

Concentrated solution rheology of an ABA poly(styrene-*b*-butadiene) copolymer in various solvents

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The critical concentrations of an SBS copolymer in cyclohexane, carbon tetrachloride, toluene, tetralin and cyclohexanone were determined. Using an equation proposed by Cornet, it was shown that at the critical concentrations the unperturbed root mean square end to end distances were, within experimental error, the same as that found for dilute solutions, indicating that the interpenetrating conformation of the blocks established for dilute solutions was maintained up to at least the critical concentrations.

Keywords Block copolymers; critical concentration; rheology; coil entanglement; hydrodynamics; phase separation

INTRODUCTION

The flow properties of concentrated ABA poly(styrene-*b*-butadiene) copolymer (SBS) solutions are practically important because of their applications as adhesives and sealing agents. In this report the rheological and hydrodynamic behaviour especially in the region of the critical concentration¹ is discussed. The viscosity-molecular weight-concentration relation above the critical concentration has been expressed¹⁻³ for homopolymers by the following equation.

$$\eta = K C^\alpha M^\beta \quad (1)$$

η is the viscosity, C is concentration and M is molecular weight. K , α and β are constants.

For polymer melts⁴ equation (2) is used.

$$\log \eta = 3.4 \log \bar{M}_w + A \quad (2)$$

\bar{M}_w is the weight average molecular weight and A is an empirical constant characteristic of a particular polymer, but independent of \bar{M}_w . For homopolymer melts the molecular weight exponent is commonly close to 3.4, but for SBS copolymers a value of 5.5 has been reported⁵ for a shear rate of 10 s^{-1} .

For dilute solutions, it has been shown⁶, for SBS in the solvents used in this study, that the polystyrene and polybutadiene blocks interpenetrate in the individual isolated random coils. Utracki *et al.*⁷ came to the same conclusion. In the solid state the blocks phase separate to give a morphology comprising polystyrene domains in a polybutadiene matrix. The critical concentration is where the effect of molecular entanglements becomes significant, but has block phase separation occurred at this concentration?

Cornet⁸ has proposed a relation between the unperturbed root mean square end-to-end distance, $(\bar{r}_0^2)^{1/2}$, and the critical concentration C_c .

$$(\bar{r}_0^2)^{1/2} = K' \left(\frac{M}{C_c} \right)^{1/2} \quad (3)$$

K' is a constant related to the packing arrangement of the random coils at the critical concentration.

In this paper equations (1) and (3), which are well established for homopolymers, are applied to an SBS copolymer.

EXPERIMENTAL

The characterization data for the polymer used in this study are shown in Table 1. It was a commercial material, Cariflex 1101, kindly donated by Shell Chemicals. The viscosity measurements were made using a Haake Rotovisko (model RVI) rheometer thermostatically controlled at $27 \pm 0.01^\circ\text{C}$. The solutions, which covered the concentration range from 5% to 30% were prepared on a

Table 1 Polymer characterization data

Parameter	Value
$\bar{M}_n \times 10^{-3a}$	100
\bar{M}_w/\bar{M}_n^b	1.48
A-B-A ^c	13.5-73-13.5
Microstructure (%) ^d	
<i>trans</i> 1,4-	45
<i>cis</i> 1,4-	38
1,2-	17

^a By membrane osmometry in toluene at 37°C

^b By gel permeation chromatography

^c Block molecular weights ($\times 10^{-3}$)

^d By 220 MHz proton n.m.r.

weight to volume basis by shaking, and, if necessary, by gentle warming. The solvents used were cyclohexane, carbon tetrachloride, toluene, tetralin and cyclohexanone. The behaviour of SBS in these solvents has been discussed⁹ in an earlier paper. To each solution was added 0.3% (w/v) *N*-phenyl-2-naphthylamine as antioxidant. This had no detectable effect on the viscosities. For each solution the flow behaviour index, n ,^{10,11} and the viscosity at a shear rate of 1 s^{-1} were determined. At low concentrations it was necessary to obtain this latter value by an extrapolation. The error in determining the viscosity at 1 s^{-1} , in those cases where extrapolation was necessary, was entirely negligible.

RESULTS AND DISCUSSION

From Table 2 it can be seen that the flow behaviour indices

Table 2 Flow data at 27°C

Solvent	Concentration (%)	η (cP)	n
Cyclohexane	5	22	1.00
	6	38	1.00
	8	90	1.00
	9	122	0.97
	10	170	0.96
	12	350	0.93
	15	917	0.91
	20	3200	0.91
	25	6600	0.94
	30	19000	1.00
Carbon tetrachloride	5	28	1.00
	6	41	1.00
	7	66	0.95
	9	130	0.93
	10	180	0.96
	12	350	0.94
	15	800	0.97
	20	2300	0.94
	25	5700	0.97
	30	12000	0.90
Toluene	5	15	1.00
	6	25	1.00
	8	52	0.98
	9	70	0.98
	10	94	0.96
	12	183	0.94
	15	500	1.00
	18	850	1.00
	20	1180	0.99
	25.1	2700	0.96
30	6200	1.00	
Tetralin	4.94	61	1.00
	6	80	0.97
	8	180	0.96
	9	250	0.96
	10	309	0.95
	12	620	0.95
	15	1394	0.93
	20	4200	0.95
	25	10000	0.93
	30	22500	0.97
Cyclohexanone	5	46	1.00
	6	77	0.98
	8	160	0.95
	9	235	0.94
	10	320	0.94
	12	660	0.95
	15	1660	0.94
	20	5900	0.91
	25	15000	0.95
	30	33000	0.95

vary in a complicated way. For homopolymer solutions it would be expected that the deviation from Newtonian behaviour would increase with concentration. However, for the SBS material a concentration will be reached where the penetrating block conformation already mentioned^{6,7} will change to the separated arrangement of blocks encountered in the solid. This process will result in structured solutions which clearly complicate the usual trend in flow behaviour index with increasing concentration.

Logarithmic plots of η versus concentration (Figure 1) in all five solvents show distinct slope changes at around 10% concentration. In these log-log plots each curve shows two linear portions whose upper and lower slopes were designated α and λ , respectively. The point of intersection corresponds to the critical concentration, η_c , at this concentration, η_c , along with α , λ and C_c are given in Table 3. The occurrence of such linear regions is common in plots of log viscosity versus either log molecular weight or log concentration^{1,7,12-14}. The following relations can be written to describe the situations above and below the critical concentration, respectively.

$$\log \eta = \log \eta_c + \alpha \log \left(\frac{C}{C_c} \right) \quad (5)$$

$$\log \eta = \log \eta_c - \lambda \log \left(\frac{C_c}{C} \right) \quad (6)$$

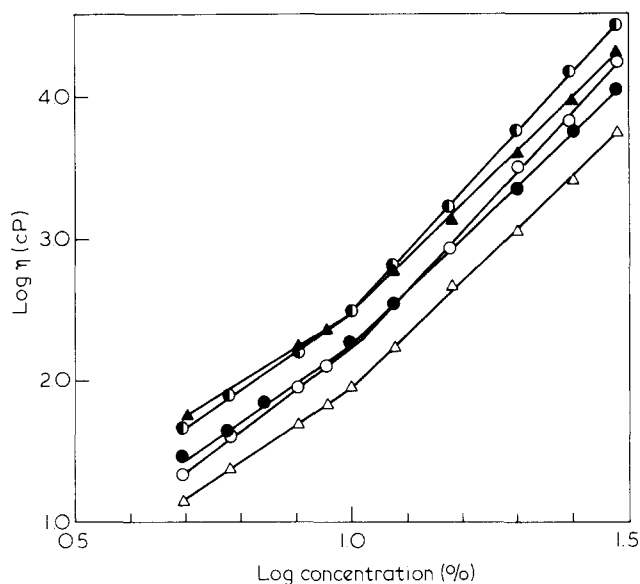


Figure 1 Log η versus log concentration plots for the copolymer in cyclohexane (○), carbon tetrachloride (●), toluene (△), tetralin (▲) and cyclohexanone (◐)

Table 3 α , λ , C_c and η_c data for the SBS copolymer in all five solvents

	α	λ	C_c (%)	η_c (cP)
Cyclohexane	4.3	2.9	10.5	200
Carbon tetrachloride	3.8	2.8	10.0	184
Toluene	3.8	2.8	10.0	114
Tetralin	3.8	2.5	10.0	309
Cyclohexanone	4.2	2.6	9.8	276

The values of α , λ and C_c for use with equations (5) and (6) are given in Table 3 for each solvent.

Dreval *et al.*¹⁵ state that the values of α for homopolymers lie between 3.5 and 7 with the average value close to 5. The α values in this work are within this range, although they differ significantly from the average value. Higher values of α (4.3–6.2) were found⁶ for four-arm star¹⁶ SBS block copolymers in cyclohexane, toluene and cyclohexanone.

It has been reported¹ that the ratio β/α varies from 0.54 to 0.72 for a range of homopolymers. This ratio has also been taken^{15,17} as being equal to the Mark–Houwink¹⁸ exponent. In this study only one SBS sample was investigated, so the molecular weight exponent, β , was not obtained directly. However, when plots of $\log \eta$ versus $\alpha \log C + \beta \log M$ are constructed with α equal to the experimentally determined values and β equal to the widely accepted^{3,15,19} value of 3.4, the graphs for this SBS sample in all five solvents have slopes very close to unity, indicating that β for SBS copolymers is also 3.4. The β/α ratios based on β equal to 3.4 and the α values from Table 3 are shown in Table 4 along with the corresponding Mark–Houwink⁶ exponents from which they differ significantly. The β/α values are also outside the range (0.54–0.72) reported¹ for homopolymers. This deviation is attributed to the rather low concentration dependence. α commonly^{3,15} has a value of around 5.0. This probably arises because the polymer selected for this work was a commercial sample which is known to contain diblock material^{20–23} as a result of incomplete coupling²³ during synthesis. Such chains would have only one end block available to locate in the ultimately formed polystyrene domains. Consequently, the network structure would be weakened and the dependence of η on concentration diminished.

As mentioned earlier for dilute solutions in these solvents, it is believed^{6,7} that the SBS molecules behave as isolated random coils in which the polystyrene end blocks interpenetrate the mid-block segments. Eventually as concentration rises substantial phase separation must occur as the solid state morphology of this sample²⁴ consists of polystyrene domains in a polybutadiene matrix. As concentration is increased, the coils may obtain a maximum packing density before block phase separation occurs. If it is assumed that the molecules in a concentrated solution are behaving as unperturbed coils and are packing as spheres, equation (3) can be used to calculate the root mean square end-to-end distance of the coils. The K' values calculated by Cornet⁸ for a face-centred cubic lattice, a body centred cubic lattice and a simple lattice were 3.04×10^{-8} mole^{1/3}, 2.64×10^{-8} mole^{1/3}

and 2.45×10^{-8} mole^{1/3}, respectively. As the three dimensional arrangement of coils at the critical concentration is not known, an average value of 2.71×10^{-8} mole^{1/3} was used.

The values of $(\bar{r}_0^2)^{1/2}$ obtained were 27 nm in carbon tetrachloride, toluene and tetralin and 26.6 nm and 27.3 nm, respectively, in cyclohexane and cyclohexanone. This value of around 27 nm compares remarkably well with a value of 26.9 ± 0.5 nm for $(\bar{r}_0^2)^{1/2}$ for this SBS copolymer obtained⁶ by dilute solution viscometry using the Stockmayer–Fixman²⁵ procedure and the Fox–Flory²⁶ equation. Bearing in mind that the sample contains some diblock material, the exactness of this agreement is certainly fortuitous. The presence of diblock will raise C_c , and hence, for a pure SBS sample $(\bar{r}_0^2)^{1/2}$ will be larger than quoted above. However, the error from this source is certainly no more than 7%. The agreement is, therefore, still good and would suggest that at C_c the end blocks are still interpenetrating the random coils and that the critical concentration is, therefore, associated with entanglements only and not with microphase separation. The concentration range over which the latter occurs will be the subject of further papers.

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Table 4 β/α values and Mark–Houwink exponents

Solvent	β/α	a^1
Cyclohexane	0.79	0.66
Carbon tetrachloride	0.89	0.72
Toluene	0.89	0.67
Tetralin	0.89	0.69
Cyclohexanone	0.82	0.63

¹Mark–Houwink exponent at 25°C