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

I—Preparation and Characterization

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An anionic polymerization procedure for preparing styrene and methyl methacrylate block copolymers is described. The products were characterized by combustion analysis, osmometry, light scattering measurement, and gel permeation chromatography. The analyses showed that the block copolymers consisted of linear three-block chains except for a few cases. The correlation between the heterogeneities of molecular weights and of composition as described by light scattering apparent molecular weights in different solvents is discussed. The heterogeneities can be described by two parameters for the polydispersities of precursor polystyrene and poly(methyl methacrylate) sub-chains and by the average composition of the block copolymer. Preliminary data on the light scattering conformational analyses are given. The results suggest that the block copolymer chains would assume the conformations similar to any flexible linear homopolymers at least in the solvents, toluene and butanone, examined in this study.

FOR preparation of block copolymers of styrene (ST) and methyl methacrylate (MMA), a number of methods have been reported and collected in several monographs[1–3]. Among them the anionic polymerization technique[4] appeared to be advantageous in obtaining good samples in large quantities. In fact, in most of the studies[5,6] reported so far on the solution properties of ST–MMA block copolymers, anionically prepared materials were used. However, some doubt still remained about the quality of samples used in such studies.

The polymerization procedure usually involves the following steps: first an anionic initiator is allowed to react with ST monomer, yielding 'living' polystyrene (PST); then MMA monomer is introduced, and 'living' PST initiates the polymerization of MMA to yield block copolymers[4]. To achieve a successful preparation, the reaction system must be free from any 'killing' impurities; initiation and propagation must be carefully controlled so that chains start growing at the same time and continue growing at the same rate; any hazardous side reaction must also be avoided. For the first purpose a high-vacuum procedure[7] was employed. To achieve an 'in-phase' growing of all the chains is difficult in practice in a rapid reaction such as polymerization of ST with sodium–naphthalene in tetrahydrofuran (THF). To avoid this difficulty Wenger[8,9] recommended use of a two-stage polymerization technique and of sodium biphenyl as an initiator; we followed the latter procedure. Freyss, Rempp and Benoit[10] pointed out a possibility of grafting 'living' PST on poly(methyl methacrylate) (PMMA) blocks; they suggested that the reaction may be suppressed by adding enough 1,1-

diphenyl ethylene (DPE) to replace polystyryl carbanions by the less reactive diphenyl methyl carbanions before adding MMA monomer. This procedure was also employed in this study.

Since sodium biphenyl is a bifunctional initiator[4], one obtains 'living' PST with two active ends, and consequently block copolymers of linear PMMA–PST–PMMA type. The products were characterized by several methods based on dilute solution studies, such as osmometry, light scattering and so on. The results will be described below. Some preliminary data on the conformational analysis by the light scattering method will also be given.

PREPARATION OF BLOCK COPOLYMERS

Materials

The solvent THF was purified according to a procedure[6,7] now routinely employed for anionic polymerization. About 1 l. each of THF had been kept until required in a storage vessel with a trace amount of sodium–biphenyl.

The monomers, ST and MMA, were also purified according to standard procedures[6]. Just prior to use, the ST monomer was purified by transferring it into a vessel containing sodium–benzophenone complex[8,11] while the MMA monomer was purified with sodium–benzyl complex[12]. From each mixture, the monomer was divided into calibrated ampoules and diluted with prepurified THF. The sodium–benzyl–MMA mixture was less stable, hence rapid operation was necessary. It is advisable also to prevent warming during the operation.

An intermediate, 1,1-diphenyl ethylene (DPE), was dried over calcium hydride (CaH_2) and distilled under a reduced pressure nitrogen atmosphere. A few drops of the freshly distilled DPE were introduced into a small ampoule.

Preparation of initiator solutions

The reactor and procedure for preparing the initiator, sodium–biphenyl–THF solution, were essentially similar to those described by Morton *et al.*[7], except that biphenyl was used here instead of naphthalene. Biphenyl was recrystallized twice from dry ether solution, dried and stored in a vacuum desiccator over phosphorus pentoxide (P_4O_{10}). The concentration of initiator solution was determined by acidimetry[7].

Synthesis of block copolymers

The apparatus used is indicated in *Figure 1*. The reactor (A) was a 1 l. round-bottomed flask. Ampoules containing THF solutions of ST (S_1, S_2), MMA (M), initiator (I), DPE (D), and a terminator, methanol (T_1, T_2), were connected to the reactor, which in turn was connected to the vacuum line and to a THF storage vessel. The whole apparatus was evacuated to 10^{-6} mm of mercury while repeatedly flamed with a hand torch, and was sealed off at the constriction (a) from the vacuum line. From the storage vessel *ca.* 800 ml of THF was distilled into the reactor (A). After the THF vessel had been removed by sealing off at the constriction (b), the initiator (I) was introduced into the reactor (A). For final elimination of any possible remaining impurities on the glass surface, every part of the

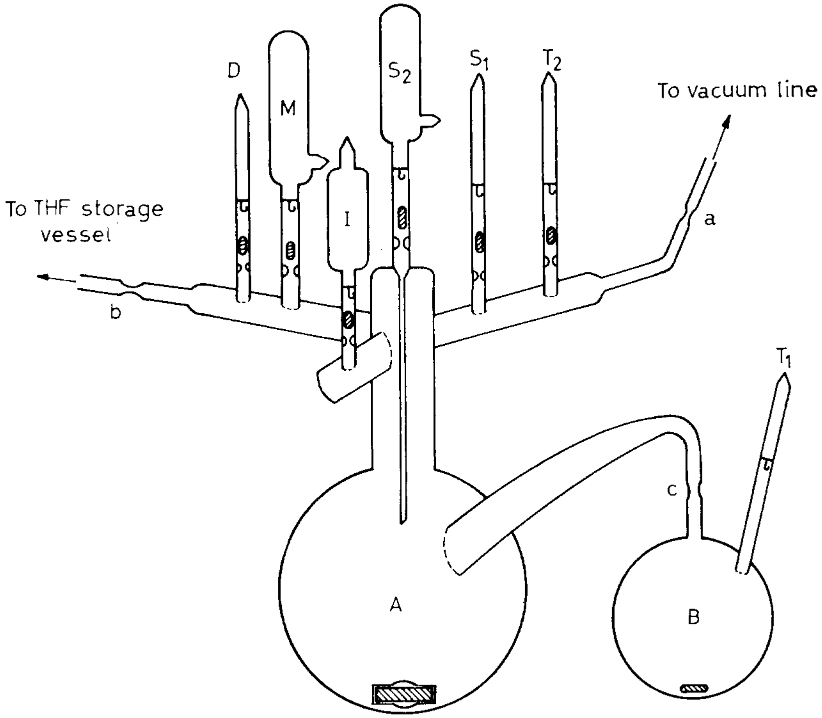

Figure 1—Sketch of apparatus for preparing block copolymers

wall was rinsed by condensing THF and then transferring the condensate back into the reactor (A).

After impurities had been thus eliminated, the small amount of ST (S_1) (usually about 0·5 ml ST in 20 ml THF) was introduced; the colour immediately changed from dark-blue to the red-orange characteristic of styryl carbanions. The system was kept under continuous stirring for about 15 min at 0°C and again cooled to −78°C; then the rest of the ST (usually about 20 ml ST in 100 ml THF) was added from the ampoule (S_2). The temperature was then raised to 0°C, and half of the 'living' PST solution was transferred into vessel (B). After the vessel (B) had been sealed off at the constriction (c), the contents of (B) were terminated with methanol–THF solution (T_1) and recovered as homo-PST (designated as series H). The rest was used as a precursor for further reaction with MMA monomer. Thus PST-H should be identical to the PST part of the product block copolymer. This fact was utilized for later analysis.

Before adding MMA monomer to the reactor (A), DPE (D) was added. An immediate colour change from orange-red to violet-red indicated that styryl carbanions were replaced by diphenyl methyl carbanions[10]. After about 30 min the reactor (A) was cooled to −78°C, and MMA solution (M) was introduced. The violet-red colour disappeared. The reaction mixture was stirred at −78°C for 30 min and then at room temperature for a further

30 min. The reaction was terminated with methanol (T_2). The product was recovered by precipitating it in a 1: 1 (by volume) water–methanol mixture plus a few drops of hydrochloric acid (HCl).

Crude block copolymers were treated by twofold precipitation from benzene solution into methanol, followed by vacuum drying at 60°C. They were then subjected to boiling point extraction with cyclohexane and acetonitrile, as suggested by Urwin and Stearne[6], to remove respectively free PST and PMMA. Finally the block copolymers were recovered by freeze drying from benzene solutions. In successful preparations no homopolymers were extracted. Some of the block copolymers were examined by a turbidimetric titration method[13]. We confirmed that the reaction proceeded quantitatively and the block copolymers contained negligible amounts of homopolymers. The average composition was determined from carbon content by a combustion analysis.

MEASUREMENTS

Osmotic pressure

Measurements were made by a Mechrolab model 502 High Speed Membran Osmometer with a variable temperature controller. Membranes used were Ultracellafilter grade *feinst* or *allerfeinst* (Membranfilter, Göttingen, Germany). For solutions of low molecular weight solutes, slight diffusion of solute through the membrane was observed. For such solutions we used Bac-T-Flex membrane filter B20 (Carl Schleicher & Schull Co.). According to Feist[14] this membrane could be successfully used for polymers with a molecular weight range of 75 000 to as low as 1 200. The solvent readings were always determined before and after measurement on each solution, and the absence of diffusion of solute was confirmed. The membranes were conditioned through 1-propanol to toluene before use.

The determination of number average molecular weight M_n was made according to the equation[15]

$$(\pi/cRT)^{1/2}=(1/M_n)^{1/2}\,[1+(A_2M_n/2)\,c] \qquad (1)$$

where π is the osmotic pressure; c is the polymer concentration, A_2 is the osmotic second virial coefficient; and R and T are the gas constant and the absolute temperature, respectively. The results for M_n are summerized in *Table 1.*

Refractive index increment and light scattering

Specific refractive index increment was measured with 436-nm wavelength light using a Shimadzu (Debye type) differential refractometer equipped with a thermostatically controlled cell.

The specific refractive index increment ν of a binary copolymer may be approximated as a linear function of (average) composition taken as independent of molecular weight[16, 17, 5]

$$\nu = x\nu_A + (1-x)\,\nu_B \qquad (2)$$

where x is the average weight fraction of constituent monomer A; and the subscripts A and B denote the quantities characteristic of parent homopolymers, poly(A) and poly(B) (here PST and PMMA, respectively). The

Table 1. Number average molecular weights of the ST–MMA block copolymers and the corresponding PST–H

Precursor PST–H		*Block copolymers*			
Code	$10^{-3}M_n^A$	*Code*	x	$10^{-3}M_n$	$10^{-3}\overline{M}_n^A$
				Without using DPE	
10H	105	10B	0·482	530	250
15H	145	15B	0·496	317	157
19H	108	19B	0·431	509	219
				With using DPE	
22H	268	22B	0·452	582	263
23H	620	23B	0·614	980	602
25H	67·2	25B	0·491	135	66·3
26H	115	26B	0·460	259	119
27H	548	27B	0·414	1240	514
28H	31·9	28B	0·473	66·2	31·3
29H	9·85	29B	0·530	19·6	10·4

approximation was found satisfactory for the block copolymers as well as for random copolymers[18]. The results are listed in *Table 2*.

Light scattering measurements were carried out with a Shimadzu (modified Brice type) light scattering photometer equipped with a constant temperature jacket[19]. A cylindrical cell with a ground glass back was used. Scattered intensities were measured at eleven different angles from 30° to 150° with vertically polarized light of 436 nm wavelength. The constant of the apparatus was evaluated with pure benzene as a reference liquid, by taking $U_u=46·4\times10^{-6}$ for the Rayleigh ratios R_{90} and $\rho_u=0·42$ for the corresponding depolarization[20, 21] at 25°C. Some block copolymers were

Table 2. Summary of light scattering $M_{\text{app.}}$ data

Code	*Solvent**	ν (436 nm)†	$10^{-3}M_{\text{app.}}$
22B	MEK	0·167	764
	DCE	0·103	769
	TOL	0·053	826
23B	MEK	0·187	1 100
25B	MEK	0·173	250
	DCE	0·110	256
	TOL	0·059	282
26B	MEK	0·168	306
	DCE	0·104	304
	TOL	0·054	328
27B	MEK	0·162	1 450
	TOL	0·049	1 410
28B	MEK	0·169	93·9

*For abbreviations, see text.
†For PST, $\nu_A=0·232$ in MEK, 0·168 in DCE and 0·113 in TOL. For PMMA, $\nu_B=0·113$ in MEK, 0·050 in DCE and 0·004 in TOL.

measured in three solvents, butanone (MEK), 1,2-dichlorethane (DCE), and toluene (TOL), at 30·0° ± 0·1°C, and some others only in MEK. Solutions and solvents were clarified by filtration through two round pieces of *mittel* grade Cellafilter. For high molecular weight samples, each stock solution was centrifuged with a Hitachi preparative ultracentrifuge model 55P at a rotor speed between 16 000 and 20 000 rev/min for about two hours at 30°C, and successively diluted by adding solvent through Cellafilter membranes directly into the light scattering cell.

Reduced scattering intensity $R(\theta, c)$ for a solution of concentration c at a scattering angle θ were calculated by using modified values of reflection corrections suggested by Kratohvil[22]. The light scattering data were treated by Zimm's procedure[23]. A typical Zimm plot is shown in *Figure 2*.

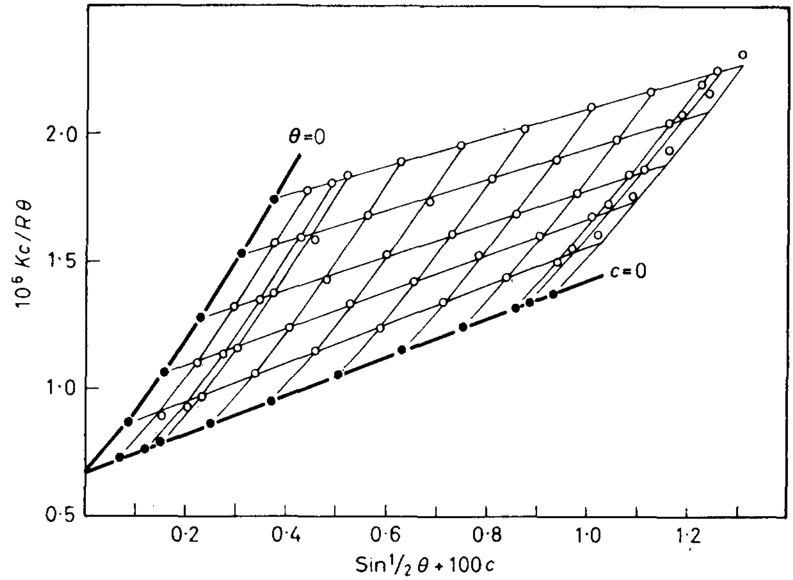

Figure 2—A typical example of Zimm plot for ST–MMA block copolymer 27B in toluene 30·0°C

As is well known, $R(\theta, c)$ can be expressed as:

$$\lim_{\theta\to 0} Kc/R(\theta, c) = 1/M_{\mathrm{app.}} + 2(A_2')_{\mathrm{app.}}\, c + \cdots \qquad (3)$$

$$\lim_{c\to 0} Kc/R(\theta, c) = (1/M_{\mathrm{app.}})\,[1 + (4/3)\,(2\pi n_0/\lambda_0)^2 \langle S^2\rangle_{\mathrm{app.}} \sin^2(\tfrac{1}{2}\theta) + \cdots] \qquad (4)$$

where $K = (4\pi^2/\lambda_0^4 N_A)(n_0\nu)^2$ is the optical constant for a vertically polarized incident beam, n_0 denotes the solvent refractive index, N_A is Avogadro's number, and λ_0 is the wavelength of light *in vacuo*. The quantities $M_{\mathrm{app.}}$, $(A_2')_{\mathrm{app.}}$ and $\langle S^2\rangle_{\mathrm{app.}}$ may be determined by extrapolating a Zimm plot. However, the extrapolations are not always simple, and use of the square root plot, $[Kc/R(\theta, c)]^{1/2}$ versus c and $\sin^2(\frac{1}{2}\theta)$, was suggested to secure more accurate estimates[24]. Thus we employed the square root plot in this study. The quantities, $M_{\mathrm{app.}}$, $(A'_2)_{\mathrm{app.}}$, and $\langle S^2\rangle_{\mathrm{app.}}$ for copolymers are apparent values, and must be distinguished from those of homopolymers[16, 17, 5].

Using the approximation of the linear dependence of ν on x, Stockmayer *et al.*[16] and Benoit *et al.*[17] have shown that $M_{\mathrm{app.}}$ can be expressed as:

$$M_{\mathrm{app.}} = M_w + 2bP + b^2Q \tag{5}$$

where

$$M_w = \Sigma\gamma_i M_i \tag{6}$$

$$P = \Sigma\gamma_i M_i\,(x_i - x) \tag{7}$$

$$Q = \Sigma\gamma_i M_i\,(x_i - x)^2 \tag{8}$$

$$b = (\nu_A - \nu_B)/\nu \tag{9}$$

Here γ_i is the weight fraction of component i, whose molecular weight is M_i and composition is x_i; the parameters P and Q represent the heterogeneity in composition; P relates to the composition variation with molecular weight, and Q to its broadness. Accordingly, equation (5) allows one to estimate not only M_w but also P and Q from light scattering data obtained in at least three solvents with different ν values. *Table 2* lists values of light scattering apparent molecular weights $M_{\mathrm{app.}}$. $(A'_2)_{\mathrm{app.}}$ and $\langle S^2\rangle_{\mathrm{app.}}$ will be discussed in a later section.

Other physicochemical measurements

Gel permeation chromatography (GPC)[25–27] was carried out by a Shimadzu GPC Model 1A[27] using a set of three columns in series packed with polystyrene gels with permeability limits 5×10^3, 4×10^4, 8×10^4Å. All runs were done with THF as the carrier solvent operating at room temperature. A flowrate of 1·0 ml/min was maintained, and in each run 0·5 ml of 0·3 per cent polymer solution was injected within 30 seconds. The column system was calibrated with nine nearly monodisperse polystyrenes, ranging in molecular weight from 2×10^3 to 6×10^6.

For some PST samples the molecular weight distribution was determined by sedimentation velocity experiments at 35·0°C in cyclohexane. A Beckman–Spinco Model E ultracentrifuge was employed. The procedure has been described elsewhere[28].

Intrinsic viscosities were determined with Ubbelohde dilution viscometers. The temperature was kept within ±0·02 deg. C at each desired value. Neither the kinetic energy correction nor the non-Newtonian correction was found to be necessary.

CHARACTERIZATION OF BLOCK COPOLYMERS

Average composition and number average molecular weight. Evidence for no branchings

Leng and Benoit[29] have shown that M_n and x may be correlated by definition as:

$$M_n = \overline{M}_n^{\mathrm{A}} + \overline{M}_n^{\mathrm{B}}; \qquad x = \overline{M}_n^{\mathrm{A}}/M_n \tag{10, 11}$$

where $\overline{M}_n^{\mathrm{A}}$ and $\overline{M}_n^{\mathrm{B}}$ are the number average molecular weights of the constituent poly(A) and poly(B) parts, respectively. Obviously $\overline{M}_n^{\mathrm{A}}$ must be equal to M_n^{A} of the precursor PST-H, if the block copolymer has no branchings.

The last column of *Table 1* shows values of $\overline{M}_n^{\mathrm{A}}$ calculated by equation (11). For some block copolymers prepared without adding DPE, $\overline{M}^{\mathrm{A}}$ is found to be twice or more larger than M_n^{A} of the precursor PST-H. This fact suggests the presence of at least one PST branch on each molecule. In one preparation (15B) without using DPE, $\overline{M}_n^{\mathrm{A}}$ is nearly equal to the M_n^{A} of PST-15H, indicating no grafting reaction. This was a rather fortuitous event. However, in all the preparations using DPE as intermediate, the agreement between $\overline{M}_n^{\mathrm{A}}$ and M_n^{A} was always satisfactory. The copolymers should consist of linear chains.

Weight average molecular weights and composition heterogeneity parameters. Test of heterogeneities

In an anionic polymerization of ST–MMA block copolymers, a more or less polydisperse 'living' PST initiates the polymerization of MMA, yielding a more or less heterogeneous product. Consequently, a heterogeneity in molecular weight inevitably leads to a heterogeneity in composition. Especially in a preparation with a bifunctional initiator, one of the two active ends could have been deactivated, and thus the product could be a mixture of 2- and 3-block type chains. Such an unsatisfactory example is revealed in GPC patterns of PST 25H and the corresponding block copolymer 25B, as demonstrated in *Figure 3*. The pattern for PST 25H shows the presence of at least two components with high and low molecular weights, and that for 25B also shows the presence of more than two components which are presumably 2- and 3-block chains. Other samples show a single peak, like the typical example shown in *Figure 3*, which implies that the preparation was satisfactory (or at least this is a necessary condition).

A correlation among average molecular weights, average composition, and their heterogeneities, may be quantitatively expressed in terms of M_w, P and Q determined from $M_{\mathrm{app.}}$ values[29,30]. For binary copolymers Leng and Benoit[29,30] gave the following equations:

$$M_w = x\overline{M}_w^{\mathrm{A}} + (1-x)\,\overline{M}_w^{\mathrm{B}} + 2\overline{M}_w^{\mathrm{AB}} \tag{12}$$

$$P = x\,(1-x)\,(\overline{M}_w^{\mathrm{A}} - \overline{M}_w^{\mathrm{B}}) + (1-2x)\,\overline{\mathrm{M}}_w^{\mathrm{AB}} \tag{13}$$

$$Q = x\,(1-x)\,[(1-x)\,\overline{M}_w^{\mathrm{A}} + x\overline{M}_w^{\mathrm{B}} - 2\overline{M}_w^{\mathrm{AB}}] \tag{14}$$

where $\overline{M}_w^{\mathrm{A}}$ and $\overline{M}_w^{\mathrm{B}}$ are the weight average molecular weights of the constituent A and B parts, respectively, and $\overline{M}_w^{\mathrm{AB}}$ is a cross (heterogeneity) coefficient[29] defined as

$$\overline{M}_w^{\mathrm{AB}} = \Sigma \gamma_i x_i\,(1-x_i)\,M_i \tag{15}$$

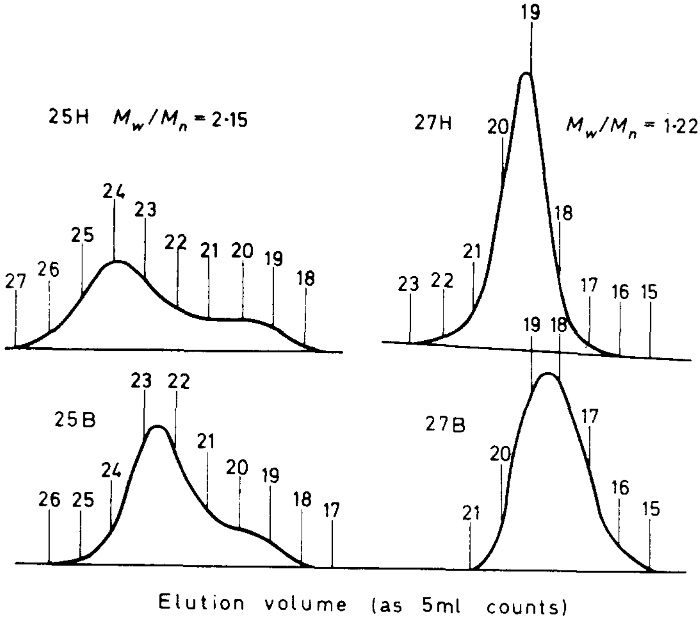

Figure 3—Typical examples of GPC patterns for 25B and 27B, and their precursor PST 25H and 27H

For block copolymer samples obtained by random coupling of poly(A) and poly(B) chains to form a mixture of poly(A)–poly(B) and poly(B)–poly(A)–poly(B) type block copolymers with the average composition x, it is easily shown that[29]:

$$\overline{M}_n^{\mathrm{B}} = (1+n)\, M_n^{\mathrm{B}} \tag{16}$$

$$\overline{M}_w^{\mathrm{B}} = M_w^{\mathrm{B}} + \{2n/(1+n)\}\, M_n^{\mathrm{B}} \tag{17}$$

$$\overline{M}_w^{\mathrm{AB}} = \overline{M}_n^{\mathrm{A}} \overline{M}_n^{\mathrm{B}} / M_n = x\,(1-x)\, M_n \tag{18}$$

where M_w^{B} and M_n^{B} are the weight and number average molecular weights of precursor poly(B) chains; and M_w^{A} and M_n^{A} are those of precursor poly(A) chains, which must be identical to $\overline{M}_w^{\mathrm{A}}$ and $\overline{M}_n^{\mathrm{A}}$, respectively; and n is the mole fraction of 3-block chains. Then Benoit's equations (12) to (14) may be rewritten as:

$$M_w/M_n \equiv 1 + Y = 1 + x^2 \overline{Y}^{\mathrm{A}} + (1-x)^2\, \overline{Y}^{\mathrm{B}} \tag{19}$$

$$P = x\,(1-x)\,[x\overline{Y}^{\mathrm{A}} - (1-x)\,\overline{Y}^{\mathrm{B}}]\, M_n \tag{20}$$

$$Q = x^2\,(1-x)^2\,(\overline{Y}^{\mathrm{A}} + \overline{Y}^{\mathrm{B}})\, M_n \tag{21}$$

with $\overline{M}_w^{\mathrm{A}}/\overline{M}_n^{\mathrm{A}} = 1 + \overline{Y}^{\mathrm{A}}$, and $\overline{M}_w^{\mathrm{B}}/\overline{M}_n^{\mathrm{B}} = 1 + \overline{Y}^{\mathrm{B}}$. One can predict values of

M_w, P and Q, and hence of $M_{\mathrm{app.}}$ in a given solvent, if values of x, M_n, $\bar{Y}^{\mathrm{A}}$ and $\bar{Y}^{\mathrm{B}}$ are known.

The quantities x and M_n are directly measurable. Also $\bar{Y}^{\mathrm{A}}$ may be determined directly from precursor PST-H. For determining M_w^{A}, we employed the light scattering method, and a somewhat indirect $[\eta]$ method with appropriate $[\eta]$ versus M_w equations for PST such as:

$$[\eta]=8{\cdot}46\times10^{-4}M_w^{1/2} \text{ in cyclohexane at } 34{\cdot}5\,^{\circ}\mathrm{C}^{30}$$

$$[\eta]=1{\cdot}20\times10^{-3}M_w^{0{\cdot}71} \text{ in toluene at } 30{\cdot}0\,^{\circ}\mathrm{C}^{31}$$

Values of $\bar{Y}^{\mathrm{A}}$ may also be determined directly by the GPC method and by the sedimentation transport method. The values determined by these methods are in reasonable agreement[28]. The results are listed in *Table 3*.

Table 3. Weight average molecular weights and heterogeneity parameters

Precursor PST–H			*Block copolymers B*					
Code	$10^{-3}M_w^{\mathrm{A}}$	$1+\bar{Y}^{\mathrm{A}}$	*Code*	$(1+\bar{Y}^{\mathrm{B}})$*	$10^{-3}M_w$	P/M_w	Q/M_w	M_w/M_n
22H	380	1·42	22B	(2·00)	807	−0·064	0·062	1·39
23H	746	1·24	23B	(1·50)	1 142	−0·009	0·036	1·16
25H	139·5	2·15	25B	(3·50)	260	−0·092	0·118	1·92
26H	144	1·24	26B	(1·50)	308	−0·031	0·037	1·19
27H	671	1·22	27B	(1·50)	1 474	−0·034	0·033	1·19
28H	52·0	1·64	28B	(2·00)	91·9	−0·040	0·071	1·42
29H†	17·8	1·83	29B‡	(3·00)	31·6	−0·054	0·098	1·61

*Values used for computing M_w, P and Q.
†M_w determined by $[\eta]$ method only.
‡Computed values only.

On the other hand there is no direct method for determining $\bar{Y}^{\mathrm{B}}$. However, it may be deduced from the polydispersity of model PMMA prepared by an anionic polymerization method from which ST monomer was omitted but which was otherwise exactly the same as the block polymerization procedure. In two trial experiments, we obtained for one sample (coded as 14M) the result that $10^{-3}M_n=72{\cdot}1$ and $10^{-3}M_w=156$ and for the other (coded as 38M) that $10^{-3}M_n=343$ and $10^{-3}M_w=581$. Hence $\bar{Y}^{\mathrm{B}}=0{\cdot}5\sim1{\cdot}00$ should be reasonable estimates. By equations (19) to (21) with directly measured values of x, M_n and $\bar{Y}^{\mathrm{A}}$ for each sample, we calculated M_w, P and Q taking $\bar{Y}^{\mathrm{B}}$ as a parameter. Then with these values, we calculated $M_{\mathrm{app.}}$ as a function of $b=(\nu_{\mathrm{A}}-\nu_{\mathrm{B}}/\nu)$ by equation (5). The results are compared with the observed values of $M_{\mathrm{app.}}$: *Figure 4* demonstrates three typical examples for nearly equimolar samples with different values of $\bar{Y}^{\mathrm{A}}$.

As is well known, the value of $M_{\mathrm{app.}}$ takes the minimum $(=M_w-P^2/Q)$ at $b=-P/Q$, which is found between $b=1$ (roughly corresponds to DCE data) and $b=2{\cdot}00$ (TOL data) for the present samples. Therefore, in these three solvents $M_{\mathrm{app.}}$ is insensitive to b. Hence unambiguous estimates of M_w, P

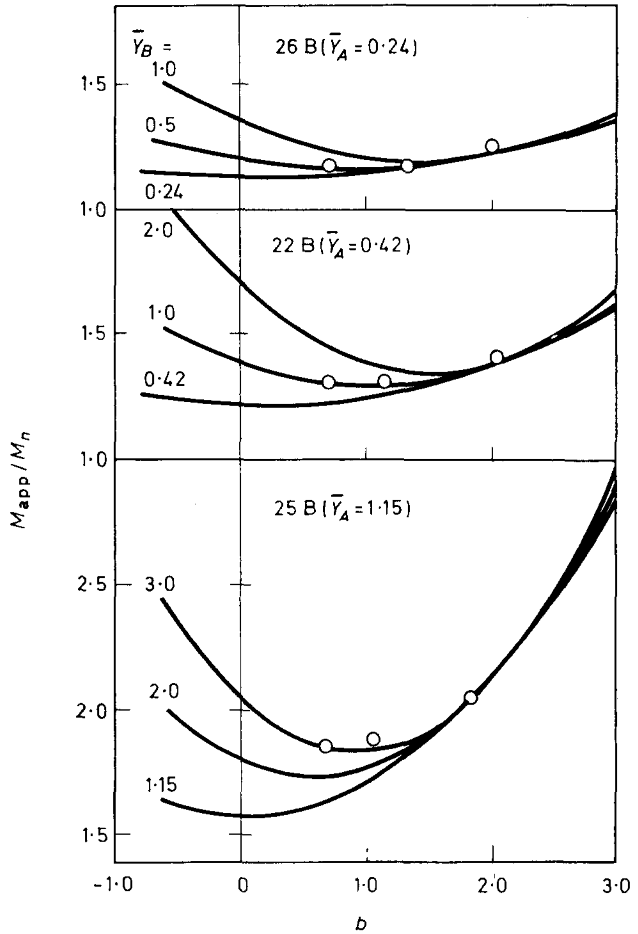

Figure 4—Light scattering apparent molecular weight $M_{app.}$ in a few solvents. In each figure solvents are butanone, dichlorethylene and toluene, respectively from left to right. Curves show calculated values of $M_{app.}/M_n$ versus b taking $\bar{Y}^B$ as a parameter as indicated

and Q from light scattering data alone are rather difficult. For such cases use of equations (19) to (21) would be helpful. It is interesting to note that $M_{app.}$ in these solvents could often be smaller than the true M_w, as opposed to an intuitive expectation. This is particularly true for materials with small $\bar{Y}^A$ values but rather large $\bar{Y}^B$ values.

From *Figure 4* it is seen that observed $M_{app.}$ versus b data are in reasonable agreement for samples 22B and 26B with calculated curves with $\bar{Y}^B = 0{\cdot}5 \sim 1{\cdot}0$, which were expected from the polydispersity of model PMMA. However, for sample 25B a choice of large $\bar{Y}^B$ (say, $2{\cdot}0 \sim 3{\cdot}0$) is necessary for attaining the agreement. The GPC analysis shows that the sample 25B is a mixture of 2- and 3-block chains; hence $\bar{Y}^B$ must be much larger than a sample consisting of purely 3-block chains should possess. *Table 3* lists the values of M_w, P and Q estimated by equations (19) to (21) with appropriate choice of $\overline{Y}^{B}$. In view of these results, we may say that the materials obtained are moderately homogeneous in both molecular weight and composition except for the two samples 25B and 29B.

Analysis of light scattering data

For $(A'_2)_{\mathrm{app.}}$, an extension of the fluctuation theory by Kirkwood and Goldberg[32] and by Stockmayer[33] readily leads to equations[34]:

$$(M_{\mathrm{app.}})^2 (A'_2)_{\mathrm{app.}} = (M_w)^2 A'_2 + 2bP_2 + b^2 Q_2 \tag{22}$$

$$(M_w)^2 A'_2 = \Sigma\Sigma\, \gamma_i \gamma_j M_i M_j B_{ij}/2 \tag{23}$$

$$P_2 = \Sigma\Sigma\, \gamma_i \gamma_j M_i M_j B_{ij}\, (x_i - x)/2 \tag{24}$$

$$Q_2 = \Sigma\Sigma\, \gamma_i \gamma_j M_i M_j B_{ij}\, (x_i - x)\,(x_j - x)/2 \tag{25}$$

$$B_{ij} = (1/RT)\,[\partial\mu_i/\partial c_j]_{T,P,c} \tag{26}$$

Here B_{ij} is the interaction parameter between components i and j; μ_i is the chemical potential per one gramme of component i; and $(M_w)^2 A'_2$ should have the same meaning as for a homopolymer system.

The apparent mean square radius $\langle S^2\rangle_{\mathrm{app.}}$ for a (heterogeneous) binary copolymer may be given as [35, 36, 29, 5]:

$$M_{\mathrm{app.}} \langle S^2\rangle_{\mathrm{app.}} = M_w \langle S^2\rangle^{\mathrm{LS}}_{Z} + 2bP_s + b^2 Q_s \tag{27}$$

$$M_w \langle S^2\rangle^{\mathrm{LS}}_{Z} = \Sigma\, \gamma_i M_i \langle S^2\rangle^{\mathrm{LS}}_{i} \tag{28}$$

$$P_s = \Sigma\, \gamma_i M_i \langle S^2\rangle^{\mathrm{LS}}_{i} (x_i - x) \tag{29}$$

$$Q_s = \Sigma\, \gamma_i M_i \langle S^2\rangle^{\mathrm{LS}}_{i} (x_i - x)^2 \tag{30}$$

The quantity $\langle S^2\rangle^{\mathrm{LS}}_{i}$ is not a mean square statistical radius but an apparent optical radius[35], and hence $\langle S^2\rangle^{\mathrm{LS}}_{Z}$ is not the Z-average mean square radius, as opposed to a homopolymer system. The optical radius $\langle S^2\rangle^{\mathrm{LS}}$ of a homogeneous copolymer fraction (for brevity, the subscript i is omitted) can be expressed as[29, 35, 36]:

$$\langle S^2\rangle^{\mathrm{LS}} = \alpha \langle S^2_{\mathrm{A}}\rangle + \beta \langle S^2_{\mathrm{B}}\rangle + \alpha\beta \langle l^2_{\mathrm{AB}}\rangle \tag{31}$$

$$\alpha = x\nu_{\mathrm{A}}/\nu;\quad \beta = (1-x)\,\nu_{\mathrm{B}}/\nu \tag{32, 33}$$

where $\langle S^2_{\mathrm{A}}\rangle$ and $\langle S^2_{\mathrm{B}}\rangle$ are the mean square statistical radii of constituent parts A and B, respectively; $\langle l^2_{\mathrm{AB}}\rangle$ is the mean square distance between the centres of gravity of the A and B parts. Apparently the optical radius $\langle S^2\rangle^{\mathrm{LS}}$ differs from the true mean square statistical radius $\langle S^2\rangle$ defined as

$$\langle S^2\rangle = x\,\langle S^2_{\mathrm{A}}\rangle + (1-x)\,\langle S^2_{\mathrm{B}}\rangle + x\,(1-x)\,\langle l^2_{\mathrm{AB}}\rangle \tag{34}$$

The quantities, $(A'_2)_{\mathrm{app.}}$ and $\langle S^2\rangle_{\mathrm{app.}}$, are sensitive to the composition heterogeneity, as shown by equations (23) to (30). Adequate estimates of

A_2' and $\langle S^2\rangle_z^{LS}$ are possible only for highly homogeneous materials. However, for optimistic cases where B_{ij} may be approximated as a constant independent of composition and molecular weight, one may reduce equation (22) to a simpler form

$$(M_{app.})^2 (A_2')_{app.} = (M_w)^2 A_2' [1 + b (P/M_w)]^2 \tag{35}$$

Since the molecular weight dependence of B_{ij} is usually insignificant[33], the approximation would be valid in a solvent such as toluene in which both PST and PMMA have similar solubility and hence the composition dependence of B_{ij} is also negligible.

Likewise in simple cases where $\langle S^2\rangle^{LS}$ may be regarded primarily as a function of molecular weight alone, one may write

$$\langle S^2\rangle_{app.} = \langle S^2\rangle_z^{LS} \tag{36}$$

which may be further reduced to a weight average value by the formula suggested by Zimm[37]

$$\langle S^2\rangle_{app.,w} = \langle S^2\rangle_{app.} (1+Y)/(1+2Y) \tag{37}$$

It is also interesting to note that in a particular solvent such as toluene in which one constituent (here PMMA) is invisible, i.e. ν_B is nearly zero, $\langle S^2\rangle_{app.}$ should reflect the (Z-average) dimensions of visible PST parts[29].

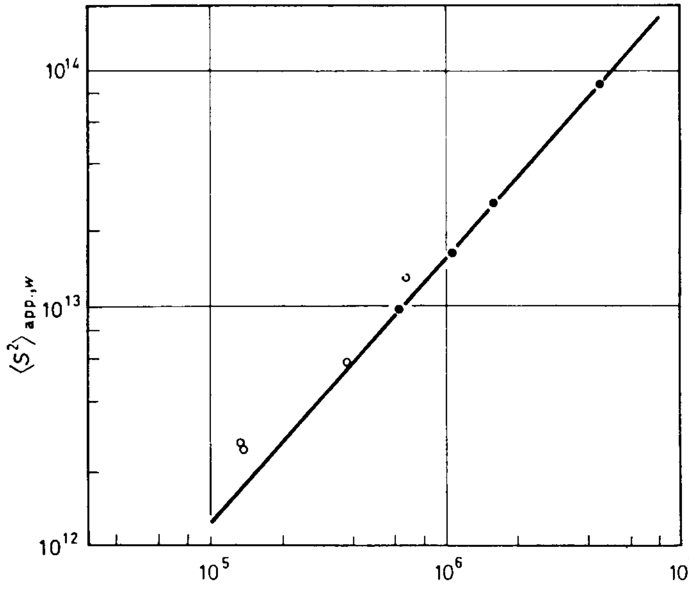

Figure 5—Apparent means square radius $\langle S^2\rangle_{app.,w}$ as a function of molecular weight of PST subchains $\overline{M}_w^A$ for ST–MMA block copolymers in toluene 30·0°C, compared with $\langle S^2\rangle$ data[24] for homo-PST–toluene systems

Table 4. Summary of light scattering data obtained in toluene at 30·0C*

Code	$10^4(A_2')_{app.}$	$10^4A_2'$	10^4A_2†	$[\eta]$	$A_2'M_w/[\eta]$†	$10^{12}\langle S^2\rangle_{app.}$	$10^{12}\langle S^2\rangle_{app.,w}$
22B	0·89	1·24	(2·65)	1·73	57·7(124)	7·72	5·96
25B	1·14	1·94	(3·81)	0·633	80·0(157)	3·80	2·48
26B	1·70	2·19	(3·28)	0·827	81·7(122)	3·27	2·73
27B	1·01	1·08	(1·87)	2·595	61·5(107)	16·0	13·6

*Units: A_2', ml mole/g²; $[\eta]$, dl/g; $\langle S^2\rangle$, cm².

†Values in parentheses are from osmometry, $A_2M_n/[\eta]$.

Table 4 summarizes light scattering data obtained in toluene at 30·0°C. Values of A_2' are computed by equation (35), while $\langle S^2\rangle_{app.,w}$ are computed by equation (37) by using $\overline{Y}^A$ instead of Y. In *Figure 5*, the values of $\langle S^2\rangle_{app.,w}$, which should be equal to $\langle S_A^2\rangle_w$, are compared with $\langle S^2\rangle$ data for the PST–toluene system reported by Berry[24]. Apparently the former are larger than the latter; the central PST subchains in PMMA–PST–PMMA block copolymers are more expanded than the corresponding homo-PST because of the interactions due to the invisible PMMA subchains. The results are qualitatively in agreement with those previously reported by Leng and Benoit[29].

Table 5. Summary of light scattering data obtained in butanone at 30·0°C*

Code	$10^4(A_2')_{app.}$	$10^4A_2'$	$[\eta]$	$A_2'M_w/[\eta]$	$10^{12}\langle S^2\rangle_{app.}$	$10^{12}\langle S^2\rangle_{app.,w}$	$10^{-21}\Phi$
22B	1·39	1·37	1·28	86·2	12·3	9·6	2·36
23B	1·92	1·80	1·55	133·0	17·6	15·5	1·98
25B	1·74	1·83	0·445	107·0	4·3	2·9	1·56
26B	1·48	1·52	0·635	74·1	5·0	4·3	1·47
27B	1·07	1·08	1·925	83·3	20·7	17·9	2·76
28B	3·00	3·28	0·284	106·0	—	—	—

*For units, see *Table 4*.

From *Table 4* it is seen that the dimensionless ratios $A_2'M_w/[\eta]$ for the block copolymers are considerably smaller than those usually found for homopolymers and also for random copolymers[16,18]. This is also true for the MEK data, as demonstrated in *Table 5*. However, the results would not necessarily imply that the block copolymer chains assume a peculiar conformation. At the moment we prefer to consider that the small values of $A_2'M_w/[\eta]$ may be due to an underestimate of A_2', i.e. equation (35) is not completely satisfactory for making the correction for composition heterogeneity. On the contrary the osmotic second virial coefficient A_2 need not be corrected for the heterogeneity, and may be larger than the light scattering A_2' yielding larger values of the osmometric dimensionless ratios $A_2M_n/[\eta]$, which are similar to the typical values of 100 to 150 (cf. *Table 4*).

Light scattering data for butanone systems are summarized in *Table 5*. From the data the Flory–Fox viscosity constants[15] Φ were computed as

$$\Phi = [\eta]\, M_w / [6 \langle S^2 \rangle_{\text{app.}, w}]^{3/2} \tag{38}$$

The values $10^{-21}\Phi$ seem to be about 2·0 to 2·8 except for the two samples 25B and 26B. Since these two samples have low molecular weights (and high composition heterogeneity for 25B also), the light scattering $\langle S^2 \rangle_{\text{app.}, w}$ data are less reliable and the low value of Φ for these samples need not be taken seriously. For other samples we may say that the values Φ are essentially the same as those usually found for homopolymer systems[15]. Obviously $\langle S^2 \rangle_{\text{app.}, w}$ are merely apparent values and differ from the true $\langle S^2 \rangle_w$. However, the difference should be small in such solvents (e.g. butanone) where ν for the block copolymers is large. The deviation of the apparent value from the true value obviously depends on the relative magnitudes of $\langle S^2_{\text{A}} \rangle$, $\langle S^2_{\text{B}} \rangle$ and $\langle l^2_{\text{AB}} \rangle$ and the factors ν_{A}/ν and ν_{B}/ν. With nearly equimolar block copolymers of PMMA–PST–PMMA type the apparent values $\langle S^2 \rangle_{\text{app.}, w}$ could be smaller than the true values $\langle S^2 \rangle_w$ [cf. equations (31) and (34)]. Anyway it is quite likely that the overall conformations of the block copolymer chains in butanone might not differ greatly from the conformations of any flexible linear homopolymer chains, as opposed to the previous conclusions by Krause[5]. The values Φ computed from the toluene data are much larger than those from the butanone data. The result may not be surprising, since $\langle S^2 \rangle_{\text{app.}, w}$ in toluene reflects the dimensions of PST subchains alone.

All these preliminary data suggest that the block copolymer chains in dilute solution may assume random coil conformations similar to flexible linear homopolymers. At the moment we cannot tell how much the so-called (extra) incompatible interactions between chemically different blocks should influence the conformations. A further quantitative analysis will be given in subsequent publications.

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REFERENCES

[1] BURLANT, W. J. and HOFFMAN, A. S. *Block and Graft Polymers*. Reinhold: New York, 1960

[2] CERESA, R. J. *Block and Graft Polymers*. Butterworths: London, 1962

[3] BATTAERD, H. A. J. and TREGEAR, G. W. *Graft Copolymers*. Interscience: New York, 1967

[4] See, for example, SZWARC, M. *Proc. Roy. Soc. A*, 1964, **279**, 260; *Fortsch. Hochpolym.Forsch.* 1960, **2**, 275

[5] KRAUSE, S. *J. phys. Chem.* 1961, **65**, 1618; 1964, **68**, 1948

[6] URWIN, J. R. and STEARNE, J. M. *Makromol. Chem.* 1964, **78**, 194 and 204

[7] Morton, M., Milkovich, R., McIntyre, E. B. and Bradley, L. J. *J. Polym. Sci.* 1963, **A1,** 443

[8] Wenger, F. *Makromol. Chem.* 1963, **64,** 151

[9] Wenger, F. *Makromol. Chem.* 1960, **36,** 200

[10] Freyss, D., Rempp, P. and Benoit, H. *J. Polym. Sci.* 1964, **2B,** 217

[11] Inoue, S., Tsuruta, T. and Furukawa, J. *Makromol. Chem.* 1960, **36,** 77

[12] Roig, A., Figueruele, J. E. and Llano, E. *J. Polym. Sci.* 1965, **3B,** 171

[13] Ohnuma, H. and Kotaka, T. Unpublished

[14] Feist, W. C. *J. Polym. Sci.* 1965, **3B,** 875

[15] Flory, P. J. *Principles of Polymer Chemistry.* Cornell University Press: Ithaca, N.Y., 1953

[16] Stockmayer, W. H., Moore Jr, L. D., Fixman, M. and Epstein, B. N. *J. Polym. Sci.* 1955, **16,** 517

[17] Bushuk, W. and Benoit, H. *Canad. J. Chem.* 1958, **36,** 1616

[18] Kotaka, T., Murakami, Y. and Inagaki, H. *J. phys. Chem.* 1968, **72,** 829

[19] Inagaki, H., Suzuki, H., Fujii, M. and Matsuo, T. *J. phys. Chem.* 1966, **70,** 1718

[20] Claesson, S. and Ohman, J. *Ark. Kemi,* 1964, **23,** 69

[21] Dezelic, G. *J. chem. Phys.* 1966, **45,** 185

[22] Kratohvil, J. P. *J. Colloid and Interface Sci.* (U.S.), 1966, **21,** 498

[23] Zimm, B. H. *J. chem. Phys.* 1948, **16,** 1093 and 1099

[24] Berry, G. C. *J. chem. Phys.* 1960, **44,** 4550

[25] Moore, J. C. *J. Polym. Sci.* 1964, **A2,** 835

[26] For recent development, see, Johnson, J. F. and Porter, R. S., Editors, *Analytical Gel Permeation Chromatography* (*J. Polym. Sci.*, **C21**). Interscience: New York, 1968

[27] Inagaki, H. and Nakazawa, A. Unpublished experiments

[28] Kotaka, T. and Donkai, N. *J. Polym. Sci.* 1968, **A2–6,** 1745

[29] Leng, M. and Benoit, W. *J. Polym. Sci.* 1962, **57,** 263

[30] Inagaki, H., Suzuki, H. and Kurata, M. *J. Polym. Sci.* 1966, **C15,** 409

[31] Oyama, T., Kawahara, K. and Ueda, M. *Nippon Kagaku Zasshi,* 1958, **79,** 727

[32] Kirkwood, J. G. and Goldberg, R. J. *J. chem. Phys.* 1950, **18,** 54

[33] Stockmayer, W. H. *J. chem. Phys.* 1950, **18,** 58

[34] Kotaka, T., Donkai, N., Ohnuma, H. and Inagaki, H. *J. Polym. Sci.* 1968, **A2–6,** 1803

[35] Benoit, H. and Wippler, C. *J. Chim. phys.* 1960, **57,** 524

[36] Leng, M. and Benoit, H. *J. Chim. phys.* 1961, **58,** 480

[37] Zimm, B. H. *J. chem. Phys.* 1948, **16,** 1099