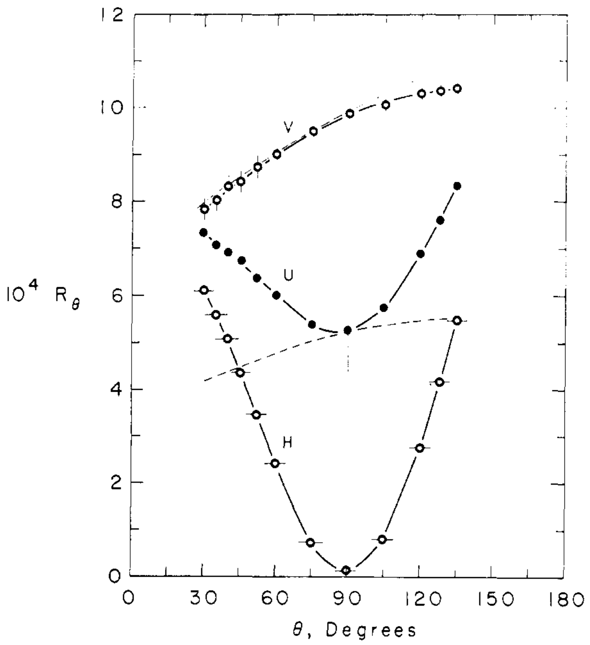

Figure 3. Angular dependence of reduced scattering ratios R_θ for poly(vinylpyridine), 0.479 g/dl in nitromethane, excited with unpolarized (U), vertically (V), and horizontally (H) polarized light. Upper and lower dashed curves are H and U corrected for geometrical dependence on angle, *viz.*, $[H - H(90°)]/\cos^2\theta$ and $U/(1 + \cos^2\theta)$.

a polyampholyte based on methacrylate.[9] Arichi[5] has shown a Zimm plot with anomalous dissymmetry very much like ours (Figure 2) for poly(2-vinylpyridine) in methanol. However, the anomaly was connected with an ionized form of the polymer, because it was suppressed by ammonia.

Ehrlich and Doty[9] tried to explain their results as the consequence of a particular kind of clustering which produced long-range interference effects. More recently Schurz, *et al.*,[7] Nakagaki,[10] and Utiyama and Kurata,[11] have shown that anomalies in the dissymmetry may be explained by optical anisotropy of the polymer segments. Utiyama and Kurata have interpreted some of Ehrlich and Doty's data with considerable success, and also their own data on atactic and isotactic polystyrene.[11,12] Although their theory in its present form can account for negative limiting slopes in the Zimm plots, it cannot account for more intense scattering in the backward direction than in the forward,[13] which is shown by some of the data of Ehrlich and Doty,[9] Arichi,[5] and us.

Schurz, *et al.*, found that their anomaly disappeared when the exciting light was vertically polarized.[7] To see if this were so in our system, and to estimate the amount of anisotropy by depolarization, we measured the intensity of scattering of vertically and horizontally polarized incident light, using a solution of the same polymer fraction as in Figure 1. A plot (Figure 3) of the reduced scattering ratios R_θ with vertically (V) and horizontally (H) polarized incident light against the angle of observation shows first that the depolarization (*i.e.*, the relative value of H at 90°) is quite small, and second, that regardless of the polarization, more light is scattered backward than forward. The angular dependences of V and of $[H - H(90°)]/\cos^2\theta$ are very similar.

The phenomenon therefore appears to be essentially different from Utiyama's,[12] for example, which can be explained as an effect of scattering segment anisotropy.[11]

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Newtonian Viscosity–Molecular Weight Relationship for Concentrated Solutions of Monodisperse Polystyrene

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In spite of its importance and the length of time that the problem has been of scientific and practical interest, there is still not complete agreement on the effect of molecular weight on the zero shear rate viscosity of concentrated polymer solutions and polymer melts. In most work on polymers with a moderately broad distribution of molecular weights, best correlations were found with weight average molecular weight.[1,2] In general, log–log plots of zero shear viscosity, η_0, *vs.* weight average molecular weight, which we will denote here simply as M, are approximated by two straight lines intersecting at a point M_c, the critical molecular weight for the inception of chain entanglement.

It has been shown[1] that for linear polymers

$$\eta_0 = \mathrm{F}(M)\mathrm{f}(\rho) \tag{1}$$

where F(M) is a function only of molecular weight and f(ρ) is a function only of the density ρ. For the case where $M \leq M_c$, F(M) is approximately proportional to M;[3,4] hence

$$\eta_0 = K_{T,M}M \tag{2}$$

for $M \leq M_c$, where $K_{T,M}$ is a coefficient depending on temperature and molecular weight M. The molecular weight dependency of $K_{T,M}$ enters through the dependence of ρ, and thus free volume, on chain ends. Clearly this dependence would be far greater in bulk polymer than in concentrated solutions. Consequently we could expect η_0 to be more nearly proportional to M in the latter.[5] For long-chain members

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of a homologous series, it is generally agreed that F(*M*) is proportional to M^a and f(ρ) is independent of *M* but dependent upon temperature. Thus we can write

$$\eta_0 = K_T M^a \tag{3}$$

for $M > M_c$. Although most investigators have found values of *a* of 3.4 and 3.5 for both narrow and broad molecular weight distribution polymers,[2,6,7] other recent experimental and theoretical values have been reported.

Chikahisha[8-10] derived an equation based on the Born and Green theory which predicts that η_0 is proportional to $M^{3.0}$ for high molecular weight polymer. The approach is equivalent in some aspects to the earlier theory of viscosity of concentrated polymer solutions developed by Bueche[11-13] (who used the Debye model of a free draining polymer molecule) which predicts a 3.5 power dependence on molecular weight. Rudd[14] reported that η_0 increases with molecular weight to the 3.14 power for nearly monodisperse polystyrene melts at 227°. Tobolsky, *et al.*,[15] on the other hand, determined that viscosities for high molecular weight polyisobutylene (of heterogeneity index 2.0) were proportional to the 3.3 power of molecular weight and later Tobolsky[16] reported a 4.0 power dependence on molecular weight from a stress relaxation experiment using narrow distribution polystyrene. Schreiber, Bagley, and West[17] reported *a* to have a value of 4.1 for polyethylene melts.

Since there has been some recent disagreement on the applicability of the most commonly reported value of 3.4 for the power dependence of viscosity on molecular weight, particularly in the case of nearly monodisperse polystyrene,[16] we felt it would be useful to report our recent experimental observations on concentrated solutions of that polymer.

Experimental Section

The narrow distribution polystyrene was obtained from Pressure Chemical Co., Pittsburgh, Pa. Molecular weights were from 2.10×10^3 to 1.80×10^6. Each batch of polymer was statistically sampled and characterized by the manufacturer. Di-2-ethyl hexyl phthalate (DOP) was chosen as the solvent because of its extremely low volatility, bp 232° (5 mm). To make certain this solvent would be suitable, its evaporation rate was estimated and found to be about 4.0×10^{-6} g/cm^2 hr at 78° (1 atm). This evaporation rate was considered negligible for our experiments since none lasted more than 72 hr. The solutions were made to within ±0.01% by weighing solvent and polymer into small air-tight glass jars that were placed in an oven at 50°. It took from 1 week to 1 month (depending on molecular weight and concentration of the solution) for the polymer to dissolve completely and yield homogeneous rubber-like solutions. Since Boundy and Boyer[18] established that pure polystyrene does not thermally degrade at temperatures below 210°, molecular weights were not checked after making the solutions.

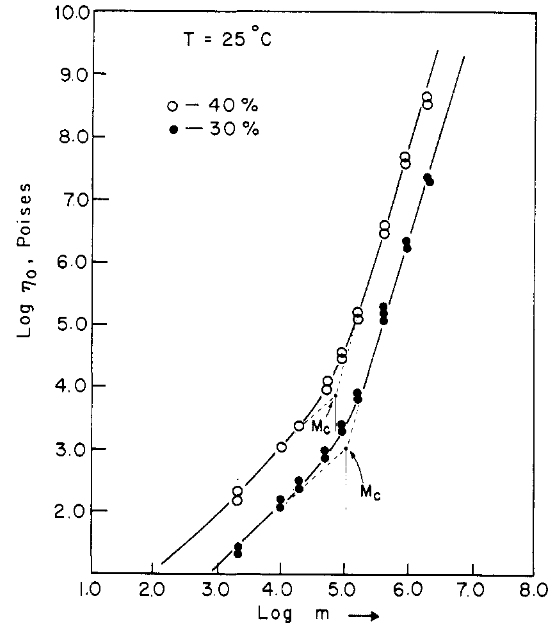

Figure 1. Viscosity–molecular weight relationship for concentrated solutions of monodisperse polystyrene at 25°.

Glass capillary viscometers were used to measure the steady-state viscosity of the concentrated polystyrene solutions at very low shear rates. The design of the viscometer was essentially that described by Fox;[7] they were basically precision-bore Pyrex capillary tubes through which solutions were forced under nitrogen pressure. By varying the capillary diameter and pressure head, viscosities were determined over a wide range of shear rates (values as low as 10^{-6} sec^{-1} for the highest molecular weights and highest polymer concentrations). For several low molecular weight samples the shear rates were of the order 10^{-2} to 10^{-1} sec^{-1}. It was established, however, that all viscosities presented here were taken in the first newtonian regime. Table I gives the newtonian viscosities of 30 and 40% polystyrene solutions at various shear rates.

Discussion

From Figure 1 it can be seen that for these systems when $M \geq M_c$, low shear-rate viscosity is proportional to $M^{3.4}$, in complete agreement with the earlier work.[2,6,19] For $M < M_c$, the slopes are 1.16 and 1.10 for 40 and 30% solution, respectively. This is because free volume, which influences viscosity, depends upon composition below the break. Although it is not clear whether or not the difference in slopes is significant, it is in the direction predicted by theory. Reducing the measured viscosities to a reference state of constant free volume should give the theoretical slopes of 1.0. Some flow data which have been corrected to "isofree" volume conditions[20] by Bueche and

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TABLE I
ZERO SHEAR VISCOSITY FOR 30 AND 40% POLYSTYRENE SOLUTION AT 25°

M_w	M_w/M_n	Viscosity η_0, poise (40% soln)	Apparent shear rate, sec^{-1}	Viscosity η_0, poise (30% soln)	Apparent shear rate, sec^{-1}
1.80×10^6	1.20	3.16×10^8	2.21×10^{-6}	2.00×10^7	3.23×10^{-6}
		4.08×10^8	2.02×10^{-6}	1.70×10^7	5.00×10^{-6}
8.60×10^5	1.15	5.00×10^7	5.23×10^{-4}	2.20×10^6	5.41×10^{-5}
		5.02×10^7	5.33×10^{-4}	1.68×10^6	9.98×10^{-4}
		5.11×10^7	5.11×10^{-4}	1.91×10^6	7.82×10^{-5}
4.11×10^5	1.06	4.01×10^6	7.99×10^{-4}	1.91×10^5	1.60×10^{-4}
		3.98×10^6	8.23×10^{-4}	1.61×10^5	2.62×10^{-4}
1.60×10^5	1.06	1.46×10^5	1.41×10^{-3}	7.20×10^3	1.16×10^{-2}
		1.44×10^5	2.01×10^{-3}	7.00×10^3	2.02×10^{-2}
		1.40×10^5	2.74×10^{-3}		
9.70×10^4	1.06	3.90×10^4	4.44×10^{-3}	1.88×10^3	2.34×10^{-2}
		3.36×10^4	4.51×10^{-3}	2.04×10^3	1.71×10^{-2}
		3.32×10^4	4.54×10^{-3}	1.97×10^3	2.22×10^{-2}
5.10×10^4	1.06	1.02×10^4	8.45×10^{-3}	7.81×10^2	1.32×10^{-2}
		9.13×10^4	1.25×10^{-2}	6.98×10^2	7.03×10^{-1}
		9.81×10^4	7.81×10^{-3}	6.97×10^2	3.00×10^{-1}
2.04×10^4	1.06	2.57×10^3	2.01×10^{-3}	2.46×10^2	2.40×10^{-1}
		2.52×10^3	3.56×10^{-3}	2.91×10^2	1.80×10^{-1}
1.03×10^4	1.06	1.15×10^3	7.82×10^{-2}	1.50×10^2	3.58×10^{-1}
		1.13×10^3	8.21×10^{-2}	1.36×10^2	4.30×10^{-1}
2.10×10^3	1.10	2.17×10^2	2.31×10^{-2}	2.82×10^1	1.21×10^{-1}
		2.20×10^2	1.23×10^{-2}	2.46×10^1	2.02×10^{-1}

Kelly[21] and by Fox and Allen[22] all yield a slope of 1.0 at low molecular weights. It is also significant to note that the log–log plot of η_0 *vs.* M does not abruptly change in slope from 1.0 to 3.4 but that it changes gradually. The region over which this change in slope occurs was defined by Sell[23] as the region of partial entanglement and was discussed further by Wolkowicz[24] and Forsman.[25] We have, then, defined M_c by the intersection of the two straight-line sections of the curve.

Apparent abrupt changes in the slope of log–log plots of η_0 *vs.* M, as well as η_0 *vs.* C, have been used as a measure of the characteristic entanglement composition,[26] and several investigators have proposed various relationships between molecular weight and concentration that determine the inception of molecular entanglement. All these equations are essentially of the same form with various power dependencies on M_c. Onogi[27] derived an expression based on a packed spheres model which predicted that $(W\rho M_c^{0.5})$ should be a constant, where W is the weight fraction of the polymer in solution. He has also recently pointed out that[28] the characteristic constant defining entanglement composition can be derived from the theory of Bueche to be $(W\rho M_c^{0.83})$. Ferry and coworkers[20] reported it to be $(W\rho M_c^{0.68})$. There are, however, other results[5,19] indicating that $(W\rho M_c)$ is constant for data on some of the same systems for which other dependencies have been given.[26] Our experimental results on concentrated solutions of narrow distribution polystyrene in di-2-ethyl hexyl phthalate agree well with this last, and simplest, expression. We found $(W\rho M_c)$ to be equal to 3.00×10^4 and 3.03×10^4 for the 40 and 30% solutions (assuming constant density), which is in good agreement with (although slightly lower than) most values reported in the literature for both bulk polymer and solutions.[26]

Acknowledgment. This work was supported by the National Science Foundation through Grant Gp 3059.

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Production of Organometallic Polymers by the Interfacial Technique. IV. Synthesis of Poly(silylalkylenediamines) by the Interfacial Technique

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Aylett[1] has recently reviewed the subject of silicon–nitrogen polymers. He notes that by contrast to Si–O polymers, polymers with Si–N bonds in the main chain have received little attention mainly because of a lack of suitable preparative methods. The review includes a review of polymer types concerned within

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