Viscosity and Normal Stresses of Linear and Star Branched Polystyrene Solutions. II. Shear-Dependent Properties[1a]

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ABSTRACT: The low-shear viscosity, η, and the primary normal stress difference coefficient, ψ, were measured for linear, 4-branched, and 6-branched narrow distribution polystyrenes in diethylbenzene (c = 25.5 g/dl) at ~20-40°. The viscosity *vs.* rate of shear, $\dot{\gamma}$, data were superimposed on the Graessley theoretical master curve computed for narrow distribution polymers, in accordance with the Wyman *et al.* results. The effective entanglement molecular weight above which the steady-state compliance, J_e, becomes independent of molecular weight was found to be: $M_{e,J} \cong 4M_c/\varphi$ or $M_{e,J} \cong M_c/\varphi^2$, where M_c is the critical entanglement molecular weight and φ the polymer volume fraction. The parameter S, which characterizes the breadth of distribution of the relaxation times, was found to be inversely proportional to the absolute value of the difference $|M_wc - M_e\rho|$. The maximum value of S at the entanglement point was found to be larger than the values predicted from the bead-and-spring model.

In the preceding paper[2] the zero-shear viscosities, η_0, of linear, 4-, and 6-branched polystyrene solutions in diethylbenzene were discussed. The concentration of these solutions was constant, c = 25.5 g/dl. The subject of this communication is the non-Newtonian behavior of these systems.

Under steady shear condition, simultaneously the tangential stress, p_{12}, and the primary normal stress difference, $p_{11} - p_{22}$, were recorded in a moderate range of rate of shear, $\dot{\gamma}$, extending only up to one decade into the non-Newtonian region. From the data, the apparent viscosity $\eta = p_{12}/\dot{\gamma}$, the primary normal stress difference coefficient, $\psi = (p_{11} - p_{22})/\dot{\gamma}^2$ and compliance, $J = \psi/2\eta^2$ were calculated as functions of $\dot{\gamma}$, T, and weight-average molecular weight of polymer, M_w. The data were compared with the results of a similar study[3] on linear polystyrenes in *n*-butylbenzene at 30°, and with the results on 4-branched polystyrene melts.[4]

Experimental Section

Polymer preparation and characterization were described previously.[5,6] The information on solvent and the method of dissolution of the polymer were given in the preceding paper.[2] The code numbers of the samples are taken from Table I in ref 2.

The rheological measurements were carried out with the cone-and-plate Weissenberg rheogoniometer, Model R18. The instrument was equipped with a new modified normal force servo system. Two pairs of platens were used: 5 and 7.5 cm diameter, both having 2° cone angle. Three torsion bars with the following spring constants K_T = 92.4, 877, and 10,080 (dyn cm)/μ were employed. The normal force spring (K_N = 6400 dyn/μ) and the torsion bars were recalibrated in our laboratory.[7] Where necessary ($\dot{\gamma} \geq 30$ sec^{-1}), the centrifugal force and shear heating effect corrections were used.[7]

The experiments were carried out isothermally ($T \pm 0.2°$) at temperatures from 23 to 36°. The data were inter- or, as in some cases, extrapolated to 30.0°. Since it was found that, owing to evaporation of diethylenebenzene (Et_2Ph), viscosity of the solutions slowly increases with time,[2] samples were sheared for less than 15 min. A small correction[2] based on the experimentally determined increase of η with time was applied.

The zero-shear primary normal stress difference coefficient

$$\psi_0 = \lim_{\dot{\gamma} \to 0} \psi$$

has been previously calculated[3] as the initial slope of the dependence $(p_{11} - p_{22})/\eta^2$ *vs.* $\dot{\gamma}^2$. It was found that for the investigated systems

$$\lim_{\dot{\gamma} \to 0} (p_{11} - p_{22}) = 0$$

and, as a consequence, the values of ψ_0 in the present paper were computed as

$$\psi_0 = \eta_0^2 \lim_{\dot{\gamma} \to 0} \psi/\eta^2$$

taking an average value of the few initial data points showing the random scatter. These values compared favorably with the low shear values of ψ_0 from the ψ *vs.* $\dot{\gamma}$ plot.

Results

The viscosity *vs.* rate of shear data were superimposed on the Graessley *et al.*[8] theoretical master curve: η/η_0 *vs.* $\dot{\gamma}\tau_0/2$ (see Figure 1). The procedure involved an assumption regarding the molecular weight distribution of the samples. After Graessley and Segal[3b] the Schulz-Zimm distribution function with the parameter Z = 10 was used. This choice, which implies that the ratio M_w/M_n = 1.09, is justified by the values 1.08 and 1.07 determined[5] for samples 15 and 43, respectively. The same type and width of the molecular weight distribution was assumed for the other samples as well. Owing to this uncertainty only the low-shear data (Newtonian and initial portion of the non-Newtonian regions) were used in the superposition procedure, allowing the high-shear data to deviate from the theoretical dependence. The superpositions are shown in Figure 1. The time characteristic parameters, τ_0, are given in Table I. Despite the limited accuracy to which these measurements are subjected, η_0, ψ_0, and τ_0 values of the linear polymer solutions are in good agreement with the data obtained in *n*-butylbenzene under otherwise identical experimental conditions.[3]

In Table I, the experimental values of zero-shear viscosity, η_0, and ψ_0 at 30.0° along with the steady-state compliance J_e calculated from these quantities are given.

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(1) (a) Part of this work was presented at the 55th Annual Meeting of the Chemical Institute of Canada, Quebec, Canada, June 5-7, 1972. (b) Department of Chemical Engineering, McGill University, Montreal, Canada. The shear-dependent properties were measured at the Gulf Oil Canada, Research Center in Ste-Anne-de-Bellevue, Quebec, Canada. (c) Division of Chemistry, National Research Council of Canada, Ottawa KIA OR9, Canada. (d) NRCC No. 13228.

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Table I
Rheological Parameters of Linear, 4-Branched, and 6-Branched Polystyrenes at 30°

Sample No.	$M_w \times 10^{-3}$	η_0 (P)	ψ_0 ((dyn sec^2)/cm^2)	$J_e \times 10^6$ (cm^2/dyn)	τ_0 (msec)	τ_N (msec)	τ_R (msec)	S	S_N
15	238	18.6	0.02	29	0.7	0.82	0.42	0.67	0.78
17	675	362 (365)	13	50	36	27	23	0.60	0.47
18	1790	13,100	16,000	47	2760	928	2200	0.49	0.17
43	351	7.5	0.0015	13	0.35	0.15	0.25	0.56	0.24
45	897	95	0.39	22	3	3.1	8.1	0.15	0.16
47	1390	569	30	46	84	40	75	0.45	0.21
66	1090	79	0.4	32	6	3.9	8.2	0.33	0.19
68	1820	347	4.8	20	21	9.9	60	0.14	0.07

Discussion

Zero-Shear Rate Parameters: η_0, ψ_0, and J_e. Recently Masuda *et al.*[4] reported on the viscoelastic properties of some 4-branched polystyrene melts. For polymers with molecular weights larger than the critical entanglement molecular weight, M_c, they observed that the shift factor a_T is the same as that for linear and comb-shaped polystyrenes. The viscosity, η_0, and the elastic coefficient $A_G = J_e\eta_0^2$, computed from the terminal zone data are lower, by the same factor, than those of linear polymers of the same molecular weight. As a result, the steady state compliance, J_e, of the branched polymers was found to be nearly one decade larger than those of the linear ones. Furthermore, for molecular weights above 4×10^4, which corresponds approximately to the critical entanglement molecular weight,[9] $M_c = 35{,}100$, J_e values for both linear and branched polymers were found to be independent of M_w.

The zero-shear parameters of Table I are in accordance with these results[4] as far as the zero-shear viscosity is concerned. For the highest molecular weight samples[2] the ratios of η_0 of a linear to a 4-branched sample and to a 6-branched sample are 10 and 39, respectively, whereas the ratios of the primary normal stress difference coefficients are approximately the square of these values. It follows that the steady-state compliance, J_e, for linear and star branched polymer solutions is of the same order of magnitude, as seen from column 5 in Table I. Furthermore, it should be noticed that only for linear samples 17 and 18, J_e reaches the plateau level: $J_e \cong 5 \times 10^{-5}$ cm^2/dyn. This would indicate that the molecular weight of the sample 15 is still below the effective entanglement molecular weight for linear polystyrenes in solutions. The values of $J_e \leq 5 \times 10^{-5}$ are found for all 4- and 6-branched samples. The J_e values for 4-branched samples follow an approximately linear dependence on molecular weight when plotted in log–log scale, reaching the linear polymer plateau level only for the highest molecular weight. Using the result of Masuda *et al.*[4] as a guide, one should expect that this trend will continue for higher molecular weight samples (or higher concentration). One should conclude that the effective entanglement molecular weight for the 4-branched polystyrenes in diethylbenzene solutions is not less than the molecular weight studied here. In both cases, for linear and 4-branched systems (data for the two 6-branched polymers are not conclusive) the expected effective entanglement molecular weight, above which J_e becomes independent of M_w, is surprisingly large: $2.38 < M_{e,J} \times 10^{-5} < 6.75$ for linear and $M_{e,J} \times 10^{-5} = 13.9$ for 4-branched polystyrenes. From the analysis of η_0 *vs.* M_w dependence the effective entanglement molecular weight was found to be related to M_c and polymer volume fraction φ by the relation[10]

$$M_{e,\eta} = M_c\varphi^{-a_1} \quad \text{for } \eta_0 \text{ } vs. \text{ } M \text{ dependence}$$

where the parameter a_1, which characterizes the solvent power, varies for flexible chain molecules from ½ to 1. The above equation is strictly valid for linear polymers. In the case of branched homologs, M_c should be divided[2] by the parameter g. Substituting the numerical values for linear polymers: $M_{e,\eta} \times 10^{-5} = 0.73\text{–}1.52$ is found, where from using the previous results,[2] $M_{e,\eta} \times 10^{-5} = 1.17\text{–}2.43$ is calculated for the 4-branched systems, in accordance with the experimental values 1.5×10^5 and 3×10^5 for linear and 4-branched polymers (for 6-branched samples $M_{e,\eta} = 5 \times 10^5$ was found). It is evident that the ratio of $M_{e,J}$ to $M_{e,\eta}$ approximately equals 4 or $1/\varphi$. In other words, the critical entanglement molecular weight for the steady-state compliance molecular weight dependence in polymer solutions is larger than that which governs the viscosity behavior and can be empirically expressed as

$$M_{e,J} = M_{e,\eta} \times 4$$

or as suggested by the empirical correlation between J_e and c in the entanglement region ($J_e \propto c^{-2}$, *e.g.*, see ref 3b) as: $M_{e,J} \cong M_{e,\eta}/\varphi \cong M_c/\varphi^2 \cong M_c/g\varphi^2$. The reason for this behavior lies in the molecular mechanism responsible for the levelling off of the J_e *vs.* M_w dependence.[11,12] The cessation of the molecular weight effect suggests a semipermanent entangled structure similar to that of cross-linked swollen polymer.

The compliance of sample 68 deviates somewhat, possibly because of a low ψ_0 for this polymer. A ψ_0 value of 10 (dyn sec^2)/cm^2 can be estimated for sample 68, when we apply $\psi_0 \propto M_w^{6.9}$, which holds for the other types of polymers. This would double the value of J_e which would still be below the plateau level of the linear polymer. Again, one would have to postulate that for the 6-branched polystyrenes $M_{e,J} \times 10^{-5} \geq 18.2$ as expected on the basis of the previous analysis.

Shear Rate Dependence of η; the Characteristic Time Constant τ_0. The shear-dependent solution viscosities of all three types of polystyrenes are superimposed on a single master curve calculated for narrow distribution polymers from the Graessley *et al.*[3,8] theory assuming Schulz–Zimm type of polydispersity function. The best fit to the theoretical curve is observed for 6-branched polymers; the worst for highest molecular weight linear polymer. This

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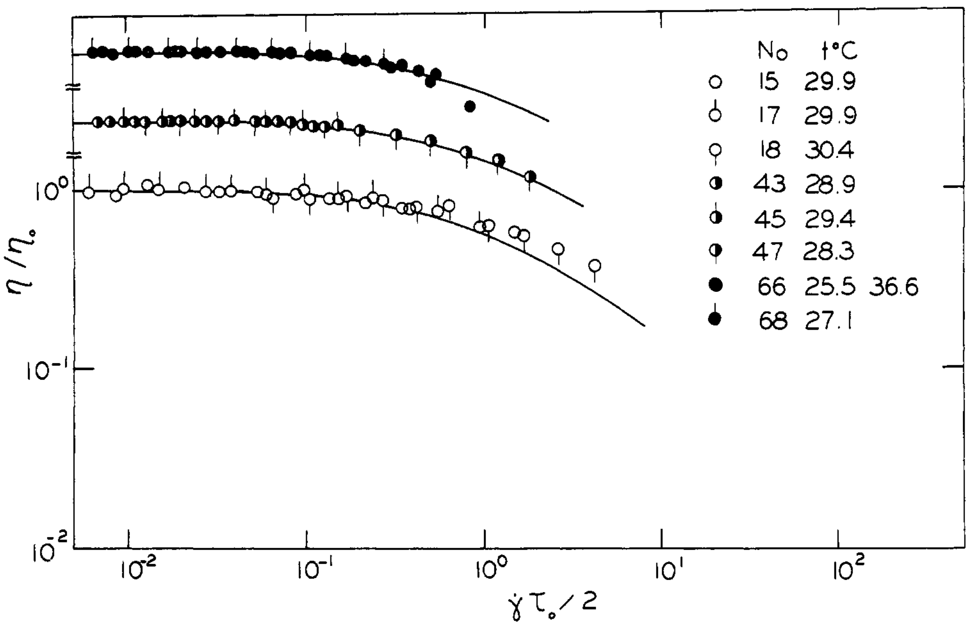

Figure 1. Superposition of η *vs.* γ data for linear and branched samples on the theoretical master curve (see text).

trend parallels the expected broadening of molecular weights. These results for $\dot{\gamma}$ extending only through the onset of the shear dependence of viscosity are in accordance with the high-shear measurements on narrow distribution linear and 4-branched polystyrene melts.[13a] The data indicate that Graessley's theory can be applied to star branched polymer solution viscosities: knowing η_0 and τ_0 one can predict the viscosity as a function of rate of shear for star branched polymers. It is worth recalling that η_0 for branched polymer can easily be calculated from η_0 of linear homologues.[2] Thus, it remains to find appropriate τ_0 for branched polymer system to generate the shear rate dependence of viscosity curve for a branched system.

In the original derivation,[8] the characteristic time constant, or the relaxation time parameter, τ_0 was postulated to be proportional to the Rouse relaxation time τ_R

$$\tau_0 = C\tau_R \tag{1}$$

where C is a constant of the order of unity and

$$\tau_R = (6/\pi^2)(\eta_0 M/cRT) \tag{2}$$

(where η_0 is the zero-shear viscosity, M is the polymer molecular weight, c is the polymer concentration, R is the gas constant, and T is the absolute temperature). However, the results on polystyrene[3b] and poly(vinyl acetate)[8c] solutions demonstrated that C was constant for unentangled systems, but decreased with concentration and molecular weight of the dissolved polymer in systems in which entanglement was expected

$$\begin{aligned} C &= \alpha/(1 + \beta cM) \\ C &= A/(1 + BE) \end{aligned} \tag{3}$$

where the average number of entanglement points $E = 2cM/\rho M_c$ and c is in g/ml (ρ is the density of undiluted polymer). Equation 3 is empirical and parameters α and β (or A and B) have to be determined for each system. There are also other reports (*e.g.*, see ref 3b, 11, and 12) on polymer melts seeming to indicate that eq 1 combined with eq 2 is valid in the range where entanglement is to be expected.

In order to gain a better perspective of the problem the rheological data, τ_0 and J_e for narrow distribution polystyrene solutions and melts were collected from the literature. The equations used for the calculations are

$$S = 0.4\tau_0/\tau_R = 2C/5 \tag{4}$$

$$S_N = cRTJ_e/M \tag{5}$$

Only for the present results and those of ref 3b, were S and S_N computed. The remaining data were calculated using the reported steady-state compliances. All the data are shown in Figure 2. Following the Graessley *et al.*[3,8] approach one should multiply S_N in eq 5 by the polydispersity factor $F = (M_w^2/M_zM_{z+1})$. As for many systems, these averages are not quoted, all but the Graessley *et al.*[3b] data are calculated assuming $F = 1.0$. The results of the latter authors are represented by broken lines calculated from eq 4 and 3 using the values of A and B quoted and with $F = 0.791$. The data cover the whole range of concentration; from very dilute systems[13b-16a] through concentrated solutions[3] (and this work) to polymer melts.[16b-18] In Figure 2 the data points of these three ranges overlap. Similarly, the regions of linear and branched samples do coincide.

The observed scatter of the data points is due not only to the experimental uncertainties but also to the differences in polydispersity of the samples used. As expected, the data[3b] corrected for molecular weight distribution tend to fall below the average value of uncorrected data points.

It is worth noting that in spite of the scatter, the resulting plot demonstrates a remarkable similarity in the rheological behavior for all these diverse systems. By con-

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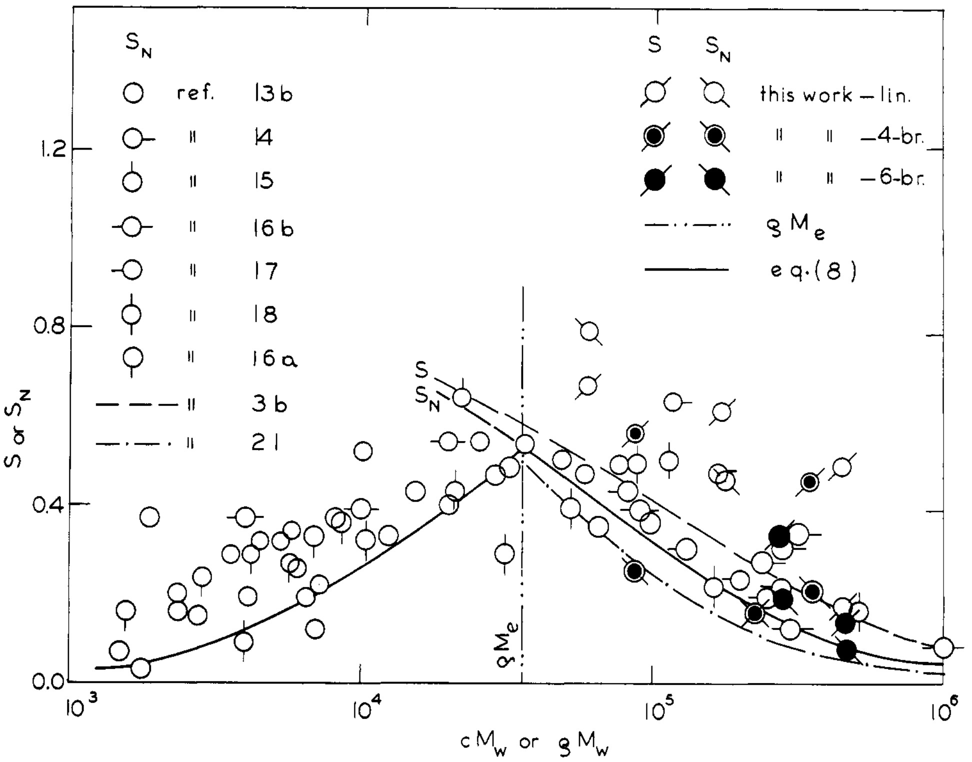

Figure 2. The experimental dependence of the parameters S and S_N, eq 6, as a function of cM (c in g/ml) for dilute solutions (ref 13b–16a) concentrated solutions (ref 3, 14, and this work) and melts (ref 16b–18) of narrow distribution polystyrenes. Only data of ref 3b were corrected for polydispersity effect.

trast with the theoretical calculations based on bead-spring model,[12] no constant value of S (or S_N) was found but rather a continuously varying dependence, in a form resembling a distribution function. The key to understanding the mechanism responsible, is the location of the apparent maximum of S, ($S_{\max} \cong 0.6$), at the onset of the entanglement region, marked by a chain line in Figure 2.

The theoretical considerations of low-frequency behavior of linear viscoelastic system leads to the following relation[12]

$$S = \sum_p^N (\tau_p/\tau_1)^2 \Big/ \left(\sum_p^N \tau_p/\tau_1\right)^2 \qquad (6)$$

where N is the number of submolecular vibrating modes, p their index, τ_1 and τ_p are the longest (or terminal) and the characteristic relaxation time of the pth vibrating mode, respectively. In view of eq 6, the dependence presented in Figure 2 suggests that linear and branched polystyrenes in solution or in melt broaden the distribution of their relaxation times when the product (cM) is increased or decreased from its entanglement value ρM_c. It is worth pointing out the high value of $S_{\max} \cong 0.6$. Assuming the inverse square relation[19] between τ_p and p and an existence of only two vibrating modes corresponding to unentangled submolecule and one with entanglement in the middle, the value of $S = 0.68$ is found; using Zimm[20] λ_p parameters $S = 0.64$ can be calculated. These numerical values computed from such simplistic assumptions serve only to illustrate the fact that the narrowing of the distribution of relaxation times in the entangling region requires very small number of relaxation modes.

From the empirical dependence in Figure 2, it follows that the theoretical value $S = 0.4$, calculated by Rouse[19] for dilute solution of bead-spring coils without hydrodynamic interactions should be expected either for unentangled (low M or low c) systems in which $cM \cong 10^4$, or for concentrated solutions or melts, in which $cM \cong 10^5$. Similarly, the theoretical value of $S = 0.206$ computed by Zimm[20] for a nondraining coil coincides with the empirical dependence for $cM \cong 3 \times 10^3$ and $cM \cong 2 \times 10^5$.

The S and S_N values of the branched samples investigated in this work fall on the empirical dependence of linear samples. As reported before[3] the values of S_N are generally lower than those of S calculated from τ_0 through eq 4 for linear, 4-, and 6-branched polymers. From the overlapping of linear and branched polymer data it follows that the width of the relaxation time distribution is not unduly affected by branching.

The values of S_N calculated for linear polystyrene melts from the Masuda *et al.*[4] J_e plateau are 0.25 and 0.05 for $M = 2 \times 10^5$ and 2×10^6, respectively, and they follow the empirical dependence of Figure 2. However, the values calculated for 4-branched polystyrene melts are 4.9 and 0.49 for $M = 10^5$ and 10^6, respectively. Especially the upper limit, being larger than unity, cannot be explained by the mechanism proposed in this paper. It can be seen that polydispersity of these samples also cannot be responsible for such large values of S_N; using $M_w/M_N = 1.18$[4], $F = 0.65$ is found—too small to lower S_N to the level of values presented in Figure 2. Interestingly, the values of J_{eN}, calculated from the rubbery plateau region for linear[11] and 4-branched polystyrene[4] melts numerically are very similar and in the range of values quoted in Figure 2.

Conclusions

It has been found that the zero-shear viscosity, η_0, and the zero-shear primary normal stress difference coefficient, ψ_0, are lower for star branched polystyrene solutions than for linear homolog of the same molecular weight. If the branched samples are compared with linear ones not

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on the basis of constant molecular weight but constant η_0 instead, the numerical values of ψ_0 of the first polymer still would be lower than that of the second.

The steady-state compliance J_e calculated from the second-order fluid theory expression $J_e = \psi_0/2\eta_0^2$ is found to be an increasing function of molecular weight for the branched samples but approximately independent of molecular weight for the two highest molecular weight linear polystyrenes; the maximum values for linear and star-branched polystyrene solutions were found to be approximately equal: $J_{e,\max} \cong 5 \times 10^{-5}$ cm²/dyn. In the framework of Graessley's[21] theory, this result would indicate that permanently entangled network is present in the investigated linear polystyrene solutions at $M_w \geq 6.75 \times 10^5$, whereas for star branched polystyrenes such a state must be expected for even higher values of cM than those investigated in this work. One can understand this behavior visualizing the polystyrene solution as a suspension of solvated macromolecular coils. The possibility of formation of entangled system will be larger for linear polymer molecules in which segment dinsity is smaller and radius of gyration larger than that of branched system. This behavior may be quite different in the melts as the Masuda *et al.*[4] results suggest.

The parameter S (or S_N) which characterizes the distribution of relaxation times τ_p was found to decrease more or less symmetrically from its maximum value ~0.6 near or at the critical entanglement point, $\rho M_c = 3.6 \times 10^4$ when cM_w product is increased or decreased. The apparent variation of the relaxation times distribution, not taken into account in the theoretical calculations,[12,19,20] finds a qualitative support in the experimental relaxation spectra[22] for high-density polyethylenes at $M_w \geq 8.6 \times 10^4$, *i.e.*, above the critical entanglement molecular weight: $M_c \cong 3800$,[9] the reported relaxation spectra was found to broaden as the molecular weight increased.

Furthermore, from the recent theory of viscoelastic behavior of entangling polymer[21] one can calculate the parameter S_N (marked by a chain line in Figure 2). The theory predicts variation of S_N from its maximum value of ½, at the entanglement region, to zero at infinitely large $E \propto cM$.

It is worth noting that eq 5 can be cast into the form of Williams'[23] equation written for $\eta_0 \gg \eta_s$, where η_s is the solvent viscosity

$$\psi_0 = 2S_N M\eta_0^2/cRT \qquad (7)$$

If the parameter S_N is taken as a constant, then $\alpha_\psi = (\mathrm{d}\log\psi_0/\mathrm{d}\log M_w) = 2(\mathrm{d}\log\eta_0/\mathrm{d}\log M) + 1$ and substituting the numerical value of the derivative[2] $(\mathrm{d}\log\eta_0/\mathrm{d}\log M_w) = 3.1$ the slope of $\log\psi_0$ *vs.* $\log M_w$, $\alpha_\psi = 7.2$ is found. This value is in a small variance with the experimental value: $\alpha_\psi = 6.9$. Furthermore, as the variables of eq 7 span few decades (eight for the systems discussed here) the variation of S_N by a factor of two will not be noticed. In consequence, eq 7 can be used to calculate an approximate value of ψ_0 from the zero-shear viscosity data. As indicated before S_N calculated for linear and branched polystyrene solutions follow the same dependence, *i.e.*, eq 7 can be used to calculate ψ_0 of star branched samples from its (or from the linear homologue[2]) zero-shear viscosity.

Finally, it should be noted that on the basis of the data presented in Figure 2, an empirical modification of eq 7 can be made. From eq 4 and definitions of E and S_N, one can find:

$$S_N = \frac{2A/5}{1 + 2B + 2B|1 - cM/\rho M_c|} \qquad (8)$$

where the absolute value of $|1 - cM/\rho M_c|$ is used to secure the symmetry of the empirical relation.[3] The dependence (eq 8) with A and B values taken from ref 3b is marked in Figure 2 as a solid line. As the original data[3b] were corrected for polydispersity, the line represents the dependence of a monodisperse system. From eq 7 and 8 putting

$$A^* = 4A/5(1 + 2B)$$
$$B^* = 1 + (1/2)B$$

and introducing the polydispersity correction[3,8] the following relation is derived

$$\psi_0^{\text{calcd}} = [A^*/(1 + B^*|1 - cM_w/\rho M_c|)] \times [M_w(\eta_0 - \eta_s)^2/cRT][M_{z+1}M_z/M_w^2]$$

Using the experimental values of A, B, ρ, and M_c, the values of ψ_0 can be computed for any polystyrene system, provided the polydispersity is known.

The behavior of the parameter S (or S_N) shown in Figure 2 is found also for other polymers, *e.g.*, poly(α-methylstyrene) in chlorinated biphenyls[24] where for the product cM_w ranging from 2×10^3 to 36×10^3 the values of S_N calculated by the authors for four polymer fractions in two solvents superimposed on the monotonically increasing (from 0.22 to 0.69) left branch of the dependence eq 8.

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