Thermodynamic and Conformational Properties of Styrene–Methyl Methacrylate Block Copolymers in Dilute Solution

II—Behaviour in Theta Solvents

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To find θ solvents for random and block copolymers of styrene and methyl methacrylate, various solvents were examined by the cloud point test. From among the solvents examined, cyclohexanol and 2-ethoxyethanol were chosen and the θ temperatures were determined by osmotic pressure measurement. In cyclohexanol two homopolymers have almost equal θ, to which the θs of the block copolymers are also quite close; while the θs of the random copolymers show a minimum at nearly equimolar composition.

Intrinsic viscosities $[\eta]$ of nearly equimolar block copolymers were examined in these two θ solvents. In contrast to random copolymers the $[\eta]_\theta$ of the block copolymers are sensitive to the type of θ solvent employed. From $[\eta]_\theta$ data in cyclohexanol the unperturbed mean square radius of gyration for the block copolymers was estimated as $10^{18}\ \langle s\rangle_0/M_w^{1/2}=6{\cdot}35$ (cm²) which is better approximated by the simple composition average of the parent homopolymers as previously suggested by Stockmayer. The behaviour of the block copolymers in a good solvent, toluene, was compared with that of the random copolymers and the homopolymers: the $[\eta]$s are smaller than those of the corresponding random copolymers but are about the average of the two homopolymers, An anomaly in $[\eta]$ which was often suggested as that due to 'intrachain phase separation' in block copolymer chains was not observed.

IN THE first article[1] of this series, we described the preparation and characterization of styrene (ST)–methyl methacrylate (MMA) block copolymers with well defined architecture. The present article is concerned with their behaviour in θ solvents in relation with that of ST–MMA random copolymers as well as of the parent homopolymers[2,3].

The concept of the θ condition for solutions of flexible chain (homo)-polymers has been fully established by Flory[4]. The θ condition is that at which the excess chemical potential due to polymer–solvent interaction is zero and deviations from ideality vanish. Consequently, at the θ condition the osmotic second virial coefficient A_2 is zero and, the polymer chain assumes a random flight conformation, its average dimensions being determined solely by short-range interactions such as fixed bond length and angles, steric hindrances between consecutive chain segments, and the like. Here we ask whether the concept may or may not be applicable to solutions of (both random and block) copolymers.

To answer the question, one should first find θ solvents[4,5]. It would be easy to obtain a θ solvent by mixing a good solvent with the appropriate amount of a non-solvent. However, the use of mixed solvent often complicates the analysis of experimental data even for homopolymers and is probably less satisfactory for copolymers. Therefore, it is desirable to find pure solvents which may bring a given copolymer to the θ condition within the workable range of temperature. With the intention of finding such solvents for ST–MMA random copolymers, Utiyama[6] has examined a variety of solvents including three ketones, eight esters of monocarboxylic acid, and three esters of dicarboxylic acid. Unfortunately the results were not successful. Recently Froelich and Benoit[7] reported that in cyclohexanol A_2 became zero at 81·6°C for ST–MMA (50 ST mol%) block copolymer and at 68·6°C for azeotropic random copolymer. Cyclohexanol has quite similar solubility for both of the parent homopolymers; in fact the θ temperature reported for polystyrene (PST) is 83·5°C[7,8] and that for poly(methyl methacrylate) (PMMA) is 77·6°C[7].

In this respect, it should be interesting to find other pure θ solvents which have different solvent power toward each of the parent homopolymers, and to examine the properties of these θ solvent systems. As far as we are aware, there have been no such solvents reported. Therefore we have made a further search for such solvents for ST–MMA random and block copolymers, and fortunately have been partially successful in the effort. We have examined the properties, particularly the molecular weight dependence of the intrinsic viscosity of the copoylmers in these θ solvents, and report the results herein.

EXPERIMENTAL

Materials

The ST–MMA block copolymers were of PMMA–PST–PMMA type prepared by an anionic polymerization technique. The detail was described in a previous paper[1]. For the sake of comparison, we used ST–MMA random copolymers, which were some fractions from low conversion copolymers prepared by a free-radical polymerization method (initiator was benzoyl peroxide; temperature was 60°C; conversion was less than ten per cent)[3]. The whole polymers, coded as SM3, SM5 and SM7, were fractionated into 10 to 12 fractions each by using the butanone and diisopropyl ether system[9]. The average composition m (in ST mole fraction) for fractions from each series was 0·29 for SM3, 0·56 for SM5 and 0·70 for SM7. The composition fluctuation was negligible. The detail has been described previously[3]. All the solvents used were carefully purified according to the method appropriate to each[10].

θ temperature determination

A simple solubility test was first performed to examine as many solvents as possible. For the test we used three random copolymer fractions with nearly equal molecular weight (cf. *Table 1*), four block copolymer samples with different compositions, and anionically prepared homopolymer samples[1]. In each case, a mixture of 15 mg polymer and 3 ml solvent was subjected to a cloud point test within the temperature range from about 95°C to room temperature, or occasionally to about 10°C. The temperature at which the first sign of cloudiness was recognized by visual inspection was recorded as the precipitation temperature. The disappearance of cloudiness upon rewarming was also checked as the dissolution temperature. The mixture which did not yield a clear solution at 95°C was recorded as 'not soluble', whereas one soluble even at deep freeze temperature (about −15°C) was recorded as 'soluble'.

After choosing 2-ethoxyethanol and cyclohexanol from among the solvents tested, we then determined the θ temperatures according to the phenomenological definition for homopolymer solutions[4,5], i.e. as the temperature at which $A_2=0$. The osmotic pressure measurements were made with a Mechrolab High Speed Membrane Osmometer Model 502 with a variable temperature controller (Mechrolab, Mt View, Calif.). The membranes used were Ultracellafilter grade *feinst* (Membranfilter, Göttingen, Germany).

Other physicochemical measurements

Whenever necessary, we determined the number average molecular weight M_n by osmotic pressure measurements and the weight average molecular weight M_w by light scattering measurements. The details have been given previously[1,3].

Intrinsic viscosity measurement was made by Ubbelohde dilution viscometers. The temperature was controlled within ± 0·02 deg. C at each desired temperature. The efflux times of the viscometers were more than 200 seconds for all solvents. Neither the kinetic energy correction nor the non-Newtonian correction was found to be necessary[1,3].

RESULTS AND DISCUSSION

Solubility test

The results of the solubility test are summarized in *Table 1,* which is helpful in obtaining a general idea of what types of solvent are capable of bringing ST–MMA copolymers to the θ condition. Among the solvents tested, alcohol ethers are non-solvents for PST but θ solvents for PMMA, while 1-chloro-*n*-hydrocarbons are the opposite. Cyclohexanol, which is known as a θ solvent for ST–MMA copolymers[7], has similar solubility for both of the parent homopolymers. Methyl cyclohexanols are more

Table 1. Precipitation temperatures T_η (°) for ST–MMA copolymers in various solvents*

Code	*PMMA*	*Random copolymers*			*Block copolymers*				*PST*
(ST mol. fr.)	*14M*	*SM3–7*	*SM5–6*	*SM7–3*	*20B*	*15B*	*16B*	*11B*	*16H*
$10^{-3} M_n$	(0)	(0·285)	(0·552)	(0·694)	(0·359)	(0·486)	(0·724)	(0·846)	(1·00)
	72·1	354	350	342	157	317	392	193	206
2-Methoxy-ethanol	< 0	29·2	65·0	89·8	(?)	(?)	(90)	N	N
2-Ethoxy-ethanol	19·5	32·0	43·4	58·6	(32)	(70)	N	N	N
2-Butoxy-ethanol	64·0	61·8	60·1	65·2	(71)	(68)	N	N	N
1-Chloro-*n*-hexane	>80	52·2	0	S	(?)	(<0)	S	S	S
1-Chloro-*n*-octane	N	N	60·3	S	N	N	(?)	(?)	S
1-Chloro-*n*-dodecane	N	N	N	95·1	N	N	N	(?)	39·2
Cyclohexanol	73·9	65·1	58·6	60·1	76·5	78·7	80·8	81·3	79·9
2-Methyl-cyclohexanol	27·9	17·4	11·1	18·9	(47)	(34)	53·7	56·5	55·2
3-Methyl-cyclohexanol	70·6	63·5	59·0	63·5	83·4	75·9	90·0	92·9	91·1
4-Methyl-cyclohexanol	66·0	59·3	55·7	62·1	(75)	(74)	76·2	N	N

*Each test was performed with 0·5 g/dl mixture.
Abbreviations: N denotes Not soluble at 95°C; S, Soluble at −15°C; Values in parentheses are ambiguous because of the gradual change in turbidity in a broad temperature range.

or less similar to cyclohexanol: among them, 2-methyl cyclohexanol has somewhat low precipitation temperatures in comparison with all other isomers. These solvents may well be θ solvents for copolymers of other derivatives of styrene and of acrylate and methacrylate, e.g. styrene–methyl acrylate copolymers[11], etc. Besides those listed in *Table 1*, several other solvents were also examined: 2-ethylbutyl aldehyde has $\theta = 22°C$ for PMMA[12] and in this solvent PST precipitates at about $-15°C$; acetoacetic acid esters are similar to alcohol ethers but appear to be slightly better solvents toward PST than alcohol ethers; some ketones such as 2-heptanone and 2-octanone[12] are similar to 1-chloro-*n*-hydrocarbons, which become poorer solvents toward PST and very much poorer toward PMMA with increasing carbon number.

Generally speaking, the block copolymers are less soluble to any solvent than the corresponding random copolymers. In some cases the random copolymers are soluble in solvents in which both homopolymers are insoluble (e.g. in cyclohexanol, methyl cyclohexanols, etc.). Solutions of the random copolymers show fairly sharp precipitation behaviour; cloudiness develops fully within a narrow range of temperature; the precipitation and dissolution temperatures agree with each other within 0·1 to 0·3 deg. C. On the other hand, solutions of the block copolymers show different behaviour depending on the type of solvent. For example, in cyclohexanol the block copolymers show a sharp precipitation behaviour: while in other solvents, the solutions became turbid at rather high temperature; the turbidity gradually increased with decreasing temperature and, finally, the precipitation (the appearance of gel-like aggregates) of the polymer took place. In such cases the temperature for phase separation was somewhat ambiguous, and is therefore given in parentheses in *Table 1*. The block copolymers would form aggregates in solvents which dissolve only one of the parent homopolymers, as previously suggested by Krause[13]. The gradual increase of turbidity in a broad temperature range is particularly evident in such solvents as 1-chloro-*n*-hydrocarbons which are poorer solvents toward PMMA than toward PST. Since the block copolymers are of PMMA–PST–PMMA type, they are apt to form aggregates in such solvents.

θ temperatures from A_2 versus T relations

Determination of θ temperatures by osmometry was made for two solvents, cyclohexanol and 2-ethoxyethanol. *Figure 1* shows typical examples of the osmotic virial expansion plot

$$\pi/c = (RT/M_n)[1 + \Gamma_2 c + \cdots] \tag{1}$$

where π is the osmotic pressure (c.g.s.); c is the polymer concentration in g/ml; R is the gas constant; T is the absolute temperature; and $\Gamma_2 = A_2 M_n$ is the second virial coefficient. On a few occasions, we found that the value of (π/cRT) at $c = 0$ became smaller as the temperature was decreased; this was particularly evident for temperatures near or below θ [cf. *Figure 1*(a)]. The reason for this is not yet clear. This might be an artefact in the measurements, or possibly due to the formation of aggregates or micelles near or below θ. In high temperature operation, say, around 85° to 95°C, we occasionally encountered a difficulty in obtaining reproducible

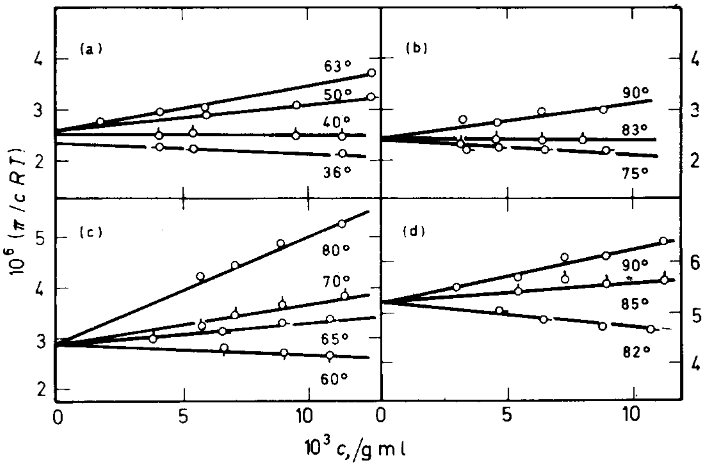


Figure 1—Examples of virial expansion plot π/cRT versus c at various temperatures as indicated. (a) SM3–7 and (b) 15B in 2-ethoxyethanol; (c) SM5–6 and (d) 11B in cyclohexanol. For sample codes, see *Table 1*

data, presumably because of thermal degradation of polymers. Therefore an error of ±1 to 2 deg. C would have been involved in the value of θ, particularly for the block copolymers in cyclohexanol. Neglecting these ambiguities for the time being, we determined A_2 as a function of T, as shown in *Figure 2*, to estimate θ and the temperature derivative of A_2 for each system.

According to the statistical mechanical theories of polymer solutions, A_2 in the vicinity of θ may be written as:

$$A_2 = 4\pi^{3/2} N_A B\,[1 - \mathrm{O}(B)] \tag{2}$$

$$B = B_0(1 - \theta/T) \tag{2a}$$

where B is the excluded volume integral for a segment pair, and B_0 is related to Flory's entropy of mixing parameter ψ_1 as:

$$(\partial A_2/\partial T)_{T=\theta} = 4\pi^{3/2} N_A B_0/\theta = (\bar{v}^2/V_1)\,\psi_1/\theta \tag{3}$$

where N_A is Avogadro's number; $\bar{v}$ is the partial specific volume of solute; and V_1 is the molar volume of solvent employed. These equations are applied to the present osmometric data, although their applicability to copolymer data is still an open question. *Table 2* lists the results. The values of ψ_1 in cyclohexanol are larger for the block copolymers than for the corresponding random copolymers.

Figure 3 shows θ as a function of ST content m (in mole fraction). In 2-ethoxyethanol, the value of θ increases with increasing ST content. The block copolymers always have higher θ temperatures than the corresponding random copolymers. In cyclohexanol the random copolymers have θs lower than those of either PST or PMMA; while the block copolymers

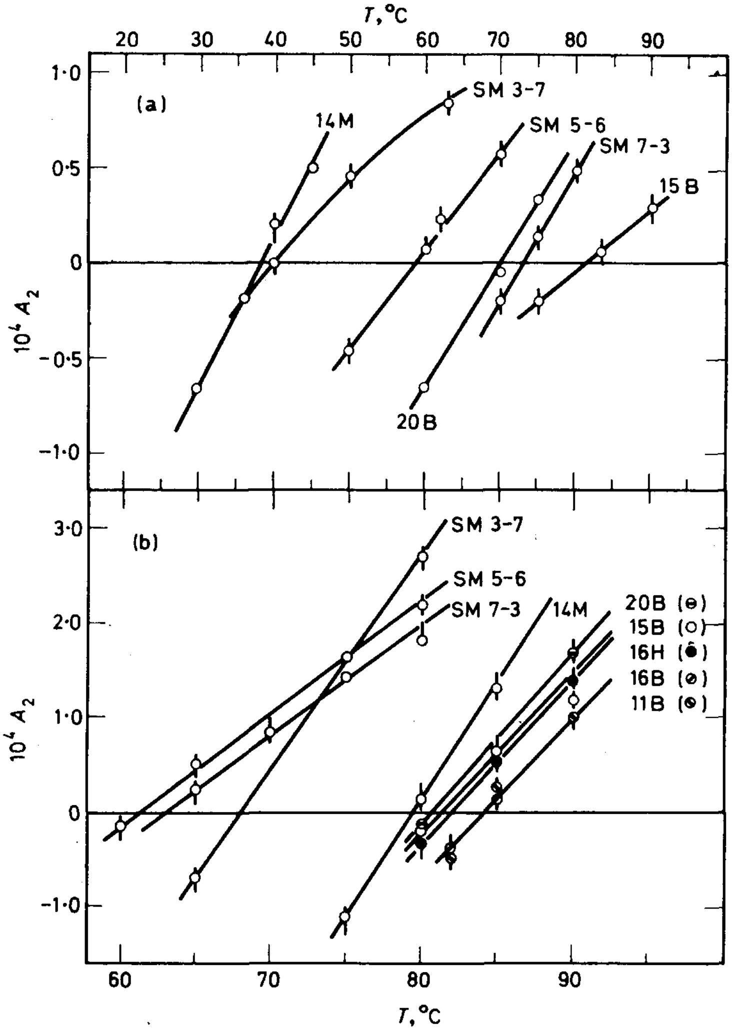


Figure 2—Osmotic second virial coefficient A_2 (c.g.s. units) as a function of temperature (°C) for the ST–MMA copolymers (a) in 2-ethoxyethanol and (b) in cyclohexanol. For sample codes, see *Table 1*

have θs which are roughly between those of PST and PMMA. Even the θ temperatures of the block copolymers 11B and 16B appear to be slightly higher than those of PST and PMMA.

The composition dependence of θ for the cyclohexanol solutions of random and block copolymers[3,7] is rather puzzling. The low values of θ for the random copolymer solutions could be interpreted as a result of incompatible (repulsive) interactions between ST and MMA units[3,7,9]. However, no depression in θ is observed for the block copolymer solutions, as opposed to an expectation that the effect of incompatible interactions between PST and PMMA portions should more or less lower the θ tem-

Table 2. Thermodynamic data for ST–MMA copolymers from A_2 versus T relationships

Code*	*2-Ethoxyethanol* θ (°C);	$10^5 (\partial A_2/\partial T)$	θ (°C);	*Cyclohexanol* $10^5 (\partial A_2/\partial T)$;	ψ_1
PMMA 14M	39·0	(0·80)	79·4	(2·5)	1·39
Random copolymers					
SM3–7	40·0	(0·46)	68·2	(2·3)	1·10
SM5–6	58·4	(0·52)	61·3	(1·3)	0·57
SM7–3	72·8	(0·70)	63·0	(1·3)	0·56
Block copolymers					
20B	69·5	(0·67)	80·5	(1·8)	0·92
15B	81·0	(0·53)	81·3	(1·8)	0·87
16B	Insoluble		84·0	(1·8)	0·84
11B	Insoluble		84·0	(1·8)	0·81
PST 16H	Insoluble		81·8	(1·7)	0·73

*For sample code, see *Table 1.*

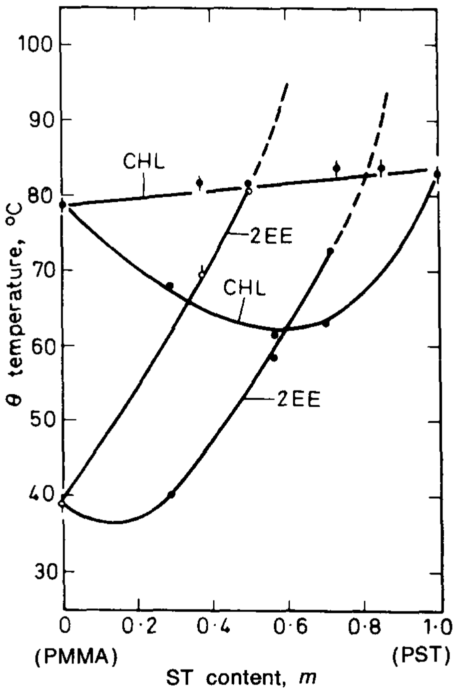


Figure 3—Values of θ (°C) as a function of ST content m (mole fraction) for the ST–MMA random and block copolymers: block copolymers in cyclohexanol (●) and in 2-ethoxyethanol (○); and random copolymers in cyclohexanol (⦶) and in 2-ethoxyethanol (⊖)

peratures of the block copolymers[14]. A preliminary test for the phase equilibrium study of the ternary system, PST–PMMA–solvent[15], showed that compatibility is better in cyclohexanol rather than in other good solvents such as toluene: for an equimolar blend of PST 26H ($10^{-3}M_n = 115$) and PMMA 14M ($10^{-3}M_n = 72{\cdot}1$) in cyclohexanol at 85°C, phase separation did not take place even at a concentration as high as $w = 0{\cdot}20$ (in g-total polymer/g-solution); while for the same mixture in toluene at 30°C, phase separation was observed at a concentration $w = 0{\cdot}11$. The fact that the effect of the incompatible interactions between PST and PMMA is insignificant in cyclohexanol explains the behaviour of the block copolymers but apparently not that of the random copolymers.

To explain these results, it appears to be necessary to reconsider the concept of 'segments' in copolymer chains. With homopolymers, the theoretical results do not depend on the particular way in which a polymer chain is divided into segments; in other words, a segment may be arbitrarily defined. On the contrary, for copolymer chains the definition of 'segments' must be a crucial problem: obviously a monomer unit need not be a segment. Murakami[16] has suggested that a sequence longer than a diad, at least, should be considered as a segment. This means that the interactions between unlike units in random copolymer chains and in block copolymer chains are entirely different in nature.

Somewhat indirect but additional evidence for this problem has been obtained in our preliminary experiments on copolymers of α-methyl styrene (MST) and MMA[15]. The two homopolymers, poly(α-methyl styrene) (PMST) and PMMA, have better compatibility[15,17] than the PST–PMMA pair: in a toluene solution of an equimolar blend of PMST and PMMA with molecular weights comparable to the PST–PMMA system described above, phase separation did not take place at concentrations as high as $w=0{\cdot}20$. Nevertheless, MST–MMA random copolymers have much lower values of θ (for example, in 2-methyl cyclohexanol) than the corresponding block copolymers and also the averages of the parent homopolymers[15]. Apparently the difference in the compatibility of parent homopolymer pairs may not necessarily account for the low value of θ of their random copolymers: the difference in the population of unlike monomer sequences between the random and block copolymer chains could be a more likely reason for the difference in θ. The thermodynamic interactions between an unlike monomer sequence and solvent molecules should be different in nature from the average (or the sum) of monomer–solvent interactions when each monomer is isolated in each homopolymer chain or in each block portion.

Analysis of intrinsic viscosity data

Table 3 gives intrinsic viscosity data for the block copolymers of nearly equimolar composition: two sets of data were taken in 2-ethoxyethanol

Table 3. Intrinsic viscosity data for PMMA–PST–PMMA block copolymers

Code	*Content* *x* (*wt fr.*)	$10^{-3}M_n$	$10^{-3}M_w$	[η] (*dl/g*); *k′* *Toluene* 30·0°*C*	*Cyclohexanol* 81·0°*C*	*2-Ethoxy-ethanol* 81·0°*C*
29B	0·530	19·6	33·9	0·176(0·79)	0·111(1·23)	0·115(0·39)
28B	0·473	66·2	91·9	0·362(0·42)	0·194(1·05)	0·216(0·16)
25B	0·499	135	260	0·624(0·37)	0·284(0·90)	—
26B	0·460	259	308	0·827(0·36)	0·329(0·61)	—
22B	0·452	582	807	1·73 (0·32)	0·578(0·93)	0·935(0·85)
23B	0·614	980	1142	2·43 (0·34)	0·675(0·97)	—
27B	0·414	1240	1474	2·59 (0·36)	0·750(1·36)	—

and in cyclohexanol at or near the θ temperature relevant to each, and another set in toluene at 30°C. The viscosity data are plotted in *Figures 4* and *5* according to a now familiar plot due to Stockmayer and Fixman[18], $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$. For the sake of comparison, our previous data[2,3] for ST–MMA random copolymers and for PST and PMMA are also plotted.

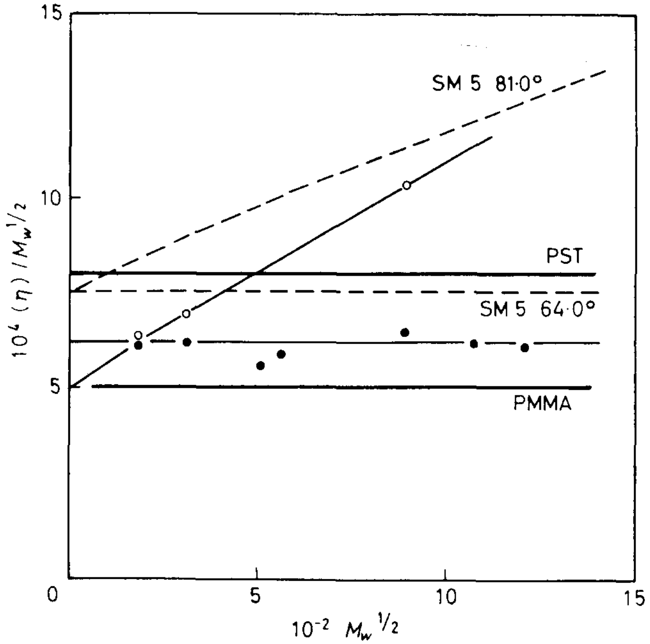


Figure 4—Plots of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ for the nearly equimolar (PMMA–PST–PMMA) block copolymers in cyclohexanol at 81·0°C (●) and in 2-ethoxyethanol at 81·0°C (○). Relevant random copolymer and homopolymer data are also shown: bold dashed curves for random copolymers SM5 in cyclohexanol at 64·0°C (θ) and at 81·0°C[3,16], bold solid curves for polystyrene–cyclohexane at 34·5°C (labelled as PST) and for poly(methyl methacrylate)-l-chloro-*n*-butane at 40·8°C (PMMA)[6]

For ST–MMA random copolymer solutions, we concluded previously[2,3] that they behave just as an ordinary homopolymer does in θ solvents: at the θ temperature where both the intra- and inter-chain excluded volume interactions should vanish simultaneously, A_2 becomes zero and an isolated chain assumes a random flight conformation as judged, for example, from the intrinsic viscosity/molecular weight relation, $[\eta]_\theta = K_0 M_w^{1/2}$. On the other hand, for the block copolymers $[\eta]_\theta$ is not necessarily proportional to $M_w^{1/2}$ even at the temperature at which $A_2 = 0$. This is particularly evident in 2-ethoxyethanol. It should be noted that 2-ethoxyethanol is a non-solvent toward PST and a moderate solvent toward PMMA at 81·0°C where A_2 vanishes and the measurements of $[\eta]$ were made. Therefore, it is likely that the block copolymer might form aggregates. It is also quite likely that even if they are molecularly dispersed, the PST portion of the block copolymer chains collapses and is tightly coiled up in this solvent, and each molecule as a whole is barely dispersed by being protected by the PMMA portions. In such a peculiar case, the block copolymer chains would not assume a random flight conformation even when $A_2=0$. Even in cyclohexanol at 81·0°C, the Stockmayer–Fixman plot appears to have a slightly negative slope. Since the θ temperature of the equimolar block copolymers is lower than that of PST and higher than that of PMMA, the PST portion is less expanded and the PMMA portions are more expanded than the corresponding random flight conformations. Therefore, the slight conformational change of the large central PST portion becomes dominant: this should be responsible for the negative slope. Nevertheless, the deviation must be small, since the three θ temperatures are quite close to one another, and the incompatible interactions between the PST and PMMA portions are not so significant in cyclohexanol.

The unperturbed dimensions of polymer chains may be estimated from $[\eta]_\theta$ by using the Flory–Fox viscosity equation[4,19]:

$$[\eta]_\theta = K_0 M_w^{1/2} = \Phi_0'(\langle s^2\rangle_0 \ /M_w)^{3/2} M_w^{1/2} \tag{4}$$

where $\langle s^2\rangle_0$ is the unperturbed mean square radius of gyration, and $\Phi_0'(=39{\cdot}4\times10^{21})$ is the viscosity constant[19,20]. The equation would be applicable to the block copolymer–cyclohexanol system, because of the reasons mentioned above. By extrapolating $[\eta]_\theta/M_w^{1/2}$ to the limit $M_w^{1/2}\to 0$, we obtain a value of $10^4K_0=6{\cdot}3$, and consequently $10^{18}(\langle s^2\rangle_0/M_w)=6{\cdot}35$ for this system.

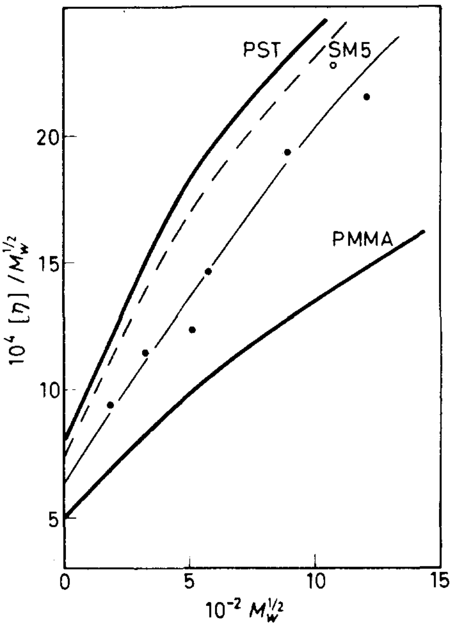
Previously Stockmayer *et al.*[9] proposed a simple additivity for $(\langle s^2\rangle_0/M_w)$ of an A–B binary copolymer as

$$(\langle s^2\rangle_0/M_w) = x_a(\langle s^2\rangle_0/M_w)_A + x_b(\langle s^2\rangle_0/M_w)_B \tag{5}$$

Here $x_a\,(=x)$ and $x_b\,(=1-x)$ are the *weight* fractions of the constituent monomers A and B, respectively; and the subscripts A and B denote the quantities characteristic of the parent homopolymers. For ST–MMA *random* copolymers, we found that the values of K_0 and hence of $(\langle s^2\rangle_0/M_w)$ are larger than those predicted by equation (4), presumably because of the effect of extra short-range interactions between consecutive ST–MMA linkages[3,21]. In contrast to this, the block copolymers have their value of K_0 about 15 per cent smaller and the value of $(\langle s^2\rangle_0/M)$ about 10 per cent smaller than those of the corresponding random copolymers. They are better approximated by the simple additivity [cf. equation (4)]. The effect of the extra short-range interactions must be negligible in the block copolymer chains, since the population of such linkages is negligible.

Figure 5 shows a plot of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ for the block copolymers in toluene at 30°C together with some homopolymer and random copolymer data[3]. Apparently the plot for the block copolymers is smaller than the corresponding random copolymers, and is between those of the parent homopolymers, as opposed to some previously reported results[13,22,23]. Presumably this is due to the fact that the former have smaller unperturbed

Figure 5—Plots of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ for the nearly equimolar block copolymers in toluene at 30·0°C (●); bold dashed curve for random copolymers SM5; bold solid curves for polystyrene (PST) and for poly(methyl methacrylate) (PMMA); all in toluene at 30·0°C[3,16]



dimensions and are subjected to a smaller influence of the excluded volume interactions.

As to the conformation of block copolymers in good solvent, it is often argued that, because of strong incompatible interactions between chemically different blocks, a phenomenon of 'intramolecular phase separation' should take place[13,22-26]. The present data neither substantiate nor deny the above interpretation. In this connection, Froelich suggested[26] that a completely segregated chain model (in which no overlapping of the domains of chemically different blocks is permitted) for a poly(A)–poly(B) type block copolymer would have the mean-square radius of gyration larger by a factor of 15 per cent than that of a corresponding random flight chain. It is hard to judge whether a deviation of this magnitude would or would not result in a significant anomaly in $[\eta]$ data.

Results of a phase equilibrium study in a ternary system (two polymer–one solvent) may be contrasted to the phenomenon of 'intrachain phase separation' (if such exists) in block copolymer chains. It is still an open question how these two phenomena could be quantitatively correlated. However, in a most optimistic view, we may expect that the intrachain phase separation would take place, if the effective segment concentration $c_{\mathrm{eff.}}$ in the domain of an isolated block copolymer chain exceeds the critical miscibility concentration c_m of the corresponding ternary system. It has been known that c_m decreases with the increasing molecular weights of the two polymers involved; while $c_{\mathrm{eff.}}$ should also decrease with increasing molecular weight of the block polymer. Therefore, there must be a delicate balance between whether the intrachain phase separation could take place or not.

Berek *et al.*[27] reported that c_m varies with $\bar{M}^{-2/3}$ where $\bar{M}=(M_A M_B)^{1/2}$ is the geometric mean of the molecular weights of the two polymers involved. For the PST–PMMA–toluene system at 30°C, they gave

$$c_m = 0{\cdot}0051 + 0{\cdot}02291\bar{M}^{-2/3} \text{ (in g/ml)}$$

for example, $c_m=0{\cdot}040$ for a blend[27] with $10^{-3}\bar{M}=573$, $c_m=0{\cdot}10$ for $10^{-3}\bar{M}=103$, and $c_m=0{\cdot}45$ for $10^{-3}\bar{M}=11$. On the other hand, by replacing an isolated polymer chain by a sphere with the radius $\langle s^2\rangle^{1/2}$, one may write

$$c_{\text{eff.}} = (3/4\pi)\,(M/N_A\langle s^2\rangle^{3/2})$$

Here we further replace $\langle s^2\rangle$ by $\langle s^2\rangle_0$ and employ the value

$$10^{18}\,\langle s^2\rangle_0/M_w = 6{\cdot}35$$

and thus obtain $c_{\text{eff.}}=2{\cdot}48\,\bar{M}_w^{-1/2}$ (in g/ml): this should be a possible maximum estimate and a real $c_{\text{eff.}}$ value must be much smaller than this, since polymer chains in a good solvent are usually more expanded. For block copolymers of a symmetrical three-block type with molecular weight M_n and composition x, the geometric mean $\bar{M}$ may be written as

$$\bar{M} = [x(1-x)/2]^{1/2}M_n$$

Thus we obtain $c_{\text{eff.}}=0{\cdot}248$ for a sample with $M_w=10^4$ which roughly corresponds to $10^{-3}\bar{M}=3{\cdot}5$, and $c_{\text{eff.}}=0{\cdot}025$ for $M_w=10^6$, i.e. $10^{-3}\bar{M}=350$ (we arbitrarily assumed $M_w=M_n$ and $x=0{\cdot}5$). Obviously at any level of M_w (or of $\bar{M}$), even the possible maximum estimate of $c_{\text{eff.}}$ is still too far below c_m. In view of these estimates, we suspect that the phenomenon of the so-called 'intrachain phase separation' could not take place at all, unless the parent homopolymer pair in the given solvent has extremely poor compatibility.

A quantitative examination will be given in a following article on the excluded volume interactions in ST–MMA block copolymer chains in several good solvents, especially placing emphasis on the correlation between their behaviour and the incompatibility of the homopolymer pair in these solvents.

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