Effect of Branch Point Position on the Linear Rheology of Asymmetric Star Polymers

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Rapid advances in theoretical understanding of the linear and nonlinear viscoelasticity of entangled polymers have led to new models that can account for the effects of both polydispersity and long-chain branching on rheology.[1−3] Since detailed information on long-chain branching is difficult or impossible to obtain from other methods,[4] it is of special interest to use molecular rheological theory to infer branching information from rheology. Recent molecular theories for long-chain-branched polymers are based on the well-known tube model for entangled polymers, in which relaxation occurs by a combination of reptation of linear chains along the tube, fluctuations of chain ends inside the tubes, and constraint release, whereby motions of surrounding chains release entanglements on the tube. These physics were included in a linear viscoelastic model developed by Milner and McLeish and applied by them to simple monodisperse linear polymers,[5] star polymers,[6] mixtures of star with linear polymers,[7] nearly monodisperse "H" polymers,[8,9] and nearly monodisperse comb polymers.[10,11] Larson[2] developed a "hierarchical model" that incorporated the physics of the Milner−McLeish model, as well as some additional physics described below, in an algorithm applicable to general mixtures of polydisperse branched and linear polymers. Park and Larson et al.[12] modified this hierarchical model to include the "early-time fluctuations". A related model was also developed by Das et al.[13] which included the effect of branches on branches, i.e., hyperbranching. However, these "hierarchical" models have only been tested for a few different model branching structures, namely stars, H, and comb polymers, which have one or more branch points. These tests allow for the effect of number and length of branches to be studied, but the effect of branch position has not been systematically examined.

Recently, however, Archer and co-workers[14] reported synthesis and rheological measurements for simple model asymmetric star polymers with a single branch point connecting a short "arm" to a long "backbone", with two different positions of the branch point along the backbone. The samples are 1,4-polyisoprene "T-shaped" A_2B73K and "Y-shaped" AB_2110K shown in Figure 1a and described in Table 1. Archer and co-workers showed that these data were consistent with a model they developed for asymmetric stars. In their model, they allowed a numerical coefficient "p^2", which relates the length of an attached arm to the mobility of its branch point, to be a function of the entanglement density of unrelaxed backbone segments,[14] while in the hierarchical model it is set to a constant value, $p^2 = 1/12$.[12] While the model of Archer et al. gives good agreement with their data, here, we use their data to evaluate independently whether or not the hierarchical model, which is a general model applicable to a wide range of polymer architectures, also accurately predicts the effect of branch point position on rheology, but without varying the parameter p^2 from the canonical value of 1/12. The parameters needed in the hierarchical model are the plateau modulus G_N^0, the entanglement spacing M_e, and the equilibration time τ_e, which can be obtained from Archer et al.,[14] namely $M_e = 4200$ g/mol, $G_N^0 = 0.6$ MPa, and $\tau_e = 7.4 \times 10^{-6}$ s at $T = 28$ °C. These parameter values are similar to those used by Park and Larson et al.[12] at $T = 25$ °C. In the hierarchical model, the "dilution exponent" α is set to the value 4/3, which was found to produce accurate predictions of other polyisoprene branched structures, such as symmetric stars.[12]

Table 1. Molecular Characterization of T- and Y-Shaped 1,4-Polyisoprene Asymmetric Stars

	M_n(SEC with LS) [g/mol] ($\times 10^{-3}$)			M in model [g/mol] ($\times 10^{-3}$)	
sample	(1) short	(2) long	(3) total	(1) short	(2) long
A_2B73K	33	73.4	169	33	73.4
AB_2110K	32.78	110.06	170.06	32.8	110

In Figures 2 and 3, we compare the predictions of the hierarchical model with experimental data for the storage and loss moduli of A_2B73K and AB_2110K. The basic idea of the hierarchical model is as follows. We consider the response of the melt to a small step strain and calculate the time-dependent linear viscoelastic relaxation modulus, which can then be converted to frequency-dependent storage and loss moduli G' and G'' using standard methods. At a short time after a small step strain, only the arms can relax inward from their tips by early time fluctuations and late-time retraction. We estimate

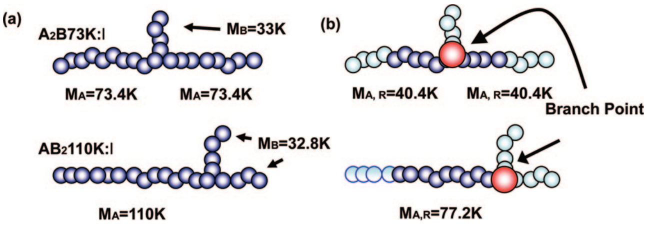

Figure 1. (a) Structure of "T-shaped" A_2B73K and "Y-shaped" AB_2110K 1,4-polyisoprene asymmetric star polymers. (b) Unrelaxed remaining backbones after relaxation of the short arms are shown in dark blue.

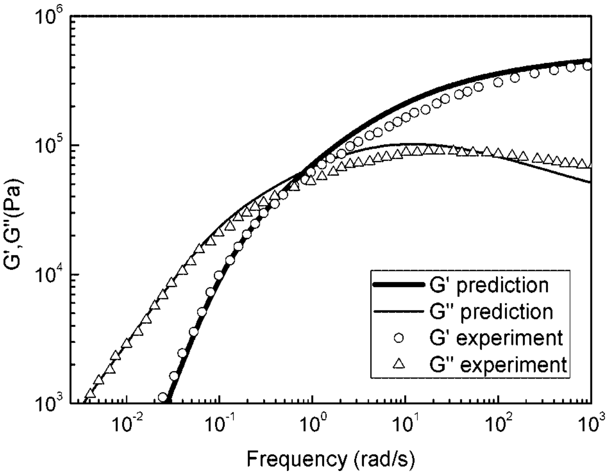

Figure 2. Dynamic moduli, $G'(\omega)$ and $G''(\omega)$, of "T-shaped" A_2B73K 1,4-polyisoprene asymmetric star polymer. The symbols are experimental data from Lee et al.[14] The solid lines are the predictions of the hierarchical model.

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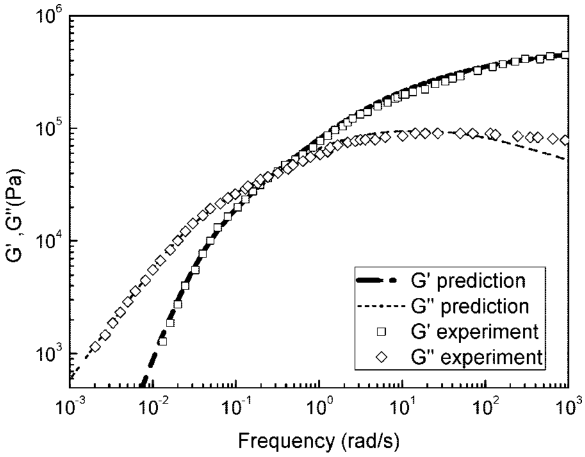

Figure 3. Same as Figure 2, except for the "Y-shaped" $AB_2$110K 1,4-polyisoprene asymmetric star polymer.

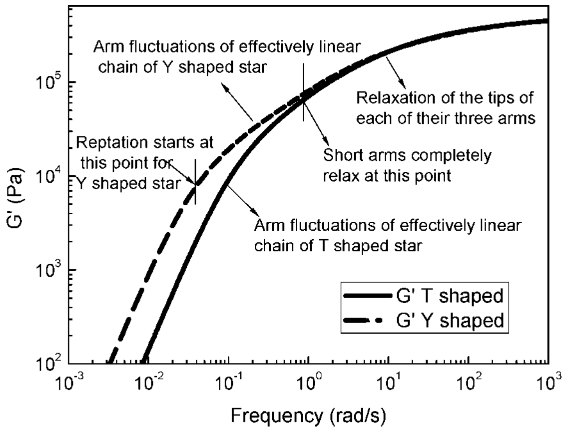

Figure 4. Comparison of dynamic moduli, $G'(\omega)$, of "T-shaped" and "Y-shaped" 1,4-polyisoprene asymmetric star polymers, as predicted by the hierarchical model.

early-time fluctuations by the function used by Milner and McLeish,[6] namely $\tau_{\mathrm{early}}(\xi) = (9/10)\pi^3\tau_e S_a{}^4\xi^4$, and the late-time arm retraction is then calculated directly from the numerical integration of $\tau_{\mathrm{late}}(\xi) = (L^2/D_{\mathrm{eff}})\int_0^{\xi} \mathrm{d}\xi' \exp[U_{\mathrm{eff}}(\xi')]\int_{-\infty}^{\xi} \mathrm{d}\xi'' \exp[-U_{\mathrm{eff}}(\xi'')]$, with $L^2/D_{\mathrm{eff}} = (3/2)\pi^2 S_a{}^3\tau_e$. In calculating the relaxation spectrum of an arm, we need the crossover equation between the early-time and the late-time functions. To obtain this, we use the equation developed by Milner and Mcleish,[12] which is $\tau_a(\xi) = \{\tau_{\mathrm{early}}(\xi) \exp[U_{\mathrm{eff}}(\xi)]\}/\{ 1 + \tau_{\mathrm{early}}(\xi) \exp[U_{\mathrm{eff}}(\xi)]/\tau_{\mathrm{late}}(\xi)\}$. At any time t, the arm will have relaxed from its free end to a point ξ obtained by equating τ_a with t; hence, $t = \tau_a(\xi) = \{\tau_{\mathrm{early}}(\xi) \exp[U_{\mathrm{eff}}(\xi)]\}/\{1 + \tau_{\mathrm{early}}(\xi) \exp[U_{\mathrm{eff}}(\xi)]/\tau_{\mathrm{late}}(\xi)\}$. When an arm is fully relaxed, it is conceptually pruned away and replaced by a bead at the branch point, which schematically represents the frictional drag contributed by that arm. Eventually, the unrelaxed molecule becomes a "linear" molecule. The final relaxation then occurs by reptation of an effectively "linear" chain, which, however, reptates slowly because of the beads representing the drag produced by the arms. The details of the hierarchical model are given by Park et al.[12] and Larson.[2]

Figure 4 shows that, over most of the frequency range, computed dynamic storage moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, of A_2B73K and $AB_2$110K are quite similar, except that the "Y-shaped" $AB_2$110K polymer relaxes somewhat slower in the terminal regime than does the "T-shaped" A_2B73K. In the high-frequency range, the "T-shaped" and "Y-shaped" molecules behave similarly because they both experience relaxation of the tips of each of their three arms. For the "T-shaped" star molecule, the short arm completely relaxes at time $t = 1.28$ s, while for "Y-shaped" molecule, the two short arms completely relax at a similar time $t = 1.36$ s. We have marked in Figure 4 the inverse times (as frequencies) at which the first short arm completely relaxes.

The difference between the rates of relaxation of the two molecules in the terminal regime can be explained as follows. For both molecules, the branch point is immobile until the short "B" arm has relaxed, after which the chain becomes effectively linear. At this point, for the "T-shaped" molecule A_2B73K, as shown at the top of Figure 1a, fluctuations are still active at both ends of what has become effectively a linear chain. If the reptation time of linear molecule, τ_d, is bigger than the present time t, the chain is not yet ready to relax by reptation.[2] The calculations using the hierarchical model show that no reptation occurs for the "T-shaped" molecule before both of the remaining arms have completely relaxed by contour length fluctuation to the point of disentanglement by dynamic dilution. On the other hand, for the "Y-shaped" molecule $AB_2$110K, both short arms relax at the same time, leaving an effectively linear chain, but with a low-mobility branch point at one end. Thus, further fluctuations are limited to the remaining long arm, which relaxes slowly by fluctuations due to its long length. The calculations with the hierarchical model show that at $t = 33.3$ s the long arm of the "Y-shaped" molecule abruptly relaxes by reptation. Therefore, in the relaxation process that occurs immediately after the molecules have become effectively linear, A_2B73K has two free ends that can relax through fluctuations while $AB_2$110K has only one free end that can relax fluctuations; hence, the former relaxes faster than the latter.

In summary, the hierarchical model given by Larson[2] and modified by Park and Larson et al.[12] yields good agreement with experimental data for long-chain branched polymers for two different branch point positions along a backbone of fixed length. Combined with earlier studies, we conclude that the hierarchical model captures not only the effects of the number and length of long-chain branches (as shown in earlier work) but also the position of the branch point.

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References and Notes

(1) McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379.
(2) Larson, R. G. *Macromolecules* **2001**, *34*, 4556.
(3) Watanabe, H. *Prog. Polym. Sci.* **1999**, *24*, 1253.
(4) Janzen, J.; Colby, R. E. *J. Mol. Struct.* **1999**, *486*, 569.
(5) Milner, S. T.; McLeish, T. C. B. *Phys. Rev. Lett.* **1998**, *81*, 725.
(6) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1997**, *30*, 2159.
(7) Milner, S. T.; McLeish, T. C. B.; Young, R. N.; Hakiki, A.; Johnson, J. M. *Macromolecules* **1998**, *31*, 9345.
(8) McLeish, T. C. B.; et al. *Macromolecules* **1999**, *32*, 6734.
(9) Daniels, D. R.; McLeish, T. C. B.; Kant, R.; Crosby, B. J.; Young, R. N.; Pryke, A.; Allgaier, J.; Groves, D. J.; Hawkins, R. J. *Rheol. Acta* **2001**, *40*, 403.
(10) Daniels, D. R.; McLeish, T. C. B.; Crosby, B. J.; et al. *Macromolecules* **2001**, *34*, 7025.
(11) Inkson, N. J.; Graham, R. S.; McLeish, T. C. B.; Groves, D. J.; Fernyhough, C. M. *Macromolecules* **2006**, *39*, 4217.
(12) Park, S. J.; Shanbhag, S.; Larson, R. G. *Rheol. Acta* **2005**, *44*, 319.
(13) Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. *J. Rheol.* **2006**, *50*, 207.
(14) Lee, J. H.; Fetters, L. J.; Archer, L. A. *Macromolecules* **2005**, *38*, 10763.

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