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Viscometric Evidence of Low Molecular Weight Polymers as Θ Solvents

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ABSTRACT: A rheological test is provided of the contention that polymer chains in melts and concentrated solutions exist with Gaussian spatial size distributions. If they do, their conformation is the same as in dilute Θ solutions, so the approach taken here is to utilize a low molecular weight polymer as solvent and a high molecular weight polymer as solute and then determine whether the former behaves as a Θ solvent for the latter. Polystyrene solutes of molecular weights 1.8×10^6 and 2.33×10^5 were dissolved at low concentrations c in solvent blends consisting of mixtures of styrene (good solvent) and a polystyrene of nominal grade $\bar{M} = 20\,000$. Plots of viscosity number $(\eta - \eta_s)/c\eta_s$ vs. c were compared for cases of differing solvent power: pure styrene, solvent blends of various composition, and several conventional Θ solvents. The solvent blends approached Θ character while styrene content was still surprisingly large, about 60% for the higher molecular weight solute and over 75% for the lower molecular weight solute. Although viscosity number plots for those blended solvents were flatter than for conventional Θ solvents (c^2 effects almost entirely suppressed), values of $[\eta]$ obtained by extrapolation were very close. Use of $[\eta] = KM^a$ yielded $a \cong 0.5$ for the Θ-type solvent blends. Results thus confirm the hypothesis and, moreover, establish the solvent blends as a new class of convenient, high-viscosity Θ solvents which should not change their behavior when temperature is varied.

A tremendous amount of effort has been directed toward the search for Θ solvents, those solvents defined by a number of unique characteristics[1] but sharing two features of special importance: (1) the spatial distributions of linear polymer solutes obey Gaussian statistics and, as a consequence, (2) the intrinsic viscosities of the solutes obey the relationship $[\eta]_\Theta = KM^{0.5}$. Whereas feature 1 has long been assumed to be shared with polymers in the melt state,[1] a test of this by exploitation of feature 2 has apparently never been made.

We describe here a rheological investigation of the proposed Gaussian nature of polymers in melts and concentrated solutions. The strategy is to mix a high molecular weight polymer "solute" in dilute proportions with a low molecular weight polymer "solvent" of the same chemical character and then determine $[\eta]$ for the former. Encouragement is afforded by a limited amount of neutron scattering work[2] with poly(dimethylsiloxanes) (PDMS) which directly measured solute spatial distributions. The result was that Gaussian coil shapes and sizes existed in the homopolymer melt but that coils expanded as the "solvent" polymer species became markedly smaller; the value of $\langle r^2 \rangle^{1/2}$ increased by about 70% as the molecular weight for the solvent was reduced to 10^3.

There is also considerable relevance of the rheology here to the polymer-processing industry, wherein a polymer liquid invariably contains a distribution of molecular weights and often residual monomer as well. Despite this fact, it is common to interpret the rheology of such systems in terms of Gaussian conventions[3] without questioning the underlying presumption (which is obviously called into doubt by the PDMS results[2]). Typically, polydisperse mixtures are analyzed in terms of strictly mechanical rules for weighting the behavior of blended *Gaussian* chains of different length. We offer here an alternate perspective, that of the low molecular weight species as a solvent which may or may not have Θ properties.

Finally, the finding that moderate molecular weight polymers are indeed Θ solvents for their larger brethren would have great utility in experimental testing of rheological theories of high-shear polymer behavior. Non-Newtonian viscosity and other nonlinear phenomena are manifested at relatively low shear *rate* if shear *stress* is sufficiently large, a goal achieved experimentally by selecting a highly viscous solvent. However, such solvents—e.g., Aroclor 1254 which has often been used with polystyrene because $\eta_s \cong 80$ poise at room temperature—are usually good solvents and do not permit even remotely the Gaussian approximation for polymer solutes. Although non-Gaussian character is itself known[4] to produce non-Newtonian behavior, this fact is often ignored when testing Gaussian-based rheological models with such systems.[5] Approximate treatments of the effect of non-Gaussian distributions have been advanced[6,7] in terms of coil size alone, with the relevant parameters being ϵ in the relationship $\langle r^2 \rangle = n^{1+\epsilon} l^2$ or α in $\langle r^2 \rangle = n(\alpha l_\Theta)^2$. However, the lack of rigor in such approximations renders their consequences suspect. It would be far preferable to secure a solvent of high viscosity having Θ character at *all temperatures*, as would be the case for low molecular weight polymer species and their concentrated solutions if the initial postulate[1] were sustained.

We present here the results of a preliminary experimental study which, despite its limited scope, tends to confirm that postulate.

Experimental Section

1. **Materials.** Polystyrene "solutes" were obtained from Pressure Chemical Co. in nominally monodisperse grades $M = 1.8 \times 10^6$ and 2.33×10^5, with $\bar{M}_w/\bar{M}_n = 1.2$ and 1.06, respectively. Polystyrene "solvents" were prepared as mixtures, in various proportion, of styrene monomer and low molecular weight polystyrenes. The latter were obtained from Polysciences, Inc., in manufacturer's grades $\bar{M} = 10^4$ and 2×10^4 which will here be designated PS_B and PS_A, respectively. Both had very broad molecular weight distributions (MWD), as shown by gel permeation chromatography (GPC) in Figure 1. These curves indicate that PS_A had $\bar{M}_w = 24\,600$ and $\bar{M}_n = 2100$, while PS_B had $\bar{M}_w = 40\,800$ and $\bar{M}_n = 3500$. The latter material was obtained years ago and is no longer available; PS_A was newly obtained and used in most of the work reported here.

Superimposed on the low-$\bar{M}$ polymer GPC curves in Figure 1 is the corresponding result for the solute with $M = 2.33 \times 10^5$; analysis of that MWD gives $\bar{M}_w = 2.41 \times 10^5$ and $\bar{M}_n = 2.20 \times 10^5$. An undesirable aspect of this curve is its overlap with those of low-$\bar{M}$ "solvent" components. For example, about 5% of PS_A has molecular weight comparable to or larger than the lower fractions of the solute, and the overlap is even more extensive with PS_B. However, subsequent results showed this not to be a major drawback, and these two samples were used without

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Table I
Properties of Solvents and Solutions

solvent	T, °C	η_s, poise	$[\eta]$, dL/g $M = 1.8 \times 10^6$	$[\eta]$, dL/g $M = 2.33 \times 10^5$	a
cyclohexane	35 (Θ)	0.0093	1.00		0.50[a]
dioxane/isopropyl alcohol (55/45)	20 (Θ)	0.013	1.02		0.50[a]
benzene/isopropyl alcohol (66/34)	20 (Θ)	0.0081	1.24		0.50[a]
styrene/polystyrene[b]					
100/0	22	0.0076	3.20	0.82	0.68
75/25 (PS_A)	25	0.066	1.27	0.43	0.53
50/50 (PS_A)	25	3.0	1.24	0.43	0.50
40/60 (PS_A)	25	18	1.24	0.43	0.50
75/25 (PS_B)	22	0.39	1.45		
50/50 (PS_B)	25	14	1.04		

[a] Reference 9b. [b] Molecular weight grade used in the blend is cited in parentheses. See Figure 1.

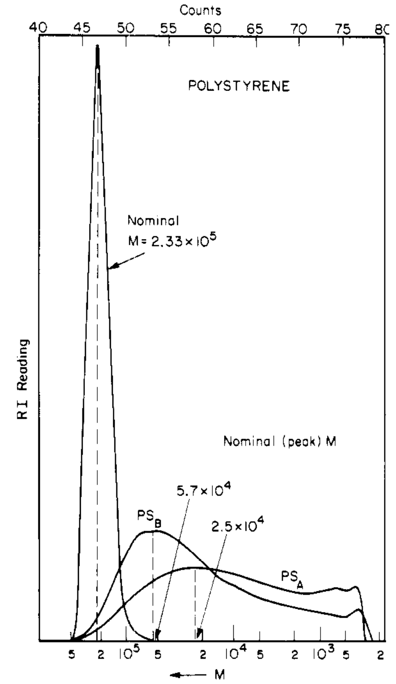

Figure 1. Gel permeation chromatograms of polystyrenes. The Polysciences, Inc., samples used here as solvent components, PS_A and PS_B, have maxima at 25 000 and 57 000, respectively; both have very broad MWD. The Pressure Chemical Co. sample is nominally $M = 233\,000$ with $\bar{M}_w/\bar{M}_n = 1.06$. Samples were dissolved in toluene at a concentration of 0.25% by weight and read by refractive index.

fractionation. We address further overtones of this matter below.

Another concern was that entanglement phenomena in the "solvent" polymer had to be avoided, since only normal solvent-like frictional interactions within the solvent phase, and between solvent and solute phases, could be tolerated. Because the critical molecular weight M_c to signal the onset of entanglement phenomena is about $\bar{M}_w = 34\,000$ for polystyrene,[8] the problem was clearly avoided for PS_A as a whole. Even the higher molecular weight fractions did not cause problems, since their concentration c_i was below criterion for entanglements in concentrated solutions ($c_i < c_{ic} = \rho M_c/M_i$, where ρ is the bulk density).

No tests were ever made for a 100% polystyrene system, since room-temperature work was desired and even low molecular weight polystyrene is glassy under these conditions. "Solvents" were therefore created as blends of styrene with the low-$\bar{M}$ polystyrene; blend compositions, expressed as polymer weight fraction, were 0.25, 0.5, and 0.6 for PS_A and 0.25 and 0.5 for PS_B. The fact that styrene content was relatively high in all cases further reduced concern about entanglements arising from the polymeric species in the blended solvents. The use of styrene proved convenient in another way, too: solutions were prepared most easily by first dissolving the high molecular weight solute directly in styrene and then using this low-viscosity fluid to dissolve the low-$\bar{M}$ polymer blend component. Such a sequence was rapid, required no heating, and could be accomplished with minimal agitation.

For comparison, several Θ solvents of the traditional sort[1] were also used for the high molecular weight solutes. These included[9] cyclohexane at 35 °C, 66% benzene/34% isopropyl alcohol at 20 °C, and 55% dioxane/45% isopropyl alcohol at 20 °C.

The viscosities and compositions of all solvents, both normal and polymer blends, are summarized in Table I.

2. **Equipment.** Capillary viscometers of the gravity-flow type were used exclusively, some being constructed with specially large diameters to accommodate the high-viscosity solvent blends and their mixtures with high molecular weight polymer solutes. Flow times were in the range of 100–1500 s, so no corrections for inertial effects had to be made. Preliminary tests with a Weissenberg rheogoniometer, operating in a cone-and-plate mode, showed that the solvent blends and their solutions were Newtonian within the range of shear rates encountered in the capillaries.

3. **Data Treatment.** From measured flow times in the capillary for a given solvent (blend) and solution of high molecular weight polymer at concentration c, the viscosity ratio $\eta(c)/\eta_s$ could be calculated directly. Then, the viscosity number $(\eta/\eta_s - 1)/c$ was plotted against c and extrapolated to $c = 0$ to obtain $[\eta]$. Subsequently, the exponent a in the relation $[\eta] = KM^a$ was evaluated by using the two Pressure Chemical Co. values of M available for the two solutes, which presumably correspond to peak GPC positions.

Results and Discussion

Figure 2 presents viscosity numbers for both solutes in the best solvent used, styrene, and in three of the conventional Θ solvents for the higher molecular weight solute. The intercepts $[\eta]$ for styrene yield $a = 0.68$, identical with that reported for the structurally similar ethylbenzene.[9a] The three Θ systems show surprising variation among themselves in viscosity number slope and intercept, although values of $[\eta]$ are within the ranges found by other workers.[9b] It should be noted that concentration dependence differs markedly between them, indicating that conventional Θ solvents may exhibit a significant range of characteristics at finite concentration.

It might have been expected that data for the styrene/polystyrene solvent *blends* would produce viscosity number curves intermediate between those for pure styrene and the Θ systems, with a gradation between them which was roughly linearly proportional to styrene content. However, Figure 3 shows that Θ behavior is achieved when styrene content is still remarkably high and that these blends exhibit a degree of uniformity which may make them more useful than conventional Θ solvents. Specific features in Figure 3 will now be discussed in detail.

1. **$M = 1.8 \times 10^6$ Solute.** The performances of all three blended PS_A solvents are close to those of the conventional

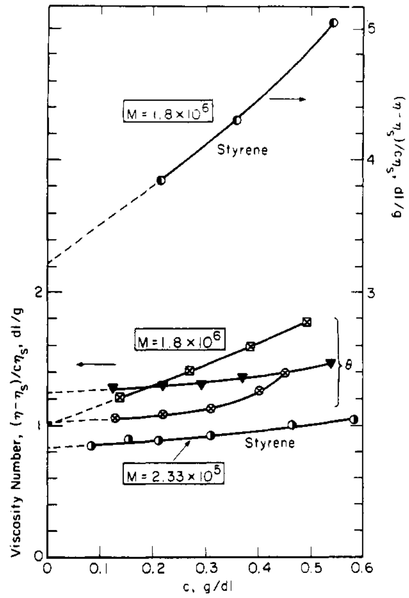

Figure 2. Role of conventional solvents. The good solvent, styrene, is shown with two polymeric solutes. (Note: the higher molecular weight solute is referred to the right-hand ordinate, which is displaced by one unit from the left-hand ordinate.) The three Θ solvents are cyclohexane (⊠), benzene/isopropyl alcohol (▼), and dioxane/isopropyl alcohol (⊗) and their behavior is not identical although they share the trait of having similar intercepts which are far lower than for styrene with the same polymer. Θ-solvent slopes can become surprisingly large, as for cyclohexane even at low concentration and dioxane/isopropyl alcohol at higher concentration.

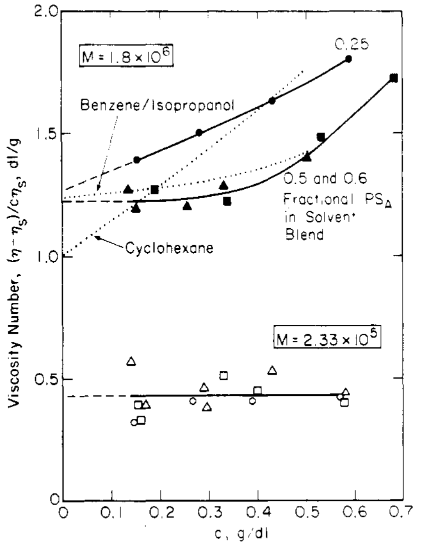

Figure 3. Role of styrene/polystyrene blended solvents, using PS$_A$ in the blend. Dotted lines represent conventional Θ-solvent systems, taken from Figure 2. Polymer weight fractions in the blends are 0.25 (●), 0.5 (▲), and 0.6 (■) with the $M = 1.8 \times 10^6$ solute and 0.25 (○), 0.5 (△), 0.6 (□) with the $M = 2.33 \times 10^5$ solute.

Θ solvents (see dashed lines in Figure 3, taken from Figure 2). This is especially unexpected for the 0.25 blend, which is far removed from good-solvent behavior despite containing 75% styrene. Indeed, the 0.25 blend curve mimics the slope of cyclohexane and the intercept of benzene/isopropyl alcohol.

There are a number of distinct trends in Figure 3 with solvent blend composition. As the styrene content is reduced, low-*c* slopes and intercepts are both reduced. Despite data scatter, it appears that a limiting condition is achieved when styrene content drops to about 50%. The low-*c* slopes become very small and may indeed be zero, which would indicate a complete suppression of c^2 effects in the expansion of $\eta(c)$ in a power series—i.e., the Huggins constant approaches zero. Apparently, no conventional Θ solvents are known to exhibit this property; Figure 2 shows that the two benzene mixtures are better approximations to it than is cyclohexane. Small slopes, of course, represent an advantage in the sense of facilitating an extrapolation to $c = 0$ for $[\eta]$ determination.

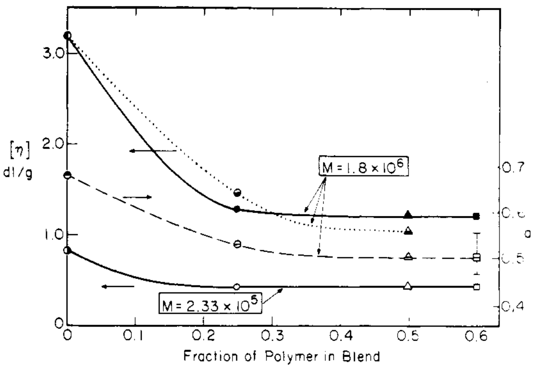

Figure 4. Dependence of viscometric parameters on blend composition: $[\eta]$ is given by solid lines (—) for blends containing PS$_A$ and by a dotted line (···) for blends containing PS$_B$; *a* is given by the dashed line (- - -) for use of PS$_A$, with the magnitude of numerical uncertainties indicated by the error bar on the $c = 0.6$ point.

At higher values of *c*, both the 0.5 and 0.6 blends exhibit upturns in viscosity which probably correspond to normal c^3 effects. These upturns are apparently not due to entanglement effects, which should not yet be a factor at such low concentrations of the $M = 1.8 \times 10^6$ solute or even the 50% or 60% PS$_A$ solvent component.

2. $M = 2.33 \times 10^5$ Solute. No trends with blend composition can be discerned within the data scatter for this smaller solute molecule in the three solvent blends. This suggests that the limiting Θ condition is achieved at compositions with more than 75% styrene. The data are essentially *c*-independent, which is not surprising in view of the fact that even pure styrene (see the lower portion of Figure 2) produces data that are insensitive to *c* in this range of solute molecular weight. The position of the horizontal curve gives $[\eta] = 0.43$ dL/g for all blends used here, this value arising from a least-squares fit which gives only half-weight to the scattered points with $c < 0.2$ g/dL.

Collectively, the evidence of Figure 3 is that monomer/polymer "solvent" blends tend to give rather flat viscosity number curves, these becoming flatter than for conventional Θ solvents when the limiting condition is reached. Values of $[\eta]$ approach Θ values at blend compositions which are surprisingly low in low-$\bar{M}$ polymer content, although the rate of approach depends on solute molecular weight (earlier approach for smaller molecular weight).

This composition dependence is illustrated explicitly for $[\eta]$ and *a* in Figure 4. Values of *a* are computed from the corresponding $[\eta]$ values for each blend, and both are listed in Table I. The asymptotic limit $a = 0.50$ is quite sensitive to the extrapolations in Figure 3, and we are not claiming great statistical confidence in this result. For example, the data scatter in viscosity numbers of Figure 3 permit uncertainties of ±0.03 dL/g for both solutes, and this translates into a range $0.46 < a < 0.55$ which is displayed in Figure 4 (at $c = 0.6$). However, we believe that the existence of essentially Θ conditions is strongly supported by the accumulated data.

So far, only results involving PS$_A$ (with $\bar{M}_w = 2.5 \times 10^4$ and a broad MWD) have been discussed. There remains

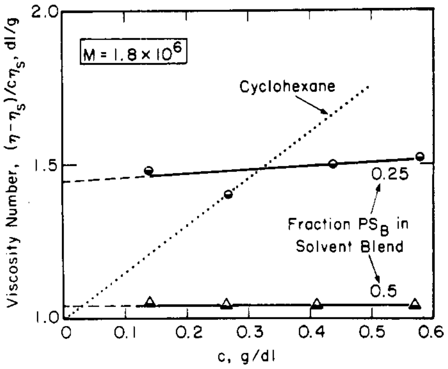

Figure 5. Viscosity numbers for $M = 1.8 \times 10^6$ solute in styrene/polystyrene blended solvents, when the latter contain PS_B. Polymer weight fractions in the blends are 0.25 (●) and 0.5 (▲). The dotted line represents cyclohexane systems, from Figure 2.

an intriguing question about how $\bar{M}$ and MWD of the low-$\bar{M}$ polymer component in the blend affect "solution" behavior. This was explored briefly by using PS_B in the solvent blend. Relative to PS_A, PS_B has an MWD skewed upward on the higher molecular weight side to give higher $\bar{M}$ but without higher molecular weight species present in the distribution. The lesser presence of very low molecular weight species might be expected to make it closer to a Θ solvent for high molecular weight polystyrene than is PS_A.

The smaller amount of PS_B available permitted only a very limited amount of data to be taken. Figure 5 displays viscosity numbers for the $M = 1.8 \times 10^6$ solute dissolved in two blends. Data scatter is minimal, and for the 0.5 blend there is less ambiguity about extrapolation to $[\eta]$ than seen in Figure 3 for the comparable blends of PS_A. This $[\eta]$ value seems clearly to be in the Θ limit, inasmuch as the curve is virtually horizontal. Both curves differ from those in Figure 3 for the corresponding concentrations of PS_A in that viscosity upturns are not exhibited in the higher c ranges.

The two values of $[\eta]$ from Figure 5 are displayed in Figure 4. Although they are close to the curve representing blends using PS_A, they differ by substantially more than the uncertainties in the PS_A and PS_B data and thus are used to define a separate dotted line. The nature of this difference is to require a higher polymer content in the blended solvent before the limiting (Θ) conditions are achieved and also a lower limit itself. Why this limiting $[\eta]$ value should be lower than for the PS_A blends is not clear, unless the latter was not truly at Θ conditions. This is certainly a possibility, since (a) our previous discussion showed that $a = 0.5$ for those systems was somewhat uncertain with existing data scatter and (b) the GPC evidence in Figure 1 shows PS_A to have such a large fraction of low molecular weight species that it may constitute a better than Θ solvent component. If this is true, then the PS_B behavior is probably closer to Θ performance. In passing, we note that its $[\eta]$ limit is extremely close to that of the Θ solvents cyclohexane and dioxane/isopropyl alcohol, whereas the limit for PS_A is close to that for benzene/isopropyl alcohol.

Conclusions

1. Rheological evidence, in the form of intrinsic viscosity data, tends to confirm the postulate that Gaussian chain statistics prevail in polymer melts and concentrated solutions. This occurs in melts having a low molecular weight tail to the MWD at least as low as 10^4 and also in solutions with good solvents present in large proportion (40–75%).

2. Low-$\bar{M}$ polymers and their solutions constitute an attractive new class of Θ solvents for high molecular weight polymers of the same chemical character. There is essentially no c dependence in the dilute viscosity number curves of such systems, making extrapolation to $c = 0$ to obtain $[\eta]$ more reliable and, indeed, making it possible to extract $[\eta]$ directly from finite-c measurements. Another notable feature is the high viscosity (which can be adjusted as desired) of these solvents, rendering them specially suitable for testing dilute-solution theories involving nonlinearities arising from stress-induced coil deformation.[10] Furthermore, such systems should remain at the Θ condition over wide ranges of temperature, so that a temperature of convenience may always be chosen.

3. This preliminary investigation has raised questions which can only be answered by further work. It is particularly important to clarify the effect of the "solvent" polymer $\bar{M}$ and MWD, especially relative to solute polymers of various molecular weights. This should be done with monodisperse "solvent" polymers and then with blends of these. The case of overlap in the MWD's of solute and solvent needs special attention, as this may be the source of the discrepancy seen here between results with PS_A and PS_B. It is also important to detect whether the chemical nature of the true solvent (here, styrene) plays a significant role or is merely acting as a free-volume diluent at the concentrations of interest.

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