Concentrated solutions of SBS block copolymers in solvent mixtures

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The viscosities of 10% and 20% solutions of linear and non-linear SBS block copolymers were measured in various solvent pairs comprising ethyl acetate/toluene, ethyl acetate/cyclohexane, ethylacetate/carbon tetrachloride, ethyl acetate/n-hexane, ethyl acetate/cyclohexanone, methyl ethyl ketone/cyclohexanone and methyl ethyl ketone/n-hexane. Addition of the second solvents to 10% solutions of the polymers in ethyl acetate or methyl ethyl ketone gave rise to peaks around 10% to 14% added solvents. These peaks are caused by phase separation involving micelles and their occurrence depends on the interplay of composition of solvent mixtures, molecular weight and solution concentration and not on polymer architecture, styrene content or state of shear.

INTRODUCTION

Ethyl acetate and methyl ethyl ketone are good solvents for polystyrene but not for polybutadiene. A block copolymer of styrene and butadiene in these two solvents is subjected to simultaneous solubilization of polystyrene and aggregation of polybutadiene segments; the result is a micellar solution. Few studies on block copolymer micelles have been reported in the literature[1-7] and most of these are on dilute solutions[1-5,7]. In this paper, the contrasting behaviour of the component segments has been studied by choice of a second solvent, concentration, molecular weight, state of shear and architecture of the block copolymer.

EXPERIMENTAL

Polymers

Samples PA5, SO2, SO1 and PH4 are linear poly(styrene-b-butadiene) triblock copolymers of the Cariflex type which were kindly supplied by Shell Chemicals for research purposes. Samples SO1 and SO2 contain diblock and homopolymers[8]. Samples ST1 and ST6 are star-shaped $(SB-)_4X$ block copolymers supplied by Professor L. J. Fetters of the University of Akron, USA. The characterization data of these polymers are shown in *Table 1*.

Solvents

All the solvents used were distilled (× 3) after drying for 24 h with a molecular sieve; only mid-cuts were taken to make the solutions.

Measurement of viscosity

The Haake Rotovisko (RVI) rotational viscometer was used to obtain the viscosities of the various solutions. Logarithmic flow curves were constructed using the Power Law in order to obtain the viscosities at the required shear rates as well as the flow behaviour indices.

RESULTS AND DISCUSSION

Figure 1 shows the viscosities of 10% solutions of sample SO1 in ethyl acetate as the second solvents were added. See also *Table 2*. Irrespective of the nature of the second solvent added, the flow patterns were the same; namely, a rise in viscosity up to about 12% of the second solvents added, then a fall through a minimum and finally a sharp

Table 1 Characterization data of SBS block copolymers

Code	Type	$\bar{M}_n \times 10^{-3}$	$\frac{\bar{M}w}{\bar{M}n}$	Microstructure of diene *trans* 1,4–(%)	 *cis* 1,4–(%)	 1,2–(%)	Styrene content (%)
PA5	SBS	60	1.05	44	40	16	27.7
SO2	SBS	64	1.44	47	38	15	25.5
SO1	SBS	100	1.48	45	38	17	27
PH4	SBS	211	1.08	42	38	20	33.0
ST6	$(SB-)_4X$	210	1.14	48	42	8	41
ST1	$(SB-)_4X$	250	1.27	44	40	16	31

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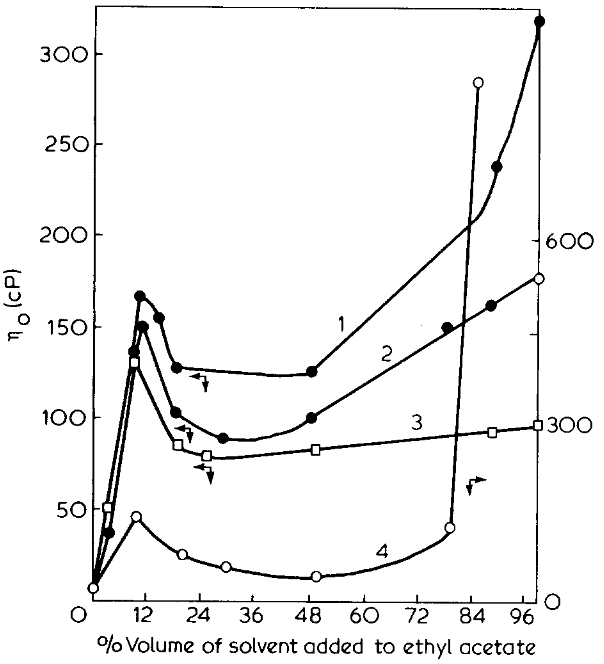

Figure 1 Plots of zero-shear viscosities of sample so1 *versus* percentage volumes of added solvents: —○—, n-hexane; —●—, carbon tetrachloride; □, toluene; ○, cyclohexanone, all in ethyl acetate

Table 2 Properties of a 10% solution of an SBS block copolymer (sample SO1) in ethyl acetate/second solvent mixtures at 27°C

Systems	Volume composition	η_0 (cP)	Flow behaviour index
Ethyl acetate-n-hexane	100 : 0	3.5	–
	90 : 10	135	0.92
	80 : 20	76	0.95
	70 : 30	60	1.0
	50 : 50	54	0.96
	20 : 80	130	0.91
	16 : 84	860	0.93
Ethyl acetate-carbon tetrachloride	100 : 0	3.5	–
	96 : 4	36	0.90
	90 : 10	150	0.94
	80 : 20	130	1.0
	70 : 30	95	0.99
	50 : 50	103	0.98
	20 : 80	154	0.95
	10 : 90	165	0.96
	0 : 100	180	0.90
Ethyl acetate-toluene	100 : 0	3.5	–
	96 : 4	65	0.80
	90 : 10	130	0.91
	75 : 25	80	0.97
	50 : 50	86	0.98
	10 : 90	97	0.97
	0 : 100	97	0.96
Ethyl acetate-cyclohexanone	100 : 0	3.5	–
	90 : 10	133	0.87
	88 : 12	167	0.90
	86 : 14	154	0.91
	84 : 16	143	0.93
	80 : 20	129	0.98
	50 : 50	129	0.98
	10 : 90	240	0.93
	0 : 100	320	0.94

or gradual rise. To form a solution in 100% ethyl acetate or 100% MEK, the solvent collapsed the polybutadiene midsegment and segregated it into a hard core which was held in solution by solubilized polystyrene segments; this is the molecular micelle. The concentration of the micelles in ethyl acetate was too low to form sufficient entanglements of segments and hence the low viscosity value which was approximately the same magnitude as that obtained in dilute solution studies[4].

On adding the second solvent, e.g. toluene, the phase separated micellar core started to disintegrate thereby releasing the segregated polybutadiene segments for solvation, entanglement and any possible network formation and hence the increase in viscosity of the medium. The polybutadiene segments still experience the contracting effects of residual ethyl acetate molecules which tend to reduce the hydrodynamic volume of the polymer. Addition of more toluene has a diluting effect on the polymer concentration. These two effects caused a fall in the viscosity of the medium. At this stage a peak therefore appeared and the solution lost its bluish cast. The viscosity fall continued until all residual contracting effects vanished at the minimum viscosity value before a slight rise occurred which continued up to 100% toluene content. In the ethyl acetate/n-hexane mixture (curve 4), the vanishing of the contracting effects of ethyl acetate on polybutadiene was thought to be followed by phase separation of polystyrene domains into stiff networks, and hence the viscosity increased enormously at about 84% added n-hexane. n-Hexane is a non-solvent for polystyrene. Behaviour of 10% (w/v) solution of sample SO1 in ethyl acetate/toluene was also repeated in ethyl acetate/cyclohexane, ethyl acetate/carbon tetrachloride (*Figure 1*) as well as in MEK/cyclohexanone and MEK/n-hexane in *Figure 2*. The values of the flow

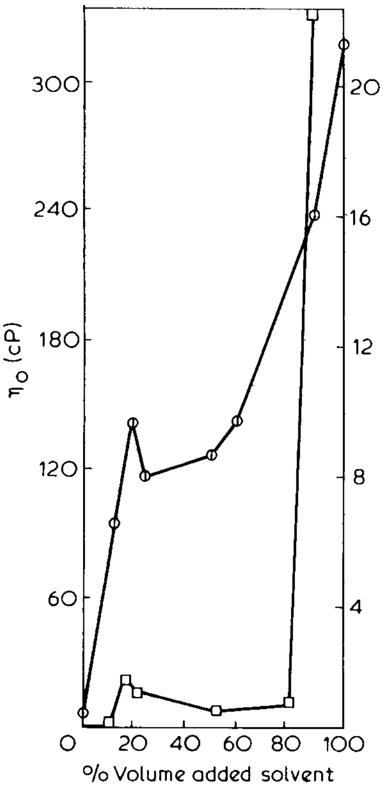

Figure 2 Plots of η_0 *versus* % volume of toluene for 10% SBS copolymer (sample So1) in MEK/cyclohexanone, ○; and MEK/n-hexane, □

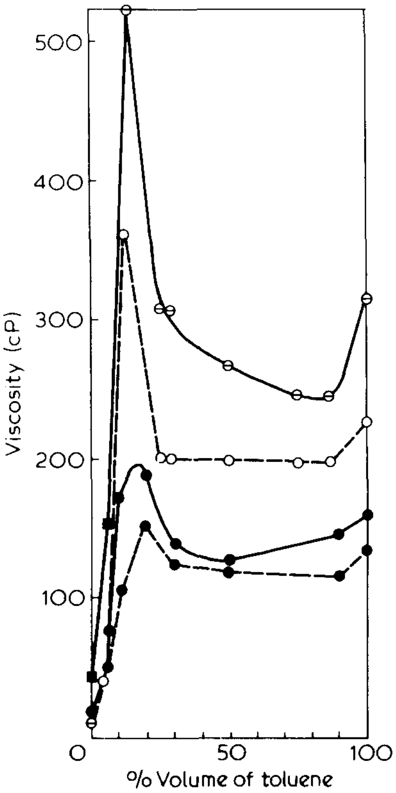

Figure 3 Plots of viscosities *versus* volume of toluene for (SB–)$_4$X block copolymers in ethyl acetate/toluene: ST1: η_0, –⊖–; η_{app} at a shear rate of 873 s^{-1}, – –●– –. ST6: η_0, –●–; – –○– –○– –, η_{app} at a shear rate of 873 s^{-1}

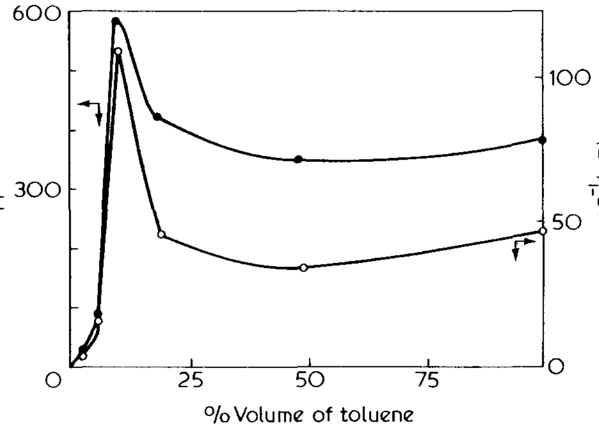

Figure 4 Plots of viscosity *versus* volume of added toluene for SBS block copolymer (sample PH4) in ethyl acetate: η_0, ○; and η_{app}, ● at a shear rate of 500 s^{-1}

behaviour indices showed that the systems were mostly mildly pseudoplastic. Since 100% ethyl acetate or MEK collapsed only the polybutadiene segment and a low viscosity was recorded, then the subsequent changes in viscosity on adding the second solvents were due mostly to changes in the conformations of the polybutadiene midsegments. The behaviour of 10% solutions of samples PH4, ST1 and ST6 (*Figure 3*) in ethyl acetate/toluene mixtures was similar to that of 10% solutions of SO1 in the different solvent mixtures studied. This remarkable similarity occurs inspite of the higher molecular weights of the three samples.

Differences in styrene content and the architecture of ST1 and ST6 did not affect the flow pattern. Sample PH4 solution showed a peak around 12% added toluene (*Figure 4*) which remained unchanged at a shear rate of 500 s^{-1}. A noticeable effect which reflected normal viscosity dependence on molecular weight appeared after about 12% added toluene; for example, increased temperature decreased the viscosity of the system. This is usual polymer solution behaviour which has been shown by SBS block copolymers in non-selective solvents[11]. On increasing the concentration of Sample SO1 to 20% (w/v) in 100% ethyl acetate, high viscosity was obtained. This is attributed to enhanced phase separation of the segments which led to the formation of a highly pseudoplastic and thixotropic jelly-like solution (*Figure 5*). The arrangement of the micelles is therefore easily disrupted by shearing forces. The micelles, without doubt, have increased in number and in size and hence the higher viscosity observed at 20% than at 10% polymer concentration. Addition of second solvent, e.g. toluene, weakened the bonds joining the micelles, and hence the viscosity fell (*Figure 6*). No peak was observed. Thixotropy persisted up to 10% added toluene though at a lower shear rate (441 s^{-1}) and higher initial shear stress (9830 dynes cm^{-2}) (*Figure 5*). A surprising result is that 10% solutions of lower molecular weight samples (PA5 and SO2) in solvent mixtures (*Figure 7*) behaved like 20% SO1 solution (*Figure 6*) and contrasts sharply with *Figure 1* for 10% solutions. It appears, therefore, that at the lower concentration (i.e. 10%) studied, samples PA5 and SO2 possessed far more micelles than the higher molecular weight samples so that in a given volume, the micelles

Table 3 Properties of 20% SBS block copolymer (sample SO1) in ethyl acetate/toluene mixtures at 27°C

Volume % toluene	η_{app} × 10^{-3} (cP) at $\dot{\gamma}$ = 10^{-1} s^{-1}	η_0 × 10^{-3} (cP)	Flow behaviour index
100	1.18	1.18	0.99
50	12.5	12.5	0.98
30	12.5	12.5	0.99
20	18	18	0.98
10	40	40	0.97
4	120	90	0.57
0	300	90	0.21

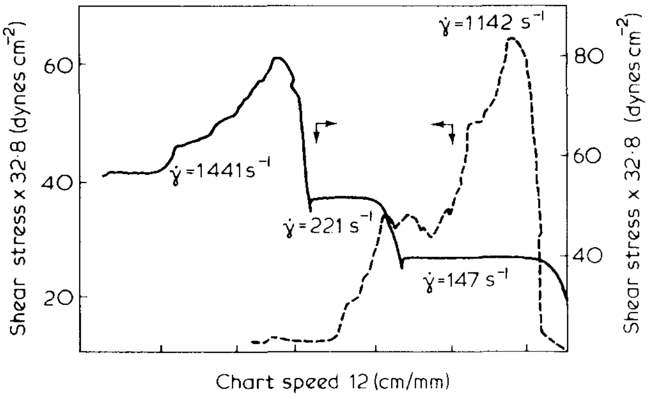

Figure 5 Thixotropic effects of 20% solutions of SBS block copolymer (sample SO1): ——, at 10% added toluene in ethylacetate/toluene mixture; – – – –, at 100% ethylacetate

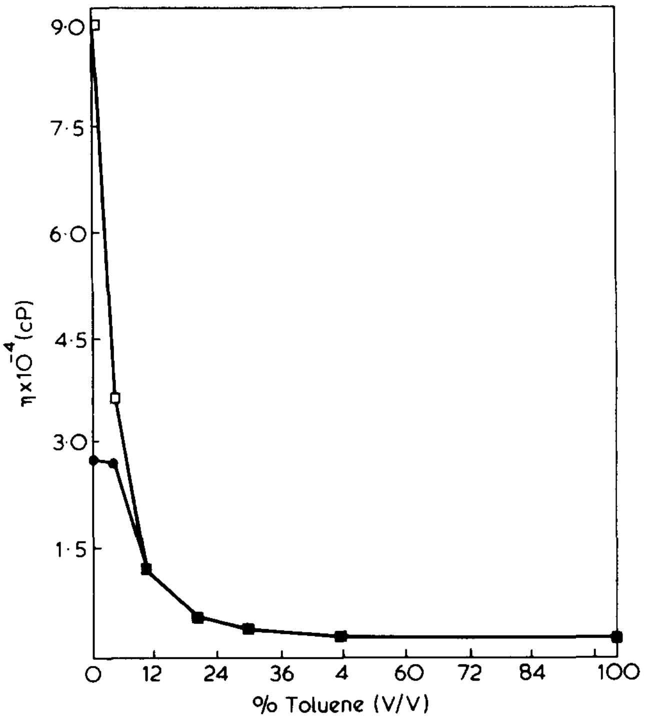

Figure 6 Plot of viscosities *versus* volume of added toluene for 20% solution of SBS block copolymer (sample SO1): η_0, □; η_{app}, ● at a shear rate of 500 s^{-1}

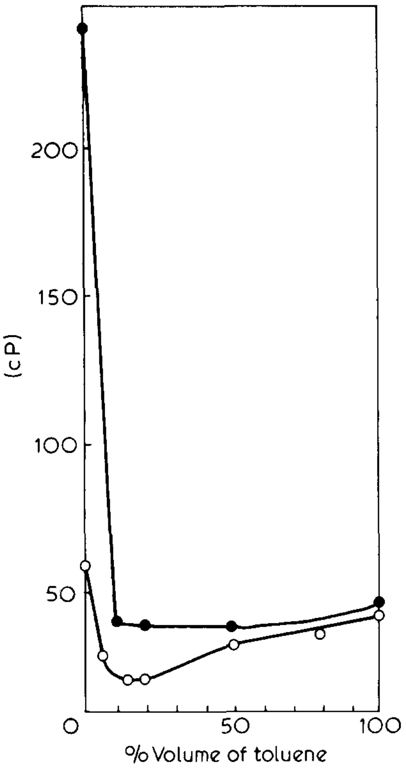

Figure 7 Plot of viscosities *versus* volume of added toluene for 10% solutions of SBS block copolymers, ●, sample SO2; ○, sample PA5

have different packing arrangements. The arrangements in PA5 and SO2 favoured higher viscosity values.

This speculative arrangement of micelles into geometric arrays has actually been demonstrated by means of electron microscopy both by the author[11] and elsewhere[12] in our laboratory. Addition of toluene has the same effect as on the 20% polymer concentration.

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