Viscoelastic Properties of 32-Arm Star Polybutadienes

We recently succeeded in making a series of regular 32-arm star 1,4-polybutadienes with narrow molecular weight distribution. The characterization and the dilute-solution properties of the polymers have been described.[1] The linear viscoelastic properties of the melts have been measured with a Rheometrics mechanical spectrometer (605 M). The dynamic mode was used with parallel platens and small deformations within the linear regime. Measurements were made at frequencies between 10^{-2} and 10^{2} rad/s. The highest temperature is dictated by the need to reach the terminal zone. The lowest temperature is about −75 °C, which is approximately 20 °C above the glass transition temperature of polybutadiene. Master curves of $G'(\omega)$ and $G''(\omega)$ have been constructed by superposing data obtained at different temperatures to the reference temperature (25.8 °C). See Figure 1.

The terminal properties of the star polymer melts $\eta_0 = \lim_{\omega\to 0} G''(\omega)/\omega$ and $J_e° = (1/\eta_0^2)\lim_{\omega\to 0} G'(\omega)/\omega^2$ are given in Table I. In this work, the longest relaxation time is phenomenologically defined as $T_{\max} = 4/\omega_{G''=G'}$,[2] where $\omega_{G''=G'}$ is the frequency of the crossover in the terminal zone (see Figure 1). $T_{\max}$ is also given in Table I. Two characteristic properties of the plateau zone are also given in Table I. The plateau modulus is derived from $G_N° = (2/\pi)\int_{-\infty}^{\infty}[G''(\omega) - G_s''(\omega)]\,\mathrm{d}\ln\omega$. In the plateau zone $G''(\omega)$ of star polymers goes through a maximum (see Figure 1). The time associated with this maximum is given as T_{eq}. T_{eq} has been identified with the time required for arm-length equilibration.[3] This process has also been considered for linear polymers.[4,5]

Many theoretical models for the time (or frequency) dependence of the modulus of melts of star polymers have been proposed.[2,6-8] All models depict the relaxation of star polymers by an arm-retraction mechanism in a mesh of entangled arms. The arms relax uncorrelated, and the relaxation process depends solely on conformational statistics. The longest relaxation time and the melt viscosity are then exponential functions of the number of entanglements per arm T_1 or $\eta_0 \propto \exp(\nu N_a)$. Furthermore, $J_e° \propto \nu' N_a$. Note that all the terminal properties are independent of f, the number of arms in the star.

Table I
Properties of Melts of 32-Arm Star Polybutadienes

sample	$M_w \times 10^{-5}$	η_0, P	$J_e° \times 10^7$, cm²/dyn	log $T_{\max}$	$G_N° \times 10^{-7}$, dyn/cm²	log T_{eq}
PBD3205B2	1.69	4.95×10^2	3.5_5	−3.92	[1.2][a]	
PBD3210B2	3.01	3.88×10^3	5.8_9	−2.82	[1.2][a]	4.2
PBD3216B2	5.58	6.58×10^4	10.5	−1.38	1.26	3.6
PBD3220B3	6.44	1.5×10^5	11.8	−1.0	1.21	3.4
PBD3237B3	13.3	$1.7_2 \times 10^7$	≥25	1.3_5	1.25	2.7

[a] Estimate because contribution of $G_s''(\omega)$ to $G''(\omega)$ is large.

Comparison of $G_N°$ in Table I with values for linear,[9] four-arm,[3] and 18-arm[10] star polymers suggests that $G_N°$ increases slightly (≈10%) for 32-arm stars. A 20% increase in $G_N°$ has been observed for multiarm stars.[11] The increase in $G_N°$ appears to be related to the increasingly non-Gaussian segment distribution of the arms in the stars as the number of arms increases. This is well documented for star polymers in dilute Θ-solvents. It carries also over to the conformation of stars in the melt.[12] For star polymers with many arms $M_e = \rho RT/G_N°$ is slightly lower than for linear polymers. In this work we have retained the classic value $M_e = 1970$ for polybutadiene[9] to calculate N_a, the number of entanglements per arm. It is difficult to determine whether $G_N°$ depends also on the molecular weight of the star at a constant number of arms. Furthermore, values of M_e may vary along the arm of the star.

For the 32-arm star polymers T_{eq} is a function of N_a^2 as previously observed for 4-arm,[3] 18-arm,[10] and multiarm star polymers.[11] Values of T_{eq} are independent of f and appear not to be sensitive to the detailed chain conformations of the stars.

In Figure 2 ln $(\eta_0/N_a^{1/2})$ is plotted against N_a. The slope is the same for all stars ($\nu = 0.4$). The absolute values of η_0 are slightly higher for the 32-arm stars than for the stars with less arms. This may be related to the small increase in $G_N°$. However, values of η_0 for the multiarm stars ($f = 270$) are 3 times higher, beyond any increase in $G_N°$ and N_a. Similar results are obtained when ln $(T_{\max}/N_a^{3/2})$ is plotted against N_a.

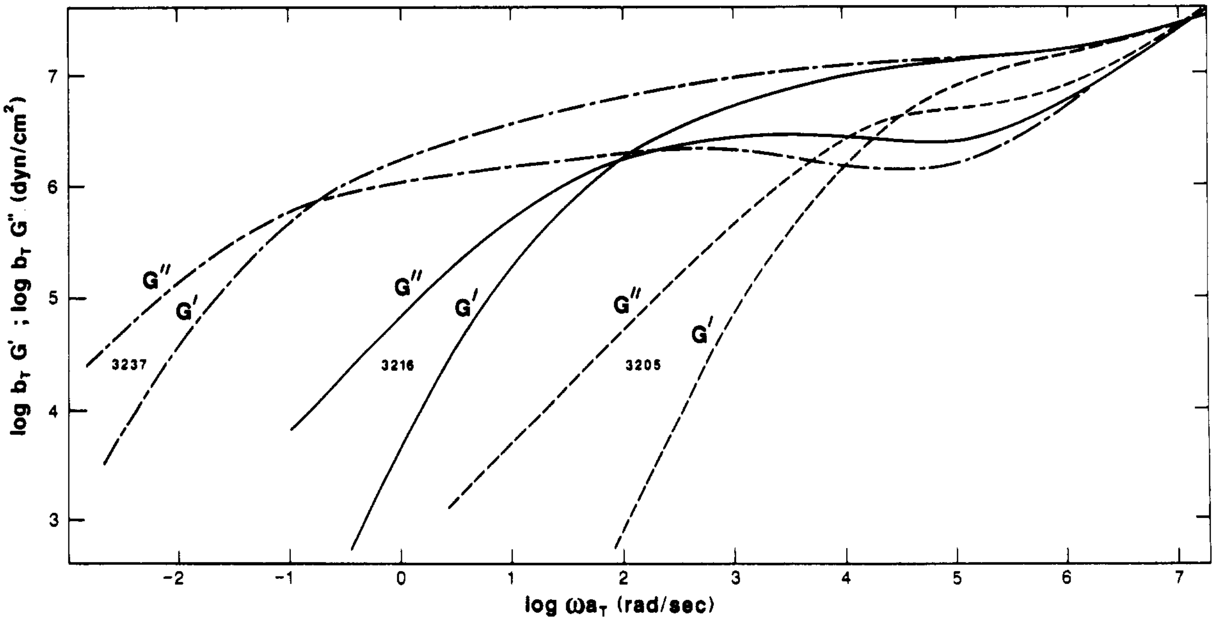

Figure 1. Master curves of $G'(\omega)$ and $G''(\omega)$ for 32-arm star polybutadienes; $T_{ref} = 25.8$ °C. The number by each pair of curves refers to the sample code in Table I.

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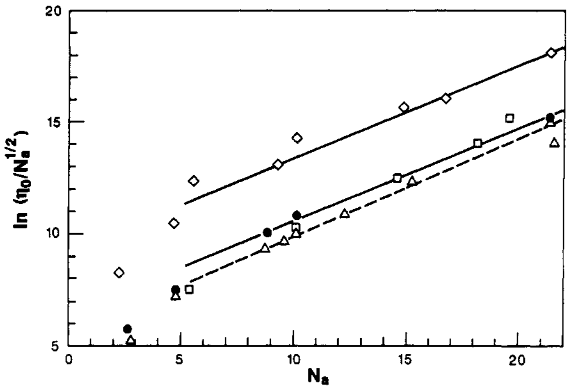

Figure 2. Plot of ln ($\eta_0/N_a^{1/2}$) against the number of entanglements per arm: (◇) multiarm star; (●) 32-arm; (△) 18-arm; (□) 4-arm star polybutadienes. T = 25.8 °C.

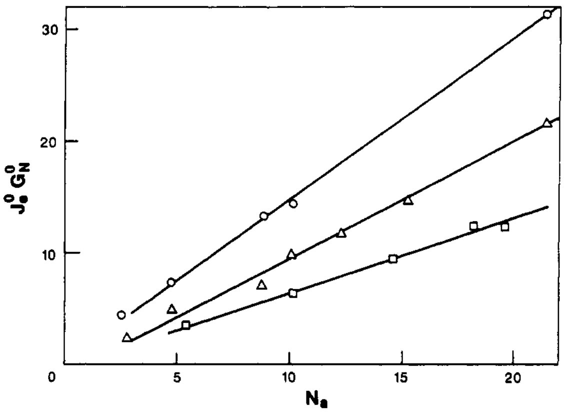

Figure 3. $J_e°G_N°$ against the number of arms: (○) 32-arm; (△) 18-arm; (□) 4-arm star polybutadienes.

In the case of $J_e°$ large differences among the star polymers with different arms are found. As shown in Figure 3, values of $J_e°$ increase rapidly with the number of arms of the star. For 32-arm stars $\nu' = 1.4$, compared with $\nu' \approx 1.0$ for 18-arm stars[10] and 0.6 for 4-arm stars.[3] This trend continues, because stars with more than 200 arms have $\nu' \geq 7.0$.[11] Contrary to theoretical expectations, there is therefore clear experimental evidence that $\nu' - \nu$ increases with the number of arms in the star. For $f \leq 8$, $\nu' \approx \nu$.[2] It is obvious from Figure 3 that the increase in $J_e°$ cannot be accounted for by a possible small increase in N_a. The terminal relaxation mechanism of star polymers changes and is extended to longer times as the number of arms of the star increases. This is evident first in increased values of $J_e°$ and for stars with many arms both in $J_e°$ and η_0.[11]

Our lack of a detailed knowledge about the conformation of star polymers makes it difficult at this time to identify unambiguously the reasons for the increase of the terminal relaxation time of star polymers with increasing number of arms. The experimental results show clearly that neither T_{eq} nor T_{max} (as defined) are affected by the number of arms. Furthermore, η_0 is independent of f for $f \leq 32$. Only $J_e°$ increases steadily with f. This suggests that the very longest relaxation times of the stars are exclusively increased when f increases. The longest relaxation times are related to the relaxation of the arm near the central core.[2] This is also the part of the chain where the chain conformation is expanded[13] and, possibly, the molecular weight between entanglements is smallest. It is therefore conceivable that the chain dynamics is selectively changed in the long-time range.

Ball and McLeish have pointed out that in the terminal zone the arm-retraction and constraint-release mechanisms are strongly coupled.[8] It is possible that constraint release is less effective in the terminal relaxation processes of stars with many arms, e.g., because other polymer chains are partially excluded from the region near the core of a star. If constraint release is absent, $\nu' = \nu = 15/8$ is expected.[14] This is not found. Indication is that ν' increases beyond 15/8.

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References and Notes

(1) Zhou, L.-L.; Toporowski, P. M.; Roovers, J.; Hadjichristidis, N., to be published in *Rubber Chem. Technol.*
(2) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*, 888.
(3) Roovers, J. *Polymer* **1985**, *26*, 1091.
(4) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1005.
(5) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(6) de Gennes, P.-G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(7) Doi, M.; Kuzuu, N. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 775.
(8) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(9) Roovers, J. *Polym. J.* **1986**, *18*, 153.
(10) Toporowski, P. M.; Roovers, J. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 3007.
(11) Roovers, J. *J. Non-Cryst. Solids* **1991**, *131-133*, 793.
(12) Horton, J. C.; et al. *Macromolecules* **1989**, *22*, 681.
(13) Richter, D.; Farago, B.; Fetters, L. J.; Huang, J. S.; Ewen, B. *Macromolecules* **1989**, *22*, 468.
(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986; p 280.

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