

Properties of the plateau zone of star-branched polybutadienes and polystyrenes

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(Received 7 August 1984; revised 29 September 1984)

The plateau zone of monodisperse star polymers has a maximum in $G''(\omega)$. The time associated with this relaxation process ($1/\omega_{\max}$) is found to depend on the square of the number of entanglements per arm. It depends also on the monomeric friction coefficient (ζ_0). These are the dependencies expected for a Rouse type process. It is found that $1/\omega_{\max}$ agrees well with T_{eq} , the characteristic time for equilibration of the arm after deformation in the Doi and Pearson-Helfand theories. T_{eq} is calculated from the zero-shear properties of the stars. The agreement of T_{eq} and $1/\omega_{\max}$ depends however on the choice of v' . Reasonable agreement is also found when T_{eq} is calculated from ζ_0 and $\langle S^2 \rangle_0$, molecular characteristics of the linear chain. This would indicate that ζ_0 for the arm contraction is essentially the same as for other long-chain motions.

(Keywords: star-shaped polymers; polybutadiene; polystyrene; zero-shear viscosity; zero-shear compliance; equilibrium time)

INTRODUCTION

Three processes are presently considered in the relaxation of a melt or a concentrated solution of an entangled regular star polymer after it has been deformed from its equilibrium configuration^{1,2}. In a first very rapid process, the arms of the stars will return, on average, to the centre of the imaginary tube in which they are embedded. Because this process involves small sections of the chains the time required for this relaxation is expected to lie in the transition zone. In a second process, the arms will regain their equilibrium length. The characteristic time for this process is given by^{1,2}:

$$T_{\text{eq}} = A \left(\frac{\zeta_0 b^2}{kT} \right) N_a^2 \quad (1)$$

where ζ_0 is the monomeric friction coefficient (for that process) b^2 is the mean square end-to-end distance per monomer unit and N_a is the number of monomer units per arm and A is a constant to be determined. Equation (1) is a typical Rouse relaxation time, dependent on M^2 and dependent on c through the dependence of ζ_0 on c only and possible dependence of b^2 on c . The third and slowest process in the relaxation of the star is a reorientation by fluctuation of the distance between the branch point and the end of each arm³. The longest time for this process is given by

$$T_{\text{max}} = T_{\text{eq}} \left(\frac{N_a}{N_e} \right) \exp \left(v' \frac{N_a}{N_e} \right) \quad (2a)$$

or

$$T_{\text{max}} = T_{\text{eq}} \left(\frac{\pi N_e}{v' N_a} \right)^{1/2} \exp \left(v' \frac{N_a}{N_e} \right) \quad (2b)$$

from refs. 1 and 2 respectively. N_e is the number of monomer units between adjacent entanglement points and $N_a/N_e = N = M_a/M_e$ is the number of entanglements per arm; v' is a constant to be determined. When $N_a/N_e > 1$, the exponentials of equations (2a) and (b) will dominate T_{max} . Therefore, for stars, η_0 , the zero-shear viscosity, which is largely determined by T_{max} , will be a function of $\exp(M_a/M_e)$. Furthermore, the zero-shear recoverable compliance $J_e^0 \propto M_a^{-1-4}$. Numerous experimental studies support these relations⁵⁻⁸.

Experimentally, less attention has been paid to the shorter time characteristics of the relaxation of star polymers. If only the chain length fluctuations are important then $G'(\omega)$ and $G''(\omega)$ curves of stars are expected to rise steeply in the terminal zone and continue a slow rise throughout the plateau zone^{1,2}, up to frequencies of the magnitude of $1/T_{\text{eq}}$. Because faster relaxation processes are expected only in the transition zone, $G''(\omega)$ may exhibit a maximum at the short time end of the plateau zone⁷. The frequency of this maximum (ω_{\max}) is found to be independent of the number of arms in the star⁷. Other branched polymers like combs and H-polymers have a similar maximum in $G''(\omega)$ which is located at the same frequency as for a star provided that $M_{\text{br}} = M_a$ ^{9,10}. The molecular weight dependence of ω_{\max} is not well established⁷ and its concentration dependence is not known.

We have prepared a series of four-arm polybutadienes and measured their dynamic mechanical properties over a wide range of frequencies and temperatures with special attention to ω_{\max} . The values of $1/\omega_{\max}$ (s) are compared with T_{eq} determined by equation (2). Furthermore we have compared $1/\omega_{\max}$ with T_{eq} calculated by equation (1). The required values of ζ_0 and b^2 are taken from independent measurements on linear polymers. In another set of experiments a 50:50 mixture of three- and four-arm polybutadienes was progressively diluted with low molecular weight polybutadiene¹¹. The ω_{\max} data from these

* Issued as NRCC 24340

experiments are used here to study the concentration dependence of ω_{\max} . Earlier results on four-arm polystyrenes are also reevaluated.

EXPERIMENTAL

A series of four-arm polybutadienes was prepared in benzene with *sec*-BuLi as initiator. Vacuum techniques and *n*-BuLi washed and solvent rinsed vessels were used. A sample of the arm prepolymer was removed before the coupling agent, 1,2 bis(methyldichlorosilyl) ethane, was added^{1,2}. The star polymer was separated from the excess arm by fractionation in a benzene-methanol mixture. The samples were dried to constant weight and kept under vacuum in the dark at all times. The micro-structure was determined by n.m.r. and is typically 36% *cis*, 54% *trans* and <10% 1,2. The weight average molecular weights of the stars were determined by light scattering in cyclohexane at 25°C. The $dn/dc = 0.114_5$ ($\lambda_0 = 436$ nm) was determined for that system. The ratio of the molecular weight of the star and that of the precursor was 4.0 ± 0.1 . Intrinsic viscosities of the stars were measured in toluene at 35°C. The molecular weight and intrinsic viscosity results are given in Table 1.

Dynamic moduli of the stars were measured with a Rheometrics mechanical spectrometer. Parallel platens were used. Checks with the cone and platen fixture were also made.

Measurements at 6 or 7 temperatures between +103°C and -77°C were routinely made. The master moduli-frequency curves are constructed by shifting data at the various temperatures to 27°C¹³. A vertical shift approximately equal to $(\rho_0 T_0)/(\rho T)$ is applied. Examples of the moduli-frequency curves are shown in Figure 1.

The frequency at which $G''(\omega)$ reaches its maximum, ω_{\max} , is determined from $G''(\omega)$ versus $\log \omega$ plots. Corrections for contributions from the transition zone, $G'_s(\omega)$, to $G''(\omega)$ are made whenever $\log \omega a_T > 3.6$ for polybutadiene and when $\log \omega a_T > -0.2$ for polystyrene at the reference temperatures. Values of $G'_s(\omega)$ were obtained from measurements on high molecular weight linear polymers (ref. 11, Figure 1, for polybutadiene, ref. 7, Figure 5, for polystyrene). Contributions from the long time relaxation processes to $G''(\omega)$ at ω_{\max} are neglected. Theoretical $G''(\omega)$ vs. ω curves for these long time processes are quite horizontal in the plateau zone^{1,2} and

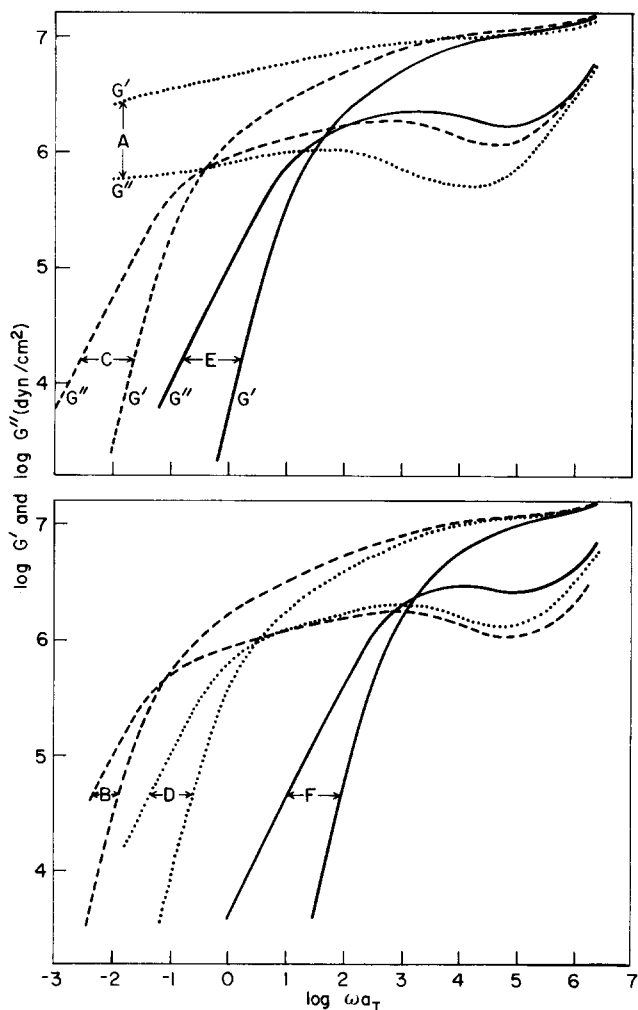


Figure 1 Log-log plot of loss and storage moduli-frequency curves for four-arm star polybutadienes at 300K. Letters refer to the samples of Table 1

will therefore have little influence on the position of the maximum.

RESULTS AND DISCUSSION

Molecular weight dependence

The characteristics of the polybutadiene stars and their rheological properties are collected in Table 1. The Table

Table 1 Characteristics of four-arm polybutadienes and polystyrenes^a

Sample ^a	$M_w 10^{-5}$	M_w/M_e	$[\eta]^{Tol}$	η_0 (P)	$J_e^0 \times 10^6$ (cm ² dyn ⁻¹)	$G_N^0 \times 10^{-7}$ (dyn cm ⁻²)	$\log \omega_{G''=G'}$
A ^c	3.95	50.8	2.45	—	—	—	—
B	1.62	20.6	—	$1.6 \cdot 10^7$	1.12	1.10	-0.91
C	1.51	19.2	1.18	$5.4 \cdot 10^6$	1.07	1.15	-0.36
D	1.21	15.4	1.01 ₆	$1.0_2 \cdot 10^6$	0.83 ₅	1.13	0.46
E	0.843	10.7	0.79 ₈	$9.4 \cdot 10^4$	0.57 ₅	1.10	1.65
F	0.452	5.7	0.51 ₅	$4.3 \cdot 10^3$	0.31	1.14 ₅	3.2 ₀
S181A ^d	10.27	14.3	2.72	$2.3 \cdot 10^8$	5.8	0.20	-2.65
S221A	8.97	12.5	—	$8.3 \cdot 10^7$	4.6	0.18	-2.15
S141AB	5.21	7.2	1.04	$6.7 \cdot 10^6$	2.4	0.20	-0.72
S161A	3.51	4.9	0.78	$1.14 \cdot 10^6$	1.9	0.18	0.19
S121A	0.935	1.3	0.30	$1.83 \cdot 10^4$	0.6	>0.16	2.45

^aReference: polybutadiene this work; polystyrene⁷

^bLog of the frequency at which $G'' = G'$ at the cross-over from the terminal to the plateau region

^cPolybutadienes at 300 K

^dPolystyrenes at 442.5 K

also includes the older data on polystyrene stars⁷. It can be seen from Table 1 that the zero-shear melt viscosities of the polybutadiene stars increase rapidly with molecular weight. On the other hand zero-shear recoverable compliance $J_e^0 \propto M$ and $G_N^0 \propto M^0$. The numerical data are in good agreement with published results on four-arm polybutadienes^{5,8}. The experimental values of ω_{\max} are given in Table 2 as $1/\omega_{\max}$ (s). The required value of ν' is derived from the experimental zero-shear properties according to²:

$$J_e^0 G_N^0 = \nu' (M_a/M_e) \quad (3a)$$

and

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^{1/2} \exp(\nu' M_a/M_e) \quad (4a)$$

The corresponding equations in the Doi-Kuzuu theory of ref. 1 are

$$\frac{4}{5} J_e^0 G_N^0 = \nu' (M_a/M_e) \quad (3b)$$

and

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^2 \exp(\nu' M_a/M_e) \quad (4b)$$

A plot of $J_e^0 G_N^0$ versus M_a/M_e is shown in Figure 2. From

Table 2 Characteristic times of the polybutadienes and polystyrenes

Sample	T_{\max} (s)		T_e (s) ^a	$\frac{1}{\omega_{\max}}$ (s)	τ_R (s) ^b
	Eq. 5	Eq. 6			
A ^c	—	—	—	14.0×10^{-3}	5.2×10^{-3}
B	35.8	31.8	2.2×10^{-3}	2.0×10^{-3}	0.86×10^{-3}
C	11.5	9.2	1.39×10^{-3}	1.4×10^{-3}	0.76×10^{-3}
D	1.7	1.4	1.23×10^{-3}	1.0×10^{-3}	0.48×10^{-3}
E	0.11	0.09	0.68×10^{-3}	0.5×10^{-3}	0.24×10^{-3}
F	0.002 ₇	0.002 ₅	0.14×10^{-3}	0.13×10^{-3}	0.068×10^{-3}
S181A ^d	2668	1787	3.22	4.46	1.66
S221A	764	565	2.12	3.38	1.26
S141AB	16.1	21	0.46	0.98	0.42
S161A	2.17	2.58	0.167	0.35	0.20
S121A	0.011	0.014	0.0026	0.0058	0.014

^a Calculated from T_{\max} in column 2 and equation (2b) with $\nu' = 0.5$

^b Equation (9)

^c Polybutadiene at 300 K

^d Polystyrene at 443 K⁷

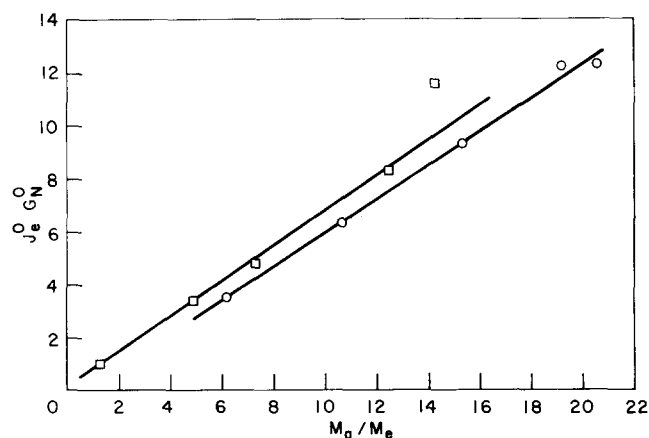


Figure 2 $J_e^0 \times G_N^0$ vs. M_a/M_e the number of entanglements per arm for four-arm star polymers. (○) polybutadienes, this work; (□) polystyrene ref. 7; The slope determines ν'

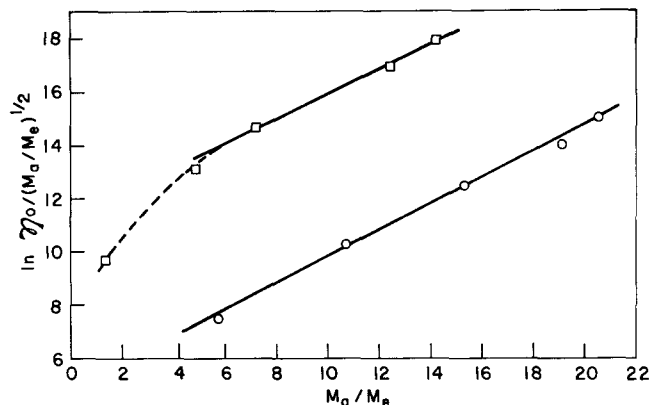


Figure 3 $\ln(\eta_0/(M_a/M_e)^{1/2})$ vs. M_a/M_e . Symbols as in Figure 2. The slope determines ν'

the slope a value of $\nu' = 0.66$ is derived using equation (3a).

With equation (3b) $\nu' = 0.53$. A plot of $\ln \left[\eta_0 \times \left(\frac{M_a}{M_e}\right)^{-1/2} \right]$ vs. M_a/M_e is shown in Figure 3. From the slope at high M_a/M_e $\nu' = 0.50$ is found. With equation (4b) $\nu' = 0.32$ is found. The older results for four-arm polystyrene stars give similar slopes. These data are also shown in Figures 2 and 3. The values of T_{\max} , the longest relaxation times, are obtained from^{1,2}:

$$T_{\max} = 2\eta_0 J_e^0 \quad (5)$$

or from²:

$$T_{\max} = 4/\omega_{G'=G''} \quad (6)$$

where $\omega_{G'=G''}$ is the frequency of the cross-over of G'' and G' at the end of the terminal and the beginning of the plateau regions. The experimental values of $\omega_{G'=G''}$ are given in Table 1. The agreement between T_{\max} from equations (5) and (6) is generally quite good.

For the calculation of T_{eq} with equation (2b) we used $\nu' = 0.50$ and T_{\max} from equation (5). The results are given in the fourth column of Table 2. The calculated T_{eq} values are compared with the experimental $1/\omega_{\max}$ data in Figure 4. One can judge from Figure 4 that $1/\omega_{\max}$ agrees well with T_{eq} in the theories of Pearson and Helfand. Similar agreement is found when T_{eq} is calculated with Doi's equation (2a) provided $\nu' = 0.32$ from the viscosity data is used.

Figure 4 shows that $1/\omega_{\max}$ depends approximately on $(M_a/M_e)^2$ for the polybutadiene stars. The earlier results for the polystyrene stars gave a slope of 2.85⁷. It is clear from Figure 4 that this high exponent is partly due to inclusion of a star with very small branches for which the theory is not expected to hold^{1,2}. It should be pointed out that T_{eq} is very sensitive to the choice of ν' . With $\nu' = 0.6$, T_{eq} is up to one order of magnitude smaller than with $\nu' = 0.5$ and almost independent of M_a/M_e . Also calculation of T_{eq} with equation (2a) would require $\nu' = 0.32$ from the zero-shear viscosity results in order to obtain $T_{eq} \propto \left(\frac{M_a}{M_e}\right)^2$.

It is of interest to check whether T_{eq} calculated from equation (2) and the experimental $1/\omega_{\max}$ are compatible with a Rouse relaxation time as defined by equation (1). The latter can be evaluated provided ζ_0 and b^2 of the polymer are known. The constant A in equation (1) has to be taken from theory. Two methods are available to determine ζ_0 .¹³ When $\eta_0 \propto M^1$, i.e. at low molecular weight near M_e :

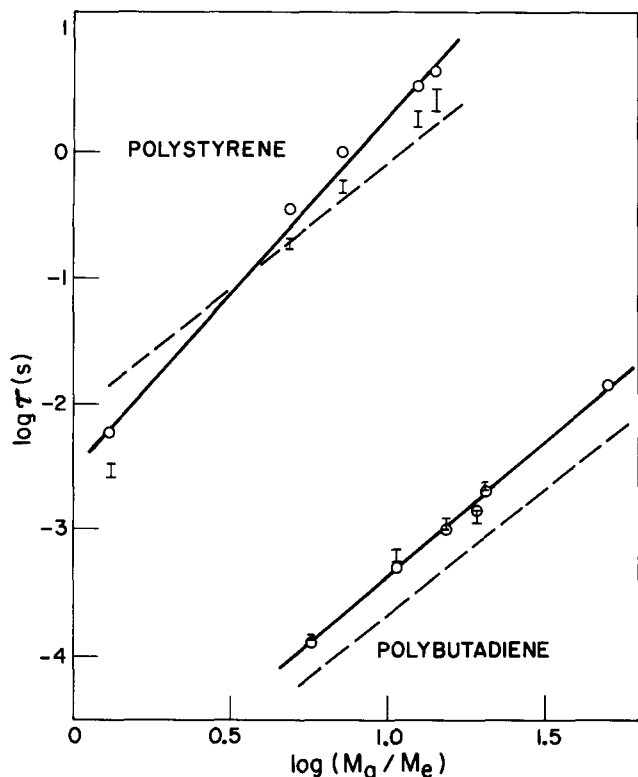


Figure 4 Log τ vs. $\log(M_a/M_e)$. Top: polystyrene. Bottom: polybutadiene. Symbols: (O) experimental $1/\omega_{\max}$; bars: T_{eq} calculated with Equation (2b) and T_{\max} from Equations (5) and (6) respectively. Dashed lines τ_R from Equation (9)

$$\zeta_0 = \frac{36\eta_0 M_0}{\rho N_A \langle r^2 \rangle_0} \quad (7)$$

with M_0 the molecular weight of the monomer unit, ρ the polymer concentration (g ml^{-1}), N_A Avogadro's number and $\langle r^2 \rangle_0$ the unperturbed end-to-end distance of the polymer.

The other method uses experimental data in the transition zone where $G' = G'' \propto \omega^{1/2}$.¹³ Then:

$$G' = G'' = \frac{b\rho N_A (\zeta_0 kT)^{1/2}}{4M_0} \omega^{1/2} \quad (8)$$

In order to evaluate ζ_0 for polybutadiene with equation (7) $\eta_0 = 10$ P when $M = 4000$ was used¹⁴⁻¹⁶. For polystyrene, $\eta_0 = 7.8 \cdot 10^3$ P at $M = 35\,500$ was used¹⁴, in good agreement with other data¹⁷⁻¹⁹. In equation (8) $\log G' = 7.4$ at $\log \omega a_T = 7.2$ is used for polybutadiene in reasonable agreement with data of Valentine²⁰. For polystyrene $\log G'' = \log G' = 6.82$ at $\log \omega a_T = 4.00$ is taken⁷, comparable with data from figures²¹. For polybutadiene $\zeta_0 = 1.1 \pm 0.5 \times 10^{-7}$ dyn.s cm^{-1} at 300 K and for polystyrene $\zeta_0 = 2.5 \pm 0.5 \times 10^{-5}$ at 443 K. If all data are included the value of ζ_0 is known within about a factor of two¹³. The r.m.s. end-to-end distance and $b^2 = \frac{\langle r^2 \rangle_0}{M} \cdot M_0$

are calculated from $\langle s^2 \rangle_0/M = 7.9 \times 10^{-18}$ cm^2 g mol^{-1} for polystyrene²² and 1.33×10^{-17} cm^2 g mol^{-1} for polybutadiene²³. No temperature correction for $\langle s^2 \rangle_0/M$ of polystyrenes is made because it is estimated to be about 5%²⁴ which is within the experimental accuracy of $\langle s^2 \rangle_0/M$. Graessley has pointed out that the configurational relaxation time of a tethered chain would be four-

times that for the same free linear chain⁴. The configurational relaxation time of a linear polymer is two times the longest Rouse time²⁵⁻²⁷, accordingly, the constant A in equation (1) equals $4/3\pi^2$ and

$$\tau_R = \frac{4}{3\pi^2} \frac{\zeta_0 b^2}{kT} N_a^2 \quad (9)$$

where τ_R is used to indicate the relaxation time from a molecular model. Values of τ_R are given in Table 2 and shown as a chain line in Figure 4.

Concentration dependence

In a preceding paper we have shown that the ω_{\max} is the same for a three-arm and a four-arm star with the same arm molecular weight¹¹. Mixing these stars has no effect on ω_{\max} . This is in agreement with the results on four- and six-arm polystyrenes⁷. We have also observed that ω_{\max} is practically unchanged when a polybutadiene star is mixed with a high molecular weight linear polybutadiene, although the maximum in $G''(\omega)$ becomes a shoulder when the star constitutes 50% or less of the mixture¹⁴. The characteristic time for the relaxation process that is observed at the G'' maximum is therefore unaffected by the concentration of the star and by its surroundings provided that the monomeric friction coefficient is unchanged.

As shown in Table 3, the frequency at the G'' maximum moves only slightly when a mixture of three- and four-arm polybutadienes is diluted with low molecular weight polybutadiene. At high dilution no maximum in G'' is observed. These shifts in ω_{\max} may well be within experimental error. In order to see whether ω_{\max} changes as ζ_0 , the latter has to be determined from a different set of experiments because there are no data for G'' and G' in the transition zone¹¹, nor are there data for η_0 below M_c at each volume fraction.

The monomeric friction coefficient can be obtained from experiments in which a high molecular weight linear polybutadiene is diluted with the same low molecular weight diluent as used for the stars. In the entanglement region:

$$\eta_0(M) = \eta_{\text{OR}}(M) \left(\frac{M}{M_c} \right)^{2.35} \quad (10)$$

with $\eta_{\text{OR}}(M)$ the hypothetical Rouse zero-shear viscosity (if no entanglements were present and $\eta_0 \propto M^1$).

With the expression for the Rouse viscosity (equation

Table 3 Frequency of G''_{\max} for polybutadiene stars at 300 K concentration dependence

Sample	ϕ	$\log \omega_{\max}$	$\Delta \log \omega_{\max}$	$\log a_\phi^{a,b}$
PBB(3+4S)3SB	1.0	2.8	—	—
PBD(3+4S)4SB	1.0	2.8	—	—
PBD(3+4S)50/50	1.0	2.8	—	—
	0.868	2.85	0.0	—
	0.75	2.85	0.0	—
	0.62	2.9	0.05	-0.02
	0.50	—	—	-0.02
	0.40	3.0	0.12	-0.04
	0.25	—	—	-0.04
	0.16	—	—	0.01
	0.089	—	—	0.139

^aCorrected for T_g

^bFrom PBD165000 diluted with PBD1800. Equation (12)

(7)) equation (10) becomes:

$$\eta_0(M) = \frac{\rho N_A \langle r^2 \rangle_0 \zeta_0}{36 M_0^2} \left(\frac{M}{M_c} \right)^{2.35} \quad (11)$$

In equation (11) only ζ_0 , ρ and M_c are expected to be concentration dependent if the diluent is a θ -solvent. With $M_c \approx 2 \cdot M_e \propto \phi^{-1}$,¹¹

$$\begin{aligned} \log \zeta_0(1.0) - \log \zeta_0(\phi) &= \log a_\phi \\ &= \log \eta_0(1.0) - \log \eta_0(\phi) + \log \phi^{3.35} \end{aligned} \quad (12)$$

Values for the concentration shift factor, $\log a_\phi$, determined from the dilution of a high molecular weight linear polymer are given in Table 3 and compared with the observed shifts in ω_{\max} . It can be seen that $\log a_\phi$ does not change on dilution with low molecular weight polybutadiene unless the latter represents 90% of the volume. The changes in $\Delta \log \omega_{\max}$ are somewhat larger but hardly outside the experimental error.

CONCLUSION

It has been shown that the experimental $1/\omega_{\max}$ is identical with the theoretical T_{eq} , the characteristic time for equilibration of the arms of a star after deformation. In agreement with theory it has been found that $1/\omega_{\max}$ depends on the square of the number of entanglements per arm and is independent of concentration provided ζ_0 is kept constant. It is also shown that $1/\omega_{\max}$ is roughly compatible with the configurational relaxation time from ζ_0 and $\langle s^2 \rangle_0$, molecular characteristics of the linear polymer.

We have observed that v' depends on the method by which it is extracted from the experimental results. v' determined from $J_e^0 \times G_N^0$ is larger than v' determined from η_0 data. Only v' from η_0 leads to $T_{\text{eq}} \propto (M_a/M_e)^2$ consistent with theory^{1,2}.

It should be pointed out that although $1/\omega_{\max}$ has Rouse-like characteristics, the dependence of $G''(\omega)$ and $G'(\omega)$ on ω at the high frequency end of the plateau is not that associated with the Rouse theory for isolated molecules or low molecular weight polymers^{1,3}.

Finally, it should be noted that the relaxation of the arms in a star polymer is the same as the B -process in the relaxation of linear polymers in the melt and concentrated solution^{2,5}. This relaxation process should appear in the plateau region of linear polymers and contribute also to

the experimental G_N^0 . For four-arm stars, the contribution of the retraction to equilibrium length of the arms to G_N^0 is probably small because the $G''(\omega)$ maximum is not marked. One could then speculate that the $G''(\omega)$ maximum may become more prominent in stars with many arms. It is certainly more important in combs with 30 branches than in stars⁹.

ACKNOWLEDGEMENT

The author thanks Mr P. M. Toporowski for help with the synthesis and characterization of the star polymer and Dr N. Hadjichristidis for making the rheological measurements on the mixtures. Dr W. W. Graessley made inspiring comments on a draft of this paper.

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