Linear viscoelastic properties of mixtures of 3- and 4-arm polybutadiene stars

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The viscoelastic properties of a three-arm and a four-arm star polybutadiene with the same arm molecular weight (M_a) were studied. The zero-shear recoverable compliance (J_e^0) and plateau modulus (G_N^0) for these stars are the same. The zero-shear viscosity (η_0) of the three-arm star is 20% lower than that of the four-arm star. Mixtures of the stars had J_e^0 and G_N^0 unchanged. A 50/50 mixture of the three- and four-arm star was diluted with a low molecular weight linear polybutadiene. $G_N^0 \propto \phi^2$; $J_e^0 \propto \phi^{-1}$ and $M_e \propto \phi^{-1}$, as expected for dilution with a θ-solvent.

(Keywords: viscoelasticity; polybutadiene; star polymer; viscosity; zero-shear compliance; dilution)

INTRODUCTION

The viscoelastic properties of regular star polymers have attracted attention in relation with the tube and reptation molecular models for polymer melts and concentrated polymer solutions. In the newest theories[1-4] it is shown that the zero-shear viscosity (η_0) of a star polymer melt depends exponentially on the number of entanglements per arm but is independent of the number of arms.

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^a \exp\left(v'\frac{M_a}{M_e}\right) \tag{1}$$

where M_a is the molecular weight of the arm and M_e is the molecular weight between two entanglements along the chain. The theories differ in the value of the exponent a. Also the product of the zero-shear recoverable compliance (J_e^0) and the plateau modulus (G_N^0) is predicted to depend solely on the number of entanglements:

$$J_e^0 \times G_N^0 = v'\frac{M_a}{M_e} \tag{2}$$

where v' is a constant.

Since it is most likely that G_N^0 is a constant dependent only on the chemical composition of the polymer, equation (2) implies that J_e^0 is a linear function of M_a/M_e.

From the method of synthesis of star polymers it is suspected that the polymers are often mixtures of stars with different functionality[5,6]. According to equations (1) and (2) this would affect the experimental η_0 and J_e^0 values little, and the necessity for pure stars would be less stringent in rheological studies. Nevertheless, it was found that mixtures of 3- and 4-arm polystyrene stars have high J_e^0 values independent of M_a[7,8]. Such mixture was recently reinvestigated and a peculiar concentration dependence was observed for J_e^0.[9]

We have prepared a three- and four-arm star polybutadiene from the same precursor (arm) polymer. The linear melt viscoelastic properties of these polymers and of their synthetic mixtures were studied over a wider range of temperature than hitherto used. The effect of solvent dilution of a 50:50 mixture of the three- and four-arm star on the viscoelastic properties was also investigated.

EXPERIMENTAL

One three- and one four-arm polybutadiene star were prepared at room temperature in benzene with sec-BuLi followed by linking with methyltrichlorosilane (3-arm star) and 1,2-bis(methyldichlorosilyl)ethane[5,6]. The linking reaction is performed with 20% excess poly(butadienyllithium). The unreacted arm material was completely removed by successive fractionations. Two linear polybutadiene samples were prepared under the same reaction conditions and terminated with t-BuOH. The molecular weight characteristics of the samples are given in *Table 1*. The microstructure of all samples is 8–10% 1,2, 36% *cis*, and 54% *trans*. Mixtures of the stars, and mixtures of the stars with PB 1800 were made in benzene. The solvent was evaporated under high vacuum to constant weight.

Dynamic loss- and storage moduli were measured with a Rheometrics mechanical spectrometer over a 10^{-2} to 10^{2} rad s^{-1} frequency range. The temperature range was from 103°C to −77°C. Measurements of the glass transition temperature of linear polybutadienes gave $T_g(°C) = -96 - 9.5 \times 10^{+3}/M_n$ in good agreement with other data[10]. Measurements of the density of PB1800 gave $\rho(t) = 0.882 - 6.6 \times 10^{-4}\ (t-27)$ which compares favourably with high molecular weight values[11].

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RESULTS

The dynamic moduli–frequency curves obtained at different temperatures were superimposed by using small vertical shifts (log b_T) and horizontal shifts (log a_T) along the frequency axis to construct master curves at 27°C[12]. The loss moduli–frequency curves of a star polymer and of a linear polymer are shown in *Figure 1*. The loss modulus of the linear polymer has a maximum at low (terminal) frequencies with a good separation between the terminal and the transition zone. The loss modulus curves of the three-arm and the four-arm star rise continuously showing only a weak maximum in the middle of the plateau region. In general, the loss and storage moduli for the three-arm and four-arm stars are numerically equal at frequencies above 10 rad s^{-1}.

The plateau moduli of each polymer and the mixtures are calculated from[12]:

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{+\infty} [G''(\omega) - G_s''(\omega)] \mathrm{d} \ln \omega \qquad (3)$$

using the experimental terminal and plateau regions. The contribution of the transition zone, $G_s''(\omega)$, used in equation (3) is shown in *Figure 1*. The data are collected in *Table 2*. It can be seen that the plateau modulus is independent of the branch structure for high molecular weight poybutadienes. The molecular weight between entanglements for polybutadiene is found from[12]:

$$M_e = \frac{\rho R T}{G_N^0} = 1970 \qquad (4)$$

in good agreement with other results[10,12].

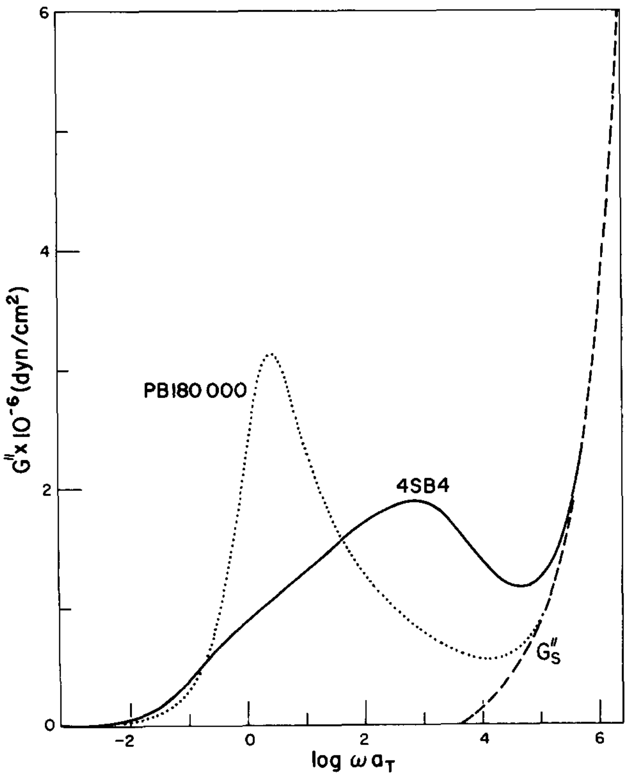

Figure 1 The loss moduli-frequency curve for a linear (PD 180 000) and a four-arm (4SB4) polybutadiene. Temperature: 27°C. G_N^0 is obtained by integrating the area under the curves. The contribution of the transition zone G_s'' is substracted

Table 1 Characteristics of polybutadiene

Sample	Type	M_a[a]	$[\eta]_\theta$[b]	$[\eta]_0$[c]	f[d]
3SB2	3-arm star	116 000	0.56_5	1.12	3.02
4SB4	4-arm star	151 000	0.57_2	1.17_5	3.92
PB180 000	linear	192 000	0.83_0	1.97	--
PB100	linear	1 800[e]	--	--	--

[a] M_w from light scattering in cyclohexane
[b] In dioxane at 26.5°C (dl g^{-1})
[c] $[\eta]$ in toluene at 25°C
[d] $(M_w)_{star}/(M_w)_a$
[e] From g.p.c.

Table 2 Rheological characteristics of polybutadiene at 27°C

Sample	$\eta_0 \times 10^{-6}$ (P)	$J_e^0 \times 10^6$ (cm^2 dyn^{-1})	$G_N^0 \times 10^{-7}$ (dyn cm^{-2})
3SB2	4.3_5	1.02	1.13
4SB4	5.4	1.07	1.15
PB180 000	3.1_5	0.18	1.11
PB1800	0.000003	—	—
(3S + 4S)50/50	4.8	1.1	1.15
(3S + 4S)25/75	5.1	1.2	1.13

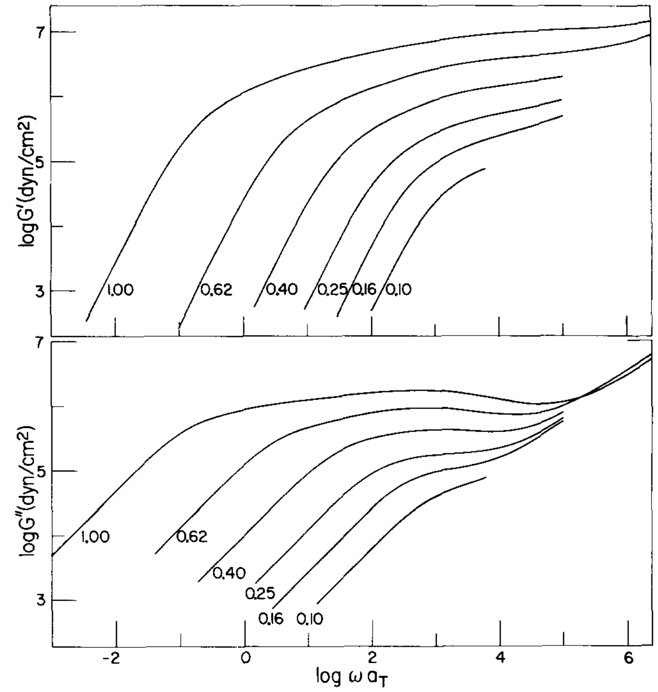

Figure 2 Moduli-frequency curves of a 50/50 mixture of a three- and four-arm star diluted with a low molecular weight linear polybutadiene (PB1800). Temperature: 27°C. The numbers with each curve indicate the volume fraction of the star

The η_0 data for the stars are also collected in *Table 2*. In our case, the η_0 of the three-arm star is about 20% lower than that of the four-arm star. The zero-shear viscosities of the mixtures of the two stars follow a linear blending law based on the weight fractions of the pure components. The zero-shear recoverable compliance (J_e^0) for the two stars are identical within experimental error. J_e^0 values for the mixtures are practically equal to those of the pure stars.

Moduli–frequency curves for the 50/50 mixture of the three- and four-arm stars when diluted with a low molecular weight linear polybutadiene (PB1800) are shown in *Figure 2*. As expected, the low frequency side of the plateau region shrinks considerably on dilution. Whenever the volume fraction of the star polymer $\phi < 0.50$, it is observed that the moduli measured below $-33°C$ slowly increased with time. The phenomenon is reversible and disappears on warming. Sufficient time is usually available to measure the high frequency moduli at lower temperatures. Differential scanning calorimetry experiments confirmed that PB1800 slowly (>1 h) crystallizes at or below $-40°C$. High molecular weight polymers do not crystallize under the same conditions. For this reason, curves with $\phi < 0.40$ in *Figure 2* are incomplete on the high frequency side. Nevertheless, the frequency range is sufficiently large to calculate G_N^0 with equation (3). The important viscoelastic properties of the dilution experiments are given in *Table 3*. It is found that $G_N^0 \propto \phi^2$ and that $J_e^0 \propto \phi^{-1}$ for $1.0 > \phi > 0.1$. These relations are shown in *Figure 3*. The zero-shear viscosities of the diluted star mixture drop precipitously from that of the bulk sample[13,14]. No power law dependence of the form $\eta_0 \propto \phi^{3.4}$ can be found as when a linear polymer is diluted with low molecular weight polybutadiene.

DISCUSSION

The results indicate that the viscoelastic properties of a three- and four-arm star with the same M_a differ little. The plateau modulus of the stars, which has not been determined previously[10,14], is found to be equal to that of linear polybutadiene. Therefore, M_e is not affected by the branch structure as suggested also by the results on polystyrene stars[15]. Values of J_e^0 for the two stars are identical within experimental error. This is in agreement with equation (2). This follows also from the Rouse–Ham theory for stars[14], accordingly:

$$(J_e^0)_f = 0.4 \frac{(15f-14)}{(3f-2)^2} \frac{fM_a}{\rho RT} \qquad (5)$$

where f is the functionality of the branch points. Equation (5) predicts $(J_e^0)_3/(J_e^0)_4 = 1.03$.

Table 3 Rheological characteristics of (3S + 4S)50/50 diluted with low *MW* polybutadiene

ϕ^a	$\eta_0{}^b$ (P)	$J_e^0 \times 10^6$ (cm^2 dyn^{-1})	$G_N^0 \times 10^{-7}$ (dyn cm^{-2})
1.00	4.8×10^6	1.1	1.15
0.868	1.4×10^6	1.33	0.85
0.750	4.2×10^5	1.54	0.64
0.620	$1.3_5 \times 10^5$	1.7	0.45
0.400	$1.1_7 \times 10^4$	2.8	0.16_8
0.250	1.6×10^3	3.9	0.069
0.160	337	6.7	0.030
0.100	79	12.0	—

[a] Volume fraction of stars
[b] Corrected to isofree volume

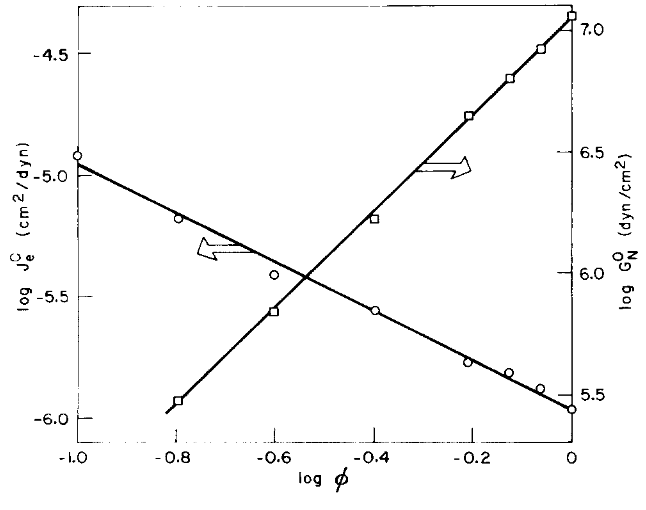

Figure 3 Dependence of J_e^0 and G_N^0 on the volume fraction of the stars when diluted with low moledular weight polybutadiene. (○) J_e^0; (□) G_N^0

The somewhat smaller zero-shear viscosity of the three-arm star represents a small departure from equation (1), that suggests that three-arm stars have an additional relaxation mechanism not available to stars with more arms[16].

The practical independence of J_e^0 on mixing three- and four-arm stars with the same M_a is in contrast with the behaviour of entangled linear polymers. Obviously, no new relaxation mechanisms are created on mixing the stars. The high values of J_e^0 found previously for four-arm polystyrenes[7,8] can therefore not be due to a simple incomplete linking reaction alone.

From equation (4) and the observed $G_N^0 \propto \phi^2$ dependence it follows that $M_e \propto \phi^{-1}$, i.e. the number of entanglements along a chain decreases linearly with the concentration of the polymer. This is the classic relation for an intermolecular process in a θ solvent[12]. It differs from $G_N^0 \propto \phi^{2.25}$ and $M_e \propto \phi^{-1.25}$ found when a polymer is diluted with a good solvent[14]. Consistent with G_N^0 constant and $M_e \propto \phi^{-1}$ we find that $J_e^0 \propto \phi^{-1}$. The experimental values of G_N^0 and J_e^0 can be used in equation (2) to calculate $v' = 0.68$. The initial decrease of J_e^0 found when a mixture of the three- and four-arm stars is diluted with 10% solvent[8] is not reproduced in this study. If such a decrease in J_e^0 is real, it must occur for a more complex mixture containing polymer other than three- and four-arm stars with the same M_a. Experiments in which a 4-arm star are mixed with a linear dimer ($M = 2M_a$) indicate that J_e^0 changes little in the presence of up to 50% dimer. A more systematic study of mixtures of starts with linear polymers may be required because the behaviour of J_e^0 may depend on the ratio of the molecular weights of the components as well as on their absolute molecular weight.

The zero-shear viscosities of the concentrated solutions can be used to test equation (1) with the exponent $a = \frac{1}{2}$ in equation (1). The experimental $v' = 0.52$ in the limit of large M_a/M_e, is less than the suggested value: $v' = 0.6$.[2] It is also smaller than the experimental $v' = 0.68$ obtained from the product $J_e^0.G_N^0$. Similar discrepancy is also found in the molecular weight study of four-arm polybutadienes[17].

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REFERENCES

1 Doi, M. and Kuzuu, N. Y. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 775
2 Pearson, D. S. and Helfand, E. *Macromolecules* 1984, **17**, 888
3 Needs, R. J. and Edwards, S. F. *Macromolecules* 1983, **16**, 1492
4 Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
5 Bauer, B. and Fetters, L. J. *Rubber Rev.* 1978, **51**, 406

6 Bywater, S. *Adv. Polym. Sci.* 1979, **30**, 90
7 Masuda, T., Ohta, Y. and Onogi, S. *Macromolecules* 1971, **4**, 763
8 Ohta, Y., Kitamura, M., Masuda, T. and Onogi, S. *Polym. J.* 1981, **13**, 859
9 Masuda, T., Ohta, Y., Kitamura, M., Minamide, M., Kato, K. and Onogi, S. *Polym. J.* 1981, **13**, 869
10 Rochefort, W. E., Smith, G. G., Rachapudy, H., Raju, V. R. and Graessley, W. W. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 1197
11 Valentine, R. H., Ferry, J. D., Homma, T. and Ninomiya, K. *J. Polym. Sci. Part A-2* 1968, **6**, 479
12 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., J. Wiley and Sons, New York, 1980
13 Kraus, G. and Gruver, J. T. *J. Polym. Sci. A-2* 1970, **8**, 305
14 Raju, V. R., Menezes, E. V., Marin, G., Graessley, W. W. and Fetters, L. J. *Macromolecules* 1981, **14**, 1668
15 Graessley, W. W. and Roovers, J. *Macromolecules* 1979, **12**, 959
16 Pearson, D. S. private communication
17 Roovers, J. *Polymer* 1985, **26**, 1091 (following paper)