THE INFLUENCE OF STRUCTURE ON THE MOLECULAR MOBILITY AND RHEOLOGY OF AMORPHOUS MACROMOLECULAR SYSTEMS

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A brief review with emphasis on the important open questions is presented of our knowledge of the factors influencing the chain mobility and mechanical properties of amorphous polymeric systems. It is necessary to give more precise meaning to the concepts of "chain entanglement" and "free volume" and to relate these to the structure of the repeating unit and to the gross chain structure of the macromolecules. From studies of the viscosity in bulk or in concentrated solution of model polymers and novel polymers, we propose to determine the influence on the mobility of heterogeneity in chain length distribution, of added diluent, and of the stereochemical chain structure. The initial data on polystyrenes of narrow distribution prepared in anionic synthesis, and of mixtures of these are presented here.

Introduction

Extensive data obtained over the past twenty-five years for amorphous polymer systems[1,2] have indicated that quite generally the chain mobility is goverened by two factors: (1) by the density of packing of the chain segments, which determines both the magnitude of the local friction factor and its temperature coefficient; and (2) by the interactions of units remote from each other in the liquid, but joined by primary valence bonds into long chains, and through "entanglements" of those chains into larger network structures. Stated more directly, both the viscosity and the time dependent rubber-like elastic response are sensitive to the total molecular chain length Z relative to the average number of chain atoms Z_c between interchain entanglements, and the temperature coefficient of these responses to stress is sensitive to the "free volume" which is itself dependent on the difference between the temperature and the glass temperature of the system.

Obviously it is important to give more precise meaning to the concepts of "chain entanglement" and "free volume," and to determine how these are influenced by the gross structural features such as chain length and its distribution, chain branching, and the dimensions of the polymer coil, and by the local structural details such as the steric and polar character of the repeating structural units and their relative stereochemical arrangements. It is the object of these studies to define more fully these relationships by viscosity studies in bulk or in concentrated solution of model polymers and of new and novel structures when they are available.

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The immediate goals in our present investigations are to determine the influence on the melt viscosity of linear polymers:

(1) of the heterogeneity in chain length distribution, employing mixtures of monodisperse polystyrenes prepared by anionic techniques

(2) of added diluent, for a variety of polymer-diluent pairs

(3) of the stereochemical structure of these polymers.

The results of the latter two studies should provide evidence on the important question[3,4] as to whether the chain entanglements are similar to those between long coiled ropes or whether specific interactions are involved. The result of the first study will provide further test of the present theory of flow, and should provide a better knowledge and understanding of the complex and incompletely defined flow relationships for polymeric substances of moderate chain length ($Z < Z_c$)[5].

Here we report the few initial results of studies of the viscosities of mixtures. Data on the effect of diluent on the viscosity of homogeneous polystyrene samples will be available soon. The results of an attempt to prepare stereoregular polyvinyl acetate are given elsewhere[6]. Further, we take this opportunity to present a brief review of the background in this field.

Background

Studies on the viscosity-temperature-molecular weight relations for fractions of polystyrene and of polyisobutylene yielded the following result[1,7,8]

$$\eta = A\, Z^{3.4} \qquad Z \geq Z_c \tag{1}$$

$$\eta = B\, Z^{a} \qquad Z \leq Z_c \tag{2}$$

$$\frac{d \log \eta}{d(1/T)} = F(T) \cdot f(1/Z) \qquad \text{any } Z \tag{3}$$

Here η is the viscosity, T is the absolute temperature, and A, B, Z_c, and $\underline{a}$ are empirical constants characteristic of the polymer type. As an approximation, the dependence in Eq. (3)

$$f(Z) \sim \left(1 - \frac{1}{Z}\right) \tag{4}$$

was observed[8] to parallel the dependence on Z of the specific volume v and of the glass temperature T_g

$$v = v_o + \frac{k_1}{Z} \tag{5}$$

$$T_g = T_g - \frac{k_2}{Z} \tag{6}$$

Values of v, T_g, and $f(Z)$ are all sensibly constant if $Z > Z_o$, and increase (or decrease) at an accelerating rate with decreasing Z below this limit.

Subsequent studies of other systems indicated that the characteristics noted above are general for different polymer systems[1]. It was suggested that the isothermal dependence of η on $Z^{3.4}$ for long chains in Eq. (1), and of η on Z^{a} for short chains (with values of a of 1 to 2.4 depending on the system) express the mutual restriction on the flow of two chain segments far removed from each other in the liquid arising from the long chain structure; the increase in the temperature coefficient with decreasing Z below Z_o was thought to be due to the decrease in "free volume" associated with the increased concentration of chain ends for shorter chains.

In an approximate theoretical treatment[9], Bueche obtained the following limiting relations for monodisperse polymer chains;

$$\eta \sim Z^{3.5} f_o \qquad Z > Z_c \qquad (1')$$

$$\eta \sim Z\, f_o \qquad Z < Z_c \qquad (2')$$

For the short chains ($Z < Z_c$) he assumed that the long range interactions mentioned above are communicated solely through the primary valence bonds in a given chain, i.e., the molecular friction factor is equal to the product of Z and the friction factor f_o per chain atom. For the long chains ($Z > Z_c$) he considers the long range interactions to be communicated through the valence bonds in a given chain and through interchain entanglements, and in this case the molecular friction factor is $Z^{3.5}f_o$. Here the flowing system is considered to consist of an infinite network of entangled chains, which tend to drag one another along as they slip over each other in flow.

Comparison of Bueche's theory with Eq. (1) and (2) suggests: that network formation occurs first when $Z/Z_c = 1$; that the behavior predicted by Eq. (1') applies when $Z/Z_c \geq 1$; and that Bueche's theory does not predict accurately the result for $Z/Z_c < 1$ since the exponent a in (2) is generally greater than the value of unity predicted in (2').

Viscosity data[7,8] on mixtures of polystyrene fractions or of polyisobutylene fractions indicated that for heterogeneous systems

$$\eta = A\, Z_w^{3.4} \qquad Z_w > Z_c;\ Z_n > Z_o \qquad (1'')$$

$$\eta = B\, Z_w^{a} \qquad Z_w < Z_c;\ Z_n > Z_o \qquad (2'')$$

$$\frac{d \log \eta}{d(1/T)} = F(T) \cdot f(1/Z_n) \qquad \text{any } Z_n \qquad (3'')$$

i.e., for such heterogeneous systems the viscosity-temperature coefficient is uniquely a function of the number average chain length, Z_n, whereas the isothermal viscosity for systems with $Z_n > Z_o$ is uniquely a function of the weight average chain length, Z_w. No adequate specification of the molecular weight dependence of η was found for heterogeneous polymers with $Z_n < Z_o$.

Recently Bueche[10] has suggested a further complication in the effect of heterogeneity of chain length distribution. Employing the aforementioned approximate theoretical treatment[9] he predicts for heterogeneous polymers with components of $Z \gg Z_c$:

$$\eta \sim Z_\eta^{3.5} \qquad Z > Z_c \qquad (7)$$

$$\text{where} \quad Z_\eta = Z_w \qquad Z_z/Z_w < 1.8 \qquad (7\text{-}1)$$

$$Z_\eta \to Z_z \qquad Z_z/Z_w > 1.8 \qquad (7\text{-}2)$$

Here Z_η is the chain length of a homogeneous polymer with a viscosity equal to that of the mixture.

Experimental and Results

Nearly twenty polystyrene samples of molecular weight ranging from 10^4 to 1.4×10^6 and of M_w/M_n of 1.01 to 1.06 prepared by the anionic polymerization techniques of Wenger and Yen[11] are available in our laboratory. These were further separated into fractions by addition at 30° of methanol to solutions of the polymer in benzene or in butanone. The molecular weights of the fractions were calculated from the measured values of the intrinsic viscosity in benzene according to the relations[12,13]

$$\log M_v = (\log [\eta] + 4.013)/0.74 \qquad M \geq 30{,}000 \qquad (8)$$

$$\log M_v = (\log [\eta] + 3.380)/0.60 \qquad M \leq 30{,}000 \qquad (9)$$

Mixtures of polymer fractions were prepared by dissolving weighed quantities in benzene, and by subsequent evaporation to dryness. A small amount (0.3 wt %) of phenyl-β-naphthylamine was added to minimize degradation during the melt viscosity determinations.

Melt viscosities were determined at 218° and at lower temperatures employing capillary viscometers and the techniques described earlier[1,7,14]. Intrinsic viscosities in benzene were measured on the sample after the melt viscosity measurement in order to determine the extent of degradation, if any.

The data on the viscosity-molecular weight relation at 218° for the present fractions of polystyrene prepared anionically are given in Table 1 and Figure 1. The lines in the latter are drawn in accord with the η-Z relations determined previously[8] for fractions of polystyrene prepared by free radical techniques. The fit of the present experimental points to these lines indicates excellent agreement between the observed behavior of the two sets of polymers.

In Table 2 the data obtained in our initial studies on mixtures of fractions are summarized. Although these data and the data assembled from the literature support (Figure 1) the earlier finding that the viscosity for heterogeneous systems with $Z_n > Z_o$ is determined by Z_w and not by Z_z, even when $Z_\eta/Z_w > 1.8$, it may be that the components of the mixtures do not satisfy Bueche's requirement that $Z \gg Z_c$. Thus conclusions on the effect of chain heterogeneity await completion of the measurements in progress on mixtures of both higher and lower chain lengths.

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TABLE I

Preliminary Viscosity Data on Fractions of Anionic Polystyrene

Designation		$\times 10^{-3}$	η_{218}	$[\eta]^b$
Polymer	Fraction	M_w^a	poises	dl/gm
		Molecular Weight Dependence		
8	AA	16.6	41.1	0.141
8	CB	18.7	42.5	0.151
8	CB	18.7	44.5	0.151
7	AA	38.1	204	0.238
7	AA	28.1	185	0.238
12	CB	45.0	220	0.277
11	CA	61.0	620	0.340
11	CA	61.0	685	0.340
D-1	CA	66.0	1,330	0.358
D-1	BA	71.0	1,390	0.378
11	BA	75.5	1,920	0.390
D-1	(Unfract.)	82.0	1,460	0.418
D-4	(Unfract.)	137.0	11,900	0.592
D-3	BA	141.0	14,600	0.620
D-4	CA	158.0	20,100	0.680
D-5	BA	195.0	43,200	0.792
D-6	BA	220.0	63,000	0.860

Temperature Dependence

		$\log \frac{\eta_{203}}{\eta_{218}}$	$\log \frac{\eta_{193}}{\eta_{218}}$	$\log \frac{\eta_{180}}{\eta_{218}}$	$\log \frac{\eta_{156}}{\eta_{213}}$
7	AA	--	0.76	1.09	2.25
11	CA	--	--	--	2.30
D-1	BA	0.69			
D-3	BA	0.35			
D-4	CA	0.34			
Reference 7		0.37	0.69	1.17	2.38

[a] $\log M_v = (\log [\eta] + 4.013)/0.74 \quad (M > 30 \times 10^3)$[7]
$\log M_v = (\log [\eta] + 3.380)/0.60 \quad (M < 30 \times 10^3)$[8]

[b] Measured in benzene at 30°C.

TABLE II

Viscosity Molecular Weight Data on Mixtures of Polymer Fractions of $Z_n > Z_o$

Mol. Wt. ($x10^{-3}$) + Wt. % of Components	calc'd M_z/M_w	M_η/M_w [a]	calc'd M_v/M_w	$x\ 10^{-3}$ calc'd M_w	$x\ 10^{-3}$ calc'd M_n	poises x 10^{-3} observed η_{218}
Present Preliminary Data on Anionic Polystyrene						
2,170 (3.85) 123 (96.15)	4.8	0.80	0.86	202	128	15.4
426 (41) 18.5 (59)	2.2	1.05	0.82	185	30	27.9
200 (50) 10 (50)	1.8	1.06	0.89	105	19	3.9
Free Radical Polystyrene[7]						
389 (50) 35 (50)	1.7	1.05	0.88	212	64	50
389 (50) 78 (50)	1.45	1.06	0.92	233	130	80.5
100 (50) 31 (50)	1.28	1.01	0.97	65.5	47.3	0.796
78 (50) 31 (50)	1.18	0.98	0.95	54.5	44.4	0.532
Polyisobutylene[7]						
233 (50) 38.2 (50)	1.5	1.00	0.83	204	66	4.56
81.5 (50) 30.0 (50)	1.2	0.98	0.96	55.8	44	0.321
Polyvinyl Acetate[15]						
2,870 (56.5) 1,040 (43.5)	1.3	0.95	0.96	2,070	1,620	--

[a] Calculated from the ratio of the molecular weight of a fraction having the same η_{218} as observed for the mixture to the calculated value of M_w for the mixture adjusted so that the calculated and observed M_v (after heating) are equal. The latter adjustment (generally indicating some degradation) was $\leq$ 6% except for the first mixture, where it was 9%.

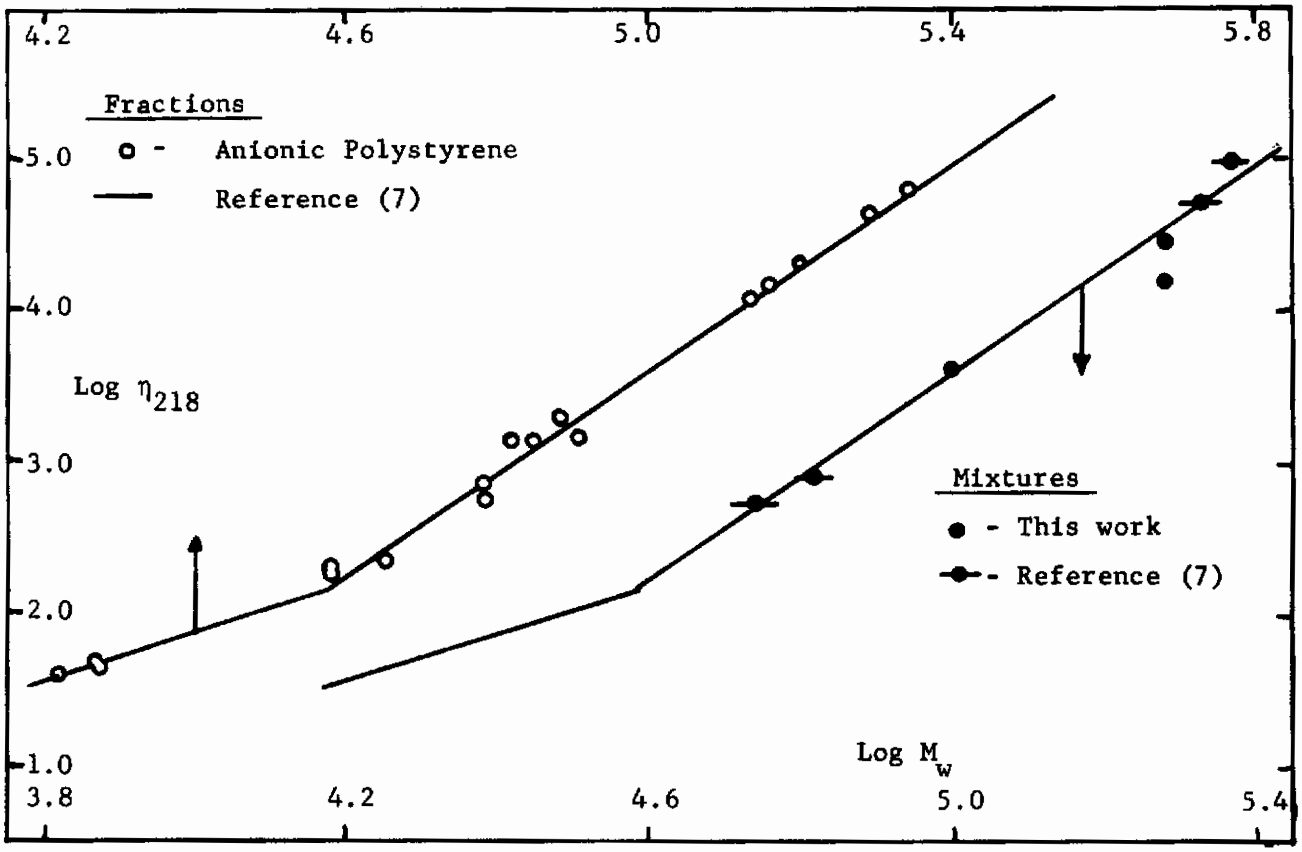

Figure 1. Preliminary η_{218}-M Data for Polystyrene Fractions and Their Mixtures.

Appendix

The various average molecular weights for heterogeneous polymers are defined by the usual equations

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad \text{number average } (M_n) \qquad \text{(A-1)}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad \text{weight average } (M_w) \qquad \text{(A-2)}$$

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \qquad \text{z-average } (M_z) \qquad \text{(A-3)}$$

$$[\eta]_{av} = \sum_i w_i [\eta]_i$$

$$M_v = \left[\frac{[\eta]_{av}}{K}\right]^{1/a} \qquad \text{viscosity average } (M_v) \qquad \text{(A-4)}$$

For a mixture of two homogeneous fractions consisting of weight fraction w_1 of molecular weight M_1 and $w_2 = 1 - w_1$ of molecular weight M_2,

$$M_n = \frac{M_2}{w_2} \left(\frac{r}{R} + 1\right)^{-1} \qquad \text{(A-5)}$$

$$M_w = w_2 M_2 \, (rR + 1) \qquad \text{(A-6)}$$

$$M_z = M_2 \left(\frac{rR^2 + 1}{rR + 1}\right) \qquad \text{(A-7)}$$

$$M_z/M_w = (r + 1) \frac{rR^2 + 1}{(rR + 1)^2} \; ; \qquad M_w/M_n = \frac{(rR + 1)(r + R)}{(r + 1)^2 \cdot R} \qquad \text{(A-8)}$$

$$\text{where } r = \frac{w_1}{w_2}; \qquad R = \frac{M_1}{M_2} \qquad \text{(A-9)}$$

In the special case where $w_1 = w_2 = 0.5$ and $r = 1$

$$M_z = \frac{M_1^2 + M_2^2}{M_1 + M_2} \; ; \qquad M_w = (M_1 + M_2)/2; \qquad M_n = \frac{2M_1M_2}{M_1 + M_2} \qquad \text{(A-10)}$$

$$\frac{M_z}{M_w} = 2 \, \frac{R^2 + 1}{(R + 1)^2} \; ; \qquad \frac{M_w}{M_n} = \frac{(R + 1)^2}{4R} \qquad \text{(A-11)}$$

It can be shown that M_z/M_w for a mixture of two fractions is maximum where $r = 1/R$. Then

$$\frac{M_z}{M_w} = \frac{(R+1)^2}{4R} \qquad r = 1/R \qquad \text{(A-12)}$$
$$\frac{M_w}{M_n} = \frac{2(R^2+1)}{(R+1)^2}$$

The relations in the following Table are useful here:

r	R	M_z/M_w	M_w/M_n
1	5	1.44	1.8
1	10	1.67	3.3
1	∞	2	∞
0.5	2	1.125	1.111
0.2	5	1.8	1.44
0.1	10	3.03	1.67
0.05	20	5.01	1.81
0.01	100	25	1.96
0	∞	∞	2