic conditions, respectively, and dynamic frequency sweeps (in the range 100−0.01 rad/s) to detect the relaxation dynamics.

The glass transition temperatures T_g were measured with a differential scanning calorimeter from Rheometric Scientific (PL-DSC), at heating/cooling rates of 10 °C.

III. Results and Discussion

III.1. Synthesis. The synthetic procedure was monitored by using SEC. A typical example is shown in Figures 1 and 2. The yield of the hydrosilylation of 1,2-PBd, found to be 75%, was calculated from the average number of branched points grafted on the backbone, and $HMeSICl_2$ was used for hydrosilylation.

The two small peaks appearing in Figure 1b,c are due to the accidentally neutralized living 1,2-PBdLi and to the excess of 1,2-PB-*b*-PSLi used for the completion of the linking reaction. The small peak appearing between the dumbbell copolymer and the excess arm (Figure 2f), having 2 times the molecular weight of the branch, is due to the linking of the 1,2-PB-*b*-PSLi with the remaining $HMeSiCl_2$, which cannot be completely eliminated in the vacuum line. The molecular characteristics of the common backbone and the final dumbbell copolymers are given in Tables 1 and 2. The molecular

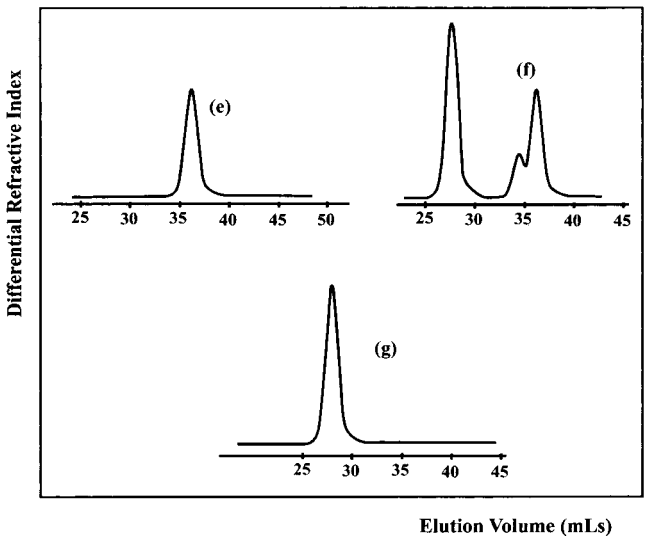


Figure 2. Monitoring the synthesis of the DB15000 by size exclusion chromatography: 1,4 PBd arm (e), the raw product of the linking reaction of the hydrosilylated backbone and living 1,4 PBd arms (f), fractionated copolymer (g).

Table 1. Molecular Characteristics of the Common Backbone 1,2-PBd-*b*-PS-*b*-1,2-PBd

sample	$M_n \times 10^3$	M_w/M_n[c]	wt % PS[d]
PBd1,2	1.20[a]	1.02	
PBd1,2-*b*-PS	6.60[b]	1.05	84
PBd1,2-*b*-PS-*b*-PBd1,2	13.0[b]	1.04	84

[a] Vapor pressure osmometry in toluene at 50 °C. [b] Membrane osmometry in toluene at 37 °C. [c] Size exclusion chromatography in THF at 30 °C. [d] ^{1}H NMR in chloroform at 25 °C.

characteristics reveal that the dumbbell copolymers exhibit a high degree of molecular and compositional homogeneity and have the expected number of branched points.

III.2. Linear Viscoelastic Properties. The measured DSC traces are depicted in Figure 3. It is clear that for all four samples there is one glass transition temperature detected, which corresponds to the 1,4-polybutadiene stars. This is an indirect proof that these block copolymer samples are disordered at all times. Indeed, the fraction of polystyrene is so small, that they are expected to remain homogeneous.[20] However, it should be noted that for the lowest arm molecular weight sample, DB1200, the polystyrene fraction is nonnegligible (Table 2), and there is some indication of local heterogeneities in the melt, manifested as a very weak endotherm in the temperature region around 70 °C, which corresponds to the glass transition of the pure polystyrene (see inset of Figure 3). This slightly different behavior of sample DB1200 is also reflected in the viscoelastic response, as discussed below.

The storage (G') and loss (G'') moduli master curves of the four samples, obtained from the frequency sweeps

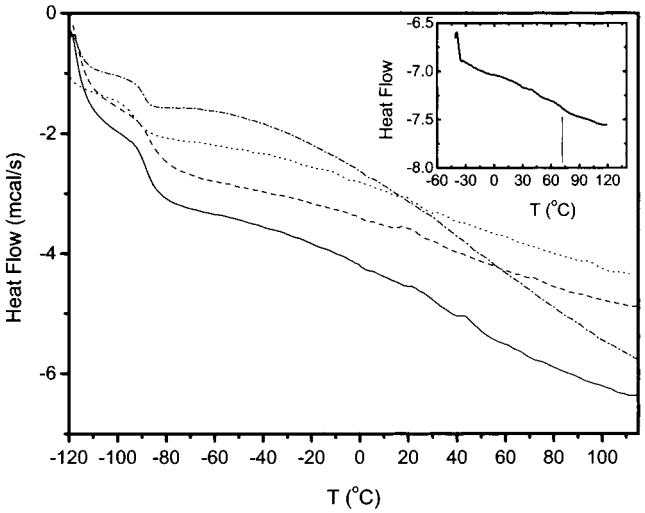


Figure 3. DSC traces of the four dumbbell polymers studied: DB1200 (dotted line), DB5000 (solid line), DB15000 (dashed−dotted line), and DB43000 (dashed line). All exhibit a glass transition temperature around -91 ± 2 °C. Inset: evidence of possible weak glass transition of polystyrene-rich component (for DB1200) at about 70 °C, indicated by vertical arrow (see text).

by applying the principle of time−temperature superposition (shifting only along the frequency axis) with reference temperature $T_{ref} = -83$ °C, are depicted in Figure 4. It can be observed that the three higher-M_a samples exhibit the same behavior, with nearly identical crossover frequency to glass (ω_c). Note that this behavior is also virtually identical to the local dynamics of a 1,4-polybutadiene star with the same functionality and very similar M_a (see also Figure 5). One can also clearly detect the presence of entanglements in the polybutadiene arms for these three samples with $M_a > M_e$. This transient network behavior is more pronounced of course for the largest M_a sample DB43000. The extracted plateau modulus value was about $G_N^0 = 1.5 \times 10^6$ Pa, which is reasonable for 1,4-polybutadiene.[21,22] It is pointed out that all stars exhibit a weak power-law relaxation rather than a true plateau (as in the case of highly entangled linear polymers).[13,21,22] This is even more pronounced in the case of sample DB5000, for which the arm molecular weight amounts to just about two entanglements, reflecting a relaxation of the transient network with $G' \sim \omega^{0.3}$. These findings, along with the most important terminal relaxation, characterized by a wide range of modes (the latter being more evident for larger M_a) suggest that the dominant mechanism of relaxation in these dumbbells is the star arm relaxation. As already established in the case of star polymers, the crossover time to terminal relaxation is assigned to the arm relaxation (τ_a).

Contrary to the above, the lowest M_a sample DB1200 exhibits a clearly different behavior. First of all, the

Table 2. Molecular Characterization of the Arms and Final Dumbbells

	arm			dumbbell copolymers			
sample	$M_n \times 10^3$	M_w/M_n[c]	$M_n \times 10^5$ [a]	$M_w \times 10^5$ [d]	M_w/M_n[c]	wt % PS[e]	f[f]
DB1200	1.20[a]	1.03	0.93[b]	0.95	1.03	13	66
DB5000	5.0[a]	1.04		3.80	1.10	3	63
DB15000	15.0[b]	1.04		11.6	1.09	1	64
DB43000	43.0[b]	1.03		28.5	1.05		63

[a] Vapor pressure osmometry in toluene at 50 °C. [b] Membrane osmometry in toluene at 37 °C. [c] Size exclusion chromatography in THF at 30 °C. [d] LALLS in THF at 25 °C. [e] ^{1}H NMR in chloroform at 25 °C. [f] Number of arms calculated by $f = [(M_{w,\,dumbbell}/I) - M_{n,\,backbone}]/M_{n,\,arm}$.

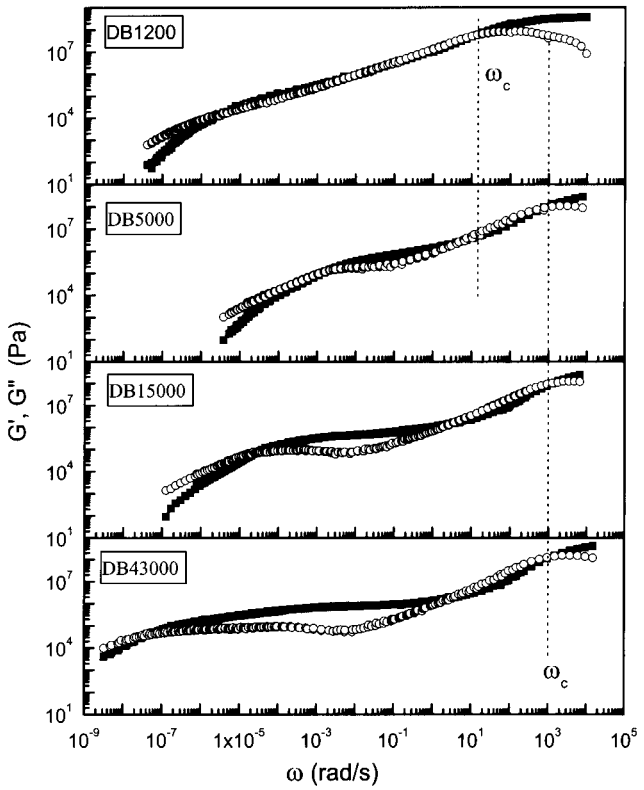


Figure 4. Master curves of storage (G', solid symbols) and loss (G'', open symbols) moduli, obtained using time−temperature superposition ($T_{ref} = -83$ °C), for the four macromolecular dumbbells studied. Vertical lines indicate the crossover frequency (ω_c) from segmental to Rouse-like dynamics (see text).

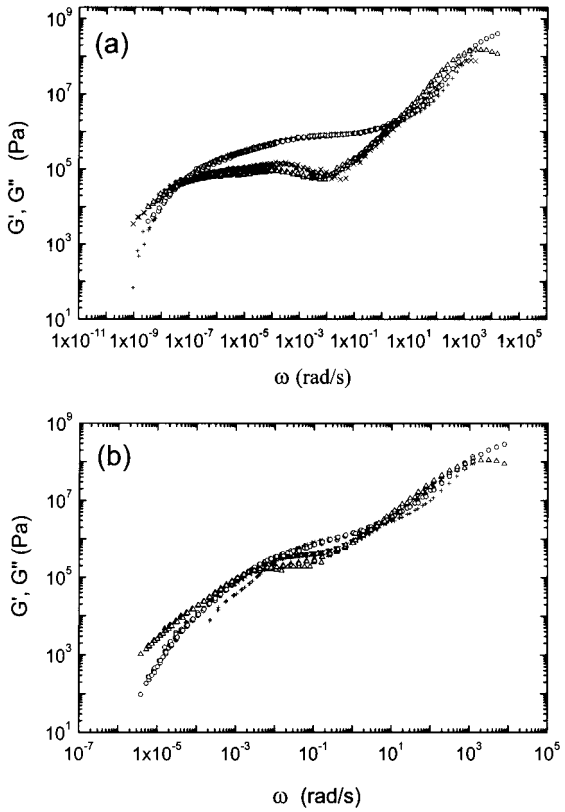


Figure 5. Comparison of linear viscoelastic spectra of dumbbells (G', ○; G'', △) and respective multiarm star polymers (G', +; G'', ×): DB43000 and 32-PBdStar37 (a); DB5000 and 64-PbdStar05 (b).

segmental dynamics is slower by nearly 1.5 decades, as demonstrated by the shift of ω_c in Figure 4. This can only be explained by the much high fraction of glassy polystyrene compared to the other samples (see Table 2), which slows down the overall dynamics of the dumbbell.[23] Furthermore, the fact that both PS and PBd star arm are unentangled is reflected in the master curve of DB1200, which exhibits a power law behavior from the glass to the terminal relaxation regions, covering about 7 decades, and characterized by a slope $G' \sim G'' \sim \omega^{0.5}$, typical of Rouse-like behavior.[22,24] This type of behavior characterizes a variety of macromolecular systems with large total molecular weight, but relaxing via branches or segments with small molecular weight below the M_e. Examples include hyperbranched polymers[25] and long-chain branched polyolefins.[26] In such cases, the response of these large systems is discussed in terms of the self-similar structure of gels.[26,27]

As already mentioned for the three larger samples, where the polystyrene represents a tiny fraction, star arm relaxation controls the dynamics. This is further demonstrated in Figure 5a, which compares the linear viscoelastic spectra of sample DB43000 and a PBd star with 32 arms and virtually the same arm molecular weight $M_a = 37\,000$ g/mol (32-PBdStar37), at the same reference temperature. Indeed, the similarity of the dynamic data is remarkable. Given the dependence of the arm relaxation process on the number of entanglements per arm, further comparison with a 64-arm star leads to similar conclusions. As seen in Figure 5b, the spectra of sample DB5000 and a star with 64 arms and $M_a = 5000$ g/mol (64-PBdStar05) are almost identical up to the arm relaxation. As lower frequencies the observed deviation is due to the structural relaxation of the 64-PBdStar05 star. Table 3 lists the isofrictional arm relaxation time (normalized to the segmental time, τ_s), τ_a/τ_s, for the four dumbbell samples as well as for various stars with different functionalities and similar arm molecular weight. These numbers confirm the assignment of the arm relaxation mode and further support the conclusion that, with the exception of sample DB1200, the star arm relaxation mechanism controls the dumbbell dynamics. The 2 decades long discrepancy between the latter sample and a star with 64 arms and similar arm molecular weight (64-PbdStar015) can be attributed to the substantial delay caused by the presence of the PS main chain (with much larger molecular weight compared to that of the star

Table 3. Isofrictional Arm Relaxation Times for Various Star and Dumbbell Polymers

sample	f	M_a (g/mol)	τ_a/τ_s
DB1200	33	1 200	4×10^6
64-PBdStar015	64	1 500	2×10^4
DB5000	33	5 000	3.2×10^5
18-PBdStar05	18	5 500	8.9×10^4
64-PBdStar05	64	5 000	10^5
270-PbdStar-LS2	267	4 500	1.6×10^5
DB15000	33	15 000	6×10^7
4-PbdStar-12	4	12 000	0.4×10^7
32-PBdStar16	32	17 400	3.47×10^7
18-PBdStar15	18	17 200	1.45×10^7
64-PBdStar15	60	12 100	0.5×10^7
128-PBdStar14	125	13 000	1.55×10^7
270-PbdStar-LS4	267	17 300	8.9×10^7
DB43000	33	43 000	2.8×10^{10}
32-PBdStar37	35	38 000	2.5×10^{10}
18-PBdStar37	18	42 300	1.6×10^{10}
270-PbdStar-LS6	263	42 300	4.7×10^{10}

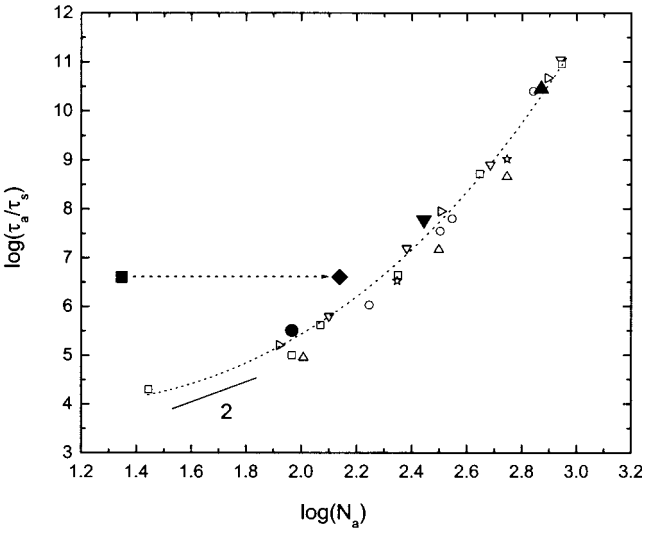


Figure 6. Normalized arm relaxation time (to the segmental time τ_s) τ_a/τ_s against arm degree of polymerization N_a for the macromolecular dumbbells (■, DB1200; ●, DB5000; ▼, DB15000; ▲, DB43000) and various star functionalities studied[12] (☆, $f = 4$; △, $f = 18$; ○, $f = 32$; □, $f = 64$; ▽ $f = 128$; tilted △, $f = 128$). The dotted line is drawn to guide the eye. The horizontal arrow points to the average overall dumbbell molecular weight accounted for its relaxation, as discussed in the text (◆). The slope of 2 is the Rouse scaling.

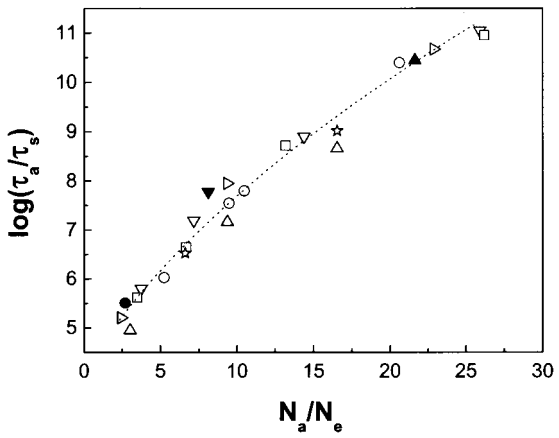


Figure 7. Normalized arm relaxation time τ_a/τ_s of entangled polymers, against the number of entanglements per arm N_a/N_e. Symbols are same as in Figure 5. The line is drawn to guide the eye.

arm); this may be enhanced by potential large fluctuations in this high-PS content block copolymer.[20]

A representation of the dependence of different isofrictional times τ_a/τ_s on the (star arm) molecular weight is illustrated in Figure 6, where selective data from various stars (including those of Table 3) are shown, along with the four dumbbells. It is evident that within experimental error the three larger dumbbells conform to the generic description of arm relaxation. For these systems possessing entangled star arms, the alternative representation of τ_a/τ_s against the number of entanglements per arm, N_a/N_e, is also possible (see Figure 7). Given the small $M_a < M_e$ of sample DB1200, its arm relaxation time should be nearly indistinguishable from its center-of-mass motion.[28] One could then envisage the relaxation of this dumbbell as the motion of an obstacle having a total average molecular weight $\langle M \rangle = M_a + M_b$, where the subscript "b" denotes the connector PS. This is smaller from the end-to-end average (span) molecular weight by one M_a, but extrapolating the pom-pom ideas,[12] we think this is appropriate. The average relaxation time can be analyzed into a fast component (independent arm relaxation) and a slower dominant component (main chain relaxation). By using $\langle M \rangle$ instead of M_a, the data nearly collapse into the "master plot" of Figure 6 (see horizontal arrow), providing an indirect confirmation of the assignment of the terminal relaxation for this sample.

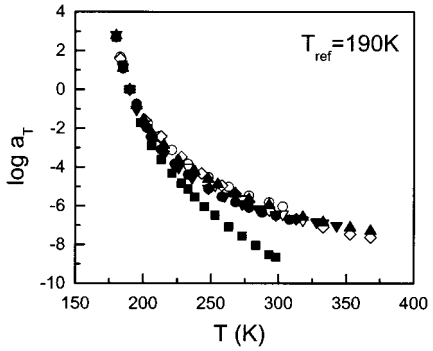


Figure 8. Frequency shift factors against temperature for the macromolecular dumbbells and various multiarm stars: ■, DB1200; ●, DB5000; ▼, DB15000; ▲, DB43000; ○, 64-PbdStar15; ▽, 32-PbdStar16; ◊, 32-PbdStar37.

In addition, rheooptical measurements provided unambiguous evidence of the polystyrene-dominated terminal relaxation. In particular, during dynamic oscillatory measurements at 25 °C with sample DB1200 at strains from 1% to 35% (being in the terminal region in the range 100−0.1 rad/s), the recorded birefringence was negative (of the order of 10^{-6});[29,30] this means that the polystyrene contribution to dumbbell flow birefringence is the dominant one (the polybutadiene possessing weak positive birefringence).

Finally, the different behavior of DB1200 compared to the other samples is also reflected on the temperature dependence of the frequency shift factors, α_T. As seen in Figure 8, for various stars and the other three dumbbells, the α_T data exhibit a virtually identical temperature dependence. For the smaller sample DB1200 there is a sharp deviation, which becomes enhanced as the temperature increases. Structural differences (due to larger PS content) can be considered as the origin of this difference.

IV. Concluding Remarks

Model dumbbell copolymers of styrene and butadiene can be synthesized by anionic high-vacuum techniques, hydrosilylation reactions, and chlorosilane linking chemistry. A series of well-defined dumbbell copolymers of $(PBd)_{32}PS(PBd)_{32}$ type with the same polystyrene (PS) connector and 32 polybutadiene (PBd) branches, on both ends, with different branch molecular weight (1200, 5000, 15 000, 43 000) were synthesized. As long as the composition of the connector is small (below 10%), the branch molecular weight controls the dumbbell dynamics, which is essentially characterized by the starlike relaxation of each branch. On the other hand, for larger connector composition, and very small branch molecular weight (below its entanglement limit), it is the total (connector and branch) molecular weight that controls the dumbbell dynamics (center-of-mass motion).

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