

Effect of Solvent Character on Polymer Entanglements

In a recent paper¹ we discussed the influence of solvent on the magnitude of the low-shear limiting viscosity ratio $\eta_r = \eta_0/\eta_s$ for polymer solutions over a wide range of concentrations. The data presented there demonstrated that thermodynamically poor solvents led to much higher viscosities at high concentrations than did good solvents. This behavior is opposite to low-concentration results, where poor solvents lead to lower viscosities because of coil shrinkage.

The traditional picture of melts and polymer solutions at high concentration attributes their generally high viscosities to the existence of entanglement networks.²⁻⁴ This concept was invoked¹ to explain the above solvent effects: In poor solvents, the entangled chains cling together more tightly and perhaps form multimolecular aggregates before entanglements occur in the classical sense.

Our objective here is to compare the onset of such phenomena with the predictions of previous theory and correlation. It is found that solvent effects, previously neglected, can lead to significant errors in such estimates.

PREDICTIONS

The onset of entanglement or aggregation phenomena can be identified by rather abrupt slope changes in plots of $\eta_r(c)$ vs. c , $\eta_r(M)$ vs. M , or $\eta_r(c,M)$ vs. cM^b . At high cM^b it is frequently reported that $\eta_r \sim c^5 M^{2.4}$, although exceptions abound, and the attainment of c^5 or $M^{2.4}$ behavior is often used to mark "critical" entanglement conditions. If the onset point for bulk polymer of density ρ is M^* , the estimate for onset in solutions has been recommended² as

$$c_{\text{ent}}M = cM_{\text{ent}} = \rho M^* \quad (1)$$

This scheme reduces the problem for solutions to finding tabulated values² of ρM^* for a given polymer, but totally ignores solvent effects.

A theory based on the packing of polymer coils at incipient overlap⁵ predicts

$$(c/M)_{\text{ent}} = 2.28 \times 10^{-23}/(\overline{R_0^2})^{3/2} \quad (2a)$$

where the mean-square end separation $\overline{R_0^2}$ is evaluated for unperturbed (θ) conditions. Thus, $\overline{R_0^2} \sim M$ and Eq. 2a becomes

$$c_{\text{ent}}M^{1/2} = cM_{\text{ent}}^{1/2} = \text{const.} \quad (2b)$$

Similar relations have been proposed and supported by others.⁶

EXPERIMENTAL

The eight combinations of polymer, solvent, and M (all nearly monodisperse) are identified in Table I. Polymer-solvent systems were chosen to represent a wide variety of thermodynamic interactions. For each polymer a good solvent and a θ solvent were selected. Polystyrene (PS) systems were intended to represent the case of nonpolar compounds with weak intermolecular forces. Strong polar forces characterize the poly-(methyl methacrylate) (PMMA) systems. Molecular weights were chosen to provide experimental access to both the entanglement and preentanglement regions at a given concentration.

Viscosimetry was performed for low- η_0 fluids with Ubbelohde U-tube viscometers, and for high- η_0 fluids with a Weissenberg rheogoniometer. Details are provided elsewhere.¹

TABLE I
 Polymer-Solvent Systems

Polymer	$\bar{M}_n \times 10^{-4}$ (osmometry)	$\bar{M}_v \times 10^{-4}$ (from $[\eta] = KM^a$)	Solvents	
			Good	θ at 25°C
Polystyrene*	5.1	5.2	toluene	decalin
	42.0	41.0	toluene	decalin
Poly(methyl methacry- late)	5.06	5.4	chlorobenzene	m-xylene
	13.0 ^b	13.1	chlorobenzene	—
	11.0 ^b	—	—	m-xylene

* Pressure Chemical Co. supplies $M = 5.10 \times 10^4$ and 41.1×10^4 , with $\bar{M}_w/\bar{M}_n < 1.06$.

^b This sample degraded slightly between the times of testing chlorobenzene and xylene systems.

DISCUSSION

Values of c_{ent} as predicted by eqs. (1) and (2) are presented in Table II. The five PS tabulations for the higher M are in reasonable agreement with each other, showing only $\pm 20\%$ variation, but the lower- M predictions differ markedly between the two schemes. The $c_{ent}M = \text{const.}$ scheme yields uncomfortably large numbers while apparently being supported by a great deal of published data in this M range, whereas the $c_{ent}M^{1/2} = \text{const.}$ method yields more reasonable numbers but is supported only by data at higher M . The three PMMA tabulations show even more puzzling variations, although it should be noted that the first line—giving far lower predictions than the other two—arises from data in a rather mediocre solvent.

The new PS data are seen in Figures 1a and 1b. For the higher- M samples, the good-solvent result is $c_{ent} \cong 10$ g/dl, and the poor-solvent result, $c_{crit} \cong 7$ g/dl. This difference is almost exactly the span of predicted values in Table II—not a wide variation, but notably one which shows viscosity enhancement beginning earlier in the poorer solvent. From the lower- M samples, poor-solvent data give $c_{crit} \cong 18$ g/dl (Fig. 1b) in fairly good agreement with the $c_{ent}M^{1/2} = \text{const.}$ scheme. Good-solvent data for low M are not extensive enough to support either correlation by themselves, being extrapolated in Figure 1a to show consistency with the $c_{ent}M = \text{const.}$ scheme, even though a superposition of Figures 1a and 1b shows consistency also with the $c_{ent}M^{1/2} = \text{const.}$ scheme.

The sum of PS data, then, shows definite variation with solvent in the region of critical (entanglement/aggregation) concentrations, with a tendency toward higher c_{crit} in good solvents being evident. A slight superiority for the $c_{ent}M^{1/2} = \text{const.}$ scheme is suggested, but all schemes fail to account for solvent effects.

Even more dramatic variations with solvent are seen in the PMMA data of Figures 2a and 2b. For the higher- M samples, the good-solvent $c_{ent} \cong 16$ g/dl (in agreement with the second $c_{ent}M = \text{const.}$ prediction of Table II) and the poor-solvent $c_{crit} \cong 8$ g/dl (close to the first $c_{ent}M = \text{const.}$ prediction, which involved the mediocre solvent). For the lower- M samples, the good-solvent $c_{ent} \cong 20$ g/dl, and the poor-solvent $c_{crit} \cong 12$ g/dl.

Thus the PMMA data, representing polar systems, show very distinctly that viscosity enhancement begins at lower concentrations in poor solvents than in good solvents. In none of the PMMA cases does the $c_{ent}M^{1/2} = \text{const.}$ scheme come close to predicting the correct c_{ent} or c_{crit} , although these data support the M dependence of $c_{crit} \sim 1/M^{1/2}$ much better than $c_{crit} \sim 1/M$.

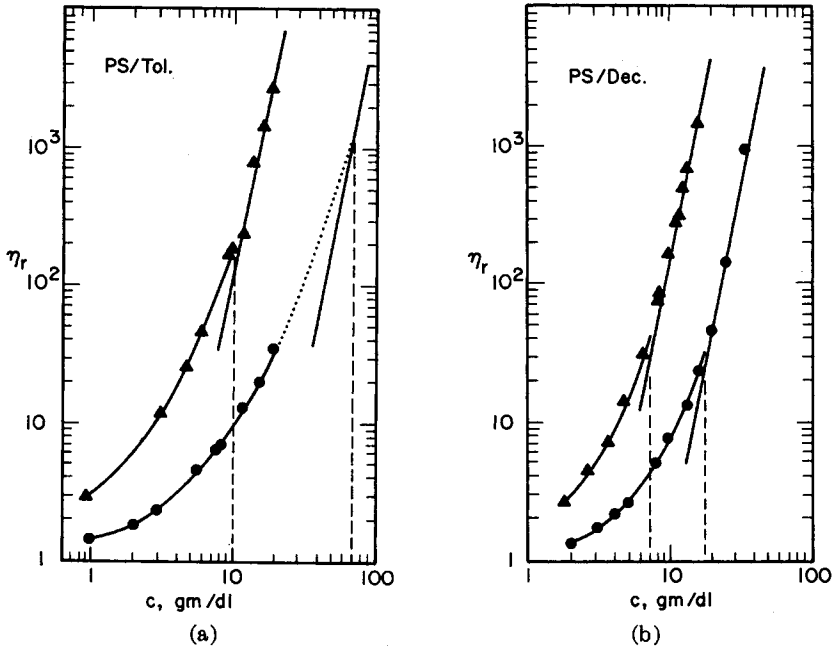


Fig. 1. Concentration dependence of zero-shear relative viscosity for polystyrene solutions. Circles represent $M = 5.1 \times 10^4$; triangles, $M = 4.1 \times 10^5$. (a) Toluene solutions; (b) decalin solutions.

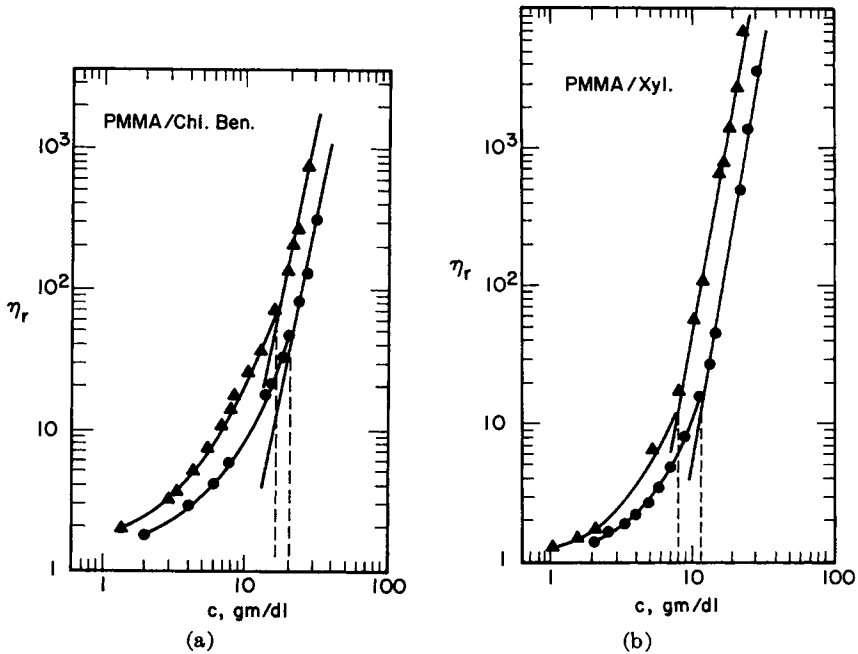


Fig. 2. Concentration dependence of zero-shear relative viscosity for poly(methyl methacrylate) solutions. Circles represent $M = 5.0 \times 10^4$; triangles, $M = 1.3 \times 10^5$ in (a) and 1.1×10^5 in (b). (a) Chlorobenzene solutions; (b) *m*-xylene solutions.

TABLE II
Estimation of Critical Entanglement Concentrations

Formula	Critical concentration, g/dl		Comments
	$M =$ 5.1×10^4	$M =$ 4.1×10^5	
Polystyrene			
$c_{\text{ent}}M = 4.4 \times 10^6$	88	10.8	from dibenzyl ether solutions, with $2.5 \times 10^4 < M < 5 \times 10^5$, quoted as especially reliable ²
$c_{\text{ent}}M = 3.75 \times 10^6$	74	9.2	average of all solution data, ² all but one solvent good
$c_{\text{ent}}M = 3.03 \times 10^6$	65	8.1	from di-2-ethylhexylphthalate solutions, ⁷ $M > 2000$
$c_{\text{ent}}M^{1/2} = 4.65 \times 10^3$	21	7.3	eq. (2), using ⁵ $(\overline{R_0^2}/M)^{1/2} = 76 \times 10^{-10}$ with R_0 in cm
$c_{\text{ent}}M^{1/2} = 5.28 \times 10^3$	24	8.3	from toluene solutions, ⁶ $M > 1.5 \times 10^5$
Poly(methyl methacrylate)			
$c_{\text{ent}}M = 10^6$	$M =$ 5×10^4	$M =$ 1.3×10^5	from diethyl phthalate solutions, ⁸ $M > 6 \times 10^4$
$c_{\text{ent}}M = 2.25 \times 10^6$	46	17.3	from bulk polymer, creep and stress relaxation ⁴
$c_{\text{ent}}M^{1/2} = 1.05 \times 10^4$	47	29	eq. (2), using ⁸ $(\overline{R_0^2}/M)^{1/2} = 60 \times 10^{-10}$ with R_0 in cm

^a Value cited is average of 5 given on pp. IV-54, 55 of ref. 9, 3 between 20°–25°C and 2 for θ solvents. Variation is about $\pm 10\%$.

CONCLUSIONS

Viscosity data $\eta_0(c)$ for both PS and PMMA suggest that sharp viscosity enhancement in good-solvent systems correspond to the classical entanglement picture and can be reliably estimated to begin at c_{ent} by traditional means. However, enhancement begins at far smaller concentrations in poor-solvent systems, probably reflecting interpolymer aggregation due to thermodynamic forces. These forces persist, of course, even when $c \geq c_{\text{ent}}$, thereby making entanglements tighter (if they form at all in the usual sense) and rendering poor-solvent viscosities higher than good-solvent viscosities over the entire range of high concentration.

This demonstrates the important role played by solvent in this regime, contrary to general understanding, and the necessity to use correlations for c_{ent} very carefully.

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