

Characterization of styrene–ethylene oxide and methyl methacrylate–styrene block copolymers by light scattering

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Several polystyrene–poly(ethylene oxide)–polystyrene (PS–PEO–PS) and poly(methyl methacrylate)–polystyrene–poly(methyl methacrylate) (PMMA–PS–PMMA) block copolymers, synthesized by free-radical polymerization, were studied in various solvents by using a light-scattering technique. The copolymers, which have different lengths of central blocks, had molecular weights within the range 3.0×10^4 to 1.6×10^6 . It was found that almost all of them were confirmed as block copolymers from the variation of the product $M_{app} \langle S_{app}^2 \rangle^{1/2}$ with $W_A v_A / v$, although they were rather heterogeneous. The copolymer compositions determined either from the additivity of the refractive index increments of its constituent parts and the copolymer or from ultra-violet analysis were in excellent agreement with each other.

(Keywords: Characterization; block copolymers; polystyrene–poly(ethylene oxide)–polystyrene; poly(methyl methacrylate)–polystyrene–poly(methyl methacrylate); light scattering)

INTRODUCTION

Light-scattering studies on dilute block copolymer solutions have been essentially restricted to some classical polymeric systems such as di- or triblock copolymers of polystyrene–poly(methyl methacrylate) (PS–PMMA)^{1–4}, polystyrene–polyisoprene (PS–PI)^{5–7} and polystyrene–polybutadiene (PS–PBD)^{8,9} prepared by anionic polymerization. Since a unified conclusion on molecular conformation and interactions of block copolymers consisting of incompatible polymer pairs does not seem to have been obtained, we thought it would be appropriate to present our experimental results on light scattering of our various block copolymers in several solvents.

In this article we will report some results of light scattering on polystyrene–poly(ethylene oxide)–polystyrene (PS–PEO–PS) and poly(methyl methacrylate)–polystyrene–poly(methyl methacrylate) (PMMA–PS–PMMA) block copolymers in benzene, carbon tetrachloride, chloroform and cyclohexane.

EXPERIMENTAL

Materials

Seven PS–PEO–PS and three PMMA–PS–PMMA triblock samples of different lengths were prepared by free-radical polymerization. To prepare PS–PEO–PS triblock copolymers, a low-molecular-weight dihydroxyl-terminated poly(ethylene oxide) glycol was reacted with an aliphatic diisocyanate (bis-(4-cyanatocyclohexyl)-methane, Hylene-W) and then with a dihydroperoxide

(2,5-dimethyl-2,5-dihydroperoxyhexane, Luperox 2,5-2,5) together with a small amount of T-12 as a catalyst; the resulting polymeric peroxy-carbamates (PEO(1), (2) or (3)) were used as a free-radical initiator for styrene polymerization^{10–13}. The mode of preparation of various copolymeric samples of PEO and PS and the sequence of reactions are given in ref. 13 in detail. To prepare PMMA–PS–PMMA block copolymers a polymeric peroxy-carbamate was prepared by reacting equivalent amounts of Hylene-W and Luperox 2,5–2,5 (ref. 10) in the presence of T-12. This multifunctional initiator is used to obtain a polystyrene which contains peroxidic segments. PMMA blocks were then attached with subsequent polymerization in methyl methacrylate¹⁴. All these copolymeric samples were characterized according to our laboratory procedures which were described elsewhere^{10–14}. Here we only list the results in Table 1.

The solvents were selected according, first, to the gross solubility of one of the parent homopolymers and, secondly, to their refractive indices, which should be different from the refractive index of one of the parent homopolymers. They were benzene, carbon tetrachloride, chloroform and cyclohexane. Benzene was purified by standard procedures and fractional distillation. The other solvents were pure analytical-grade reagents.

Methods

Light-scattering measurements were made in a Brice-Phoenix light-scattering photometer with unpolarized blue light ($\lambda = 436$ nm). The refractive-index increments

Table 1 Characteristics of PS-PEO-PS and PMMA-PS-PMMA block copolymer samples

Copolymer no.	Type	PS content of copolymers (wt%)		$M_n \times 10^{-4}$		$[\eta]^e$ (dl g ⁻¹)
		Eq. (1)	U.v. analysis	PEO	PS	
1	PS-PEO-PS	94.1	93.8	0.55 ^a	—	0.964
2	PS-PEO-PS	94.3	95.7	4.0 ^b	—	0.495
3	PS-PEO-PS	93.0	95.3	4.0	—	0.493
4	PS-PEO-PS	87.9	84.4	4.0	—	0.518
5	PS-PEO-PS	92.5	89.5	4.0	—	0.505
6	PS-PEO-PS	90.0	68.9	2.0 ^{c,d}	—	1.625
7	PS-PEO-PS	93.1	83.6	2.0	—	2.300
8	PMMA-PS-PMMA	42.3	40.0	—	7.4	1.750
9	PMMA-PS-PMMA	49.3	47.0	—	11.0	1.650
10	PMMA-PS-PMMA	66.0	69.0	—	11.0	1.400

^a PEO(1)

^b PEO(3)

^c PEO(2): for characterization of these peroxy-carbonates refer to Table 1, Nos. 1, 6 and 2 respectively in Ref. 15

^d $M_w = 2.6 \times 10^4$ for PEO(2) determined by LS

^e In benzene, at 30°C

($v = dn/dc$) were determined at 30°C and 436 nm wavelength with Brice-Phoenix refractometer. Care has been taken by using the same batch of pure solvent for both light-scattering and refractive-index measurements. The error in dn/dc measurements is less than 1%. Molecular-weight distributions of copolymers were determined with Waters-GPC-200 model gel permeation chromatography. For light-scattering measurements, solutions are injected into the cell by filtering through 0.45 μm (type HA) Millipore membrane filters.

EXPERIMENTAL RESULTS

Refractive-index increments

The specific refractive-index increments of the copolymers and their parent homopolymers were determined in benzene, carbon tetrachloride, cyclohexane and chloroform. The results are given in Table 2. Since the refractive-index increment of a copolymer is a linear function of its composition^{15,16}, we used the data given in Table 2 in the following relation to calculate chemical compositions of copolymeric samples:

$$v = W_A v_A + (1 - W_A) v_B \quad (1)$$

where v , v_A and v_B denote the refractive-index increments of the copolymer and homopolymers of A and B respectively, and W_A indicates the weight fraction of component A in the copolymer. The chemical compositions of 10 copolymeric samples were expressed as per cent by weight of PS content and given in Table 1. (Per cent values of PS content were the average values for measurements in benzene, carbon tetrachloride and cyclohexane or chloroform.) We have also determined the PS content of the copolymeric samples by measuring the absorbance of pure PS in copolymers at 269 nm^{13,14}. It is seen that there is good agreement on chemical compositions evaluated with these two methods for all copolymeric samples except sample no. 6.

Light-scattering measurements

A series of light-scattering measurements was performed on all copolymeric samples in three solvents. The angular measurements from 45° to 135° for PS-PEO-PS block copolymers (samples 1-7) were

Table 2 Refractive-index increments of the polymers and the copolymers in various solvents at 30°C and 436 nm

Samples	dn/dc (ml g ⁻¹)			
	Benzene (S ₁)	Carbon tetrachloride (S ₂)	Cyclohexane (S ₃)	Chloroform (S ₄)
Polymers				
PS ^a	0.116	0.162	0.191	0.157
PMMA ^b	0.006	0.033	—	0.056
PEO(1) ^c	-0.035	0.047	-0.165	—
PEO(2) ^c	-0.037	0.047	-0.165	—
PEO(3) ^d	-0.047	0.050	-0.210	—
Copolymers ^d				
1	0.108	0.157	0.161	—
2	0.106	0.157	0.164	—
3	0.105	0.154	0.162	—
4	0.100	0.151	0.123	—
5	0.104	0.153	0.162	—
6	0.096	0.152	0.160	—
7	0.105	0.151	0.176	—
8	0.050	0.080	—	0.101
9	0.061	0.103	—	0.100
10	0.075	0.118	—	0.126

^a $M_w = 2.5 \times 10^5$

^b $M_w = 1.5 \times 10^5$

^{c,d} Refer to Table 1

carried out in benzene, carbon tetrachloride and cyclohexane. For PMMA-PS-PMMA block copolymers (samples 8-10), benzene, carbon tetrachloride and chloroform were used as solvents.

The typical Zimm plots obtained are shown in Figures 1-3. Normal Zimm plots were observed for most of the copolymer solutions¹⁷. Since the temperature of the measuring cell was 30°C, inverted Zimm plots (Figure 1c) were always obtained when the solvent was cyclohexane (a theta-solvent for PS) regardless of the PEO content of the copolymer. For samples 4 and 7-9, if carbon tetrachloride was used as solvent, inverted Zimm plots (Figures 2 and 3b) only were observed. This behaviour is expected since carbon tetrachloride is a poor solvent for both PEO and PMMA components. When PEO or PMMA content in the copolymers reached 10 or 50% respectively, poor solvent effect became dominant.

To evaluate light-scattering data, standard procedures

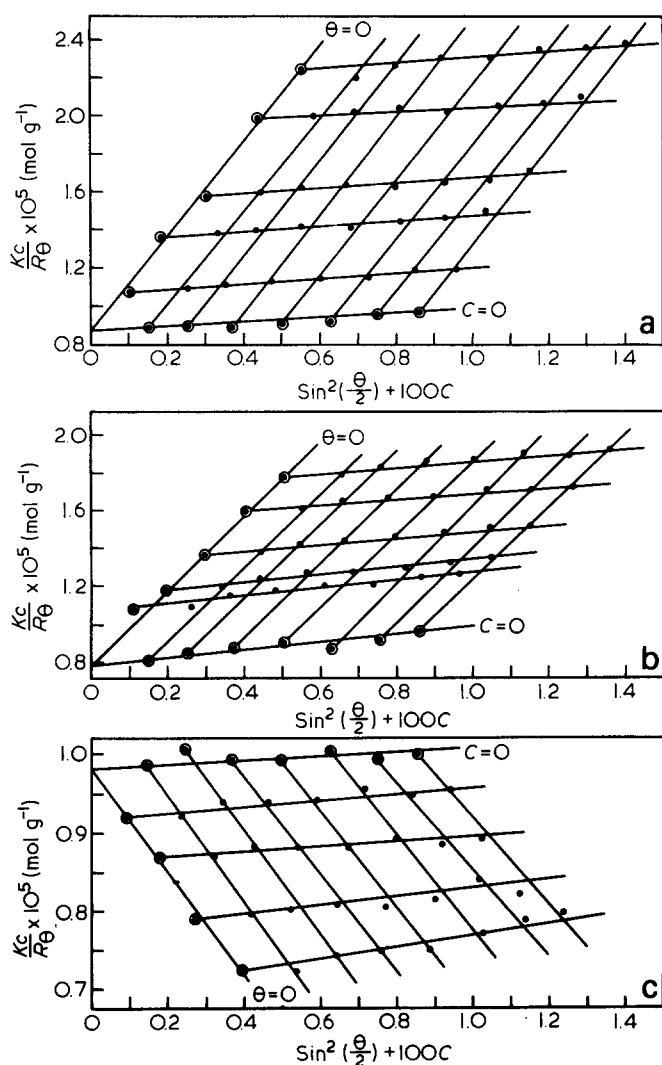


Figure 1 Zimm plots for PS-PEO-PS copolymer 1 in (a) benzene, (b) carbon tetrachloride, and (c) cyclohexane

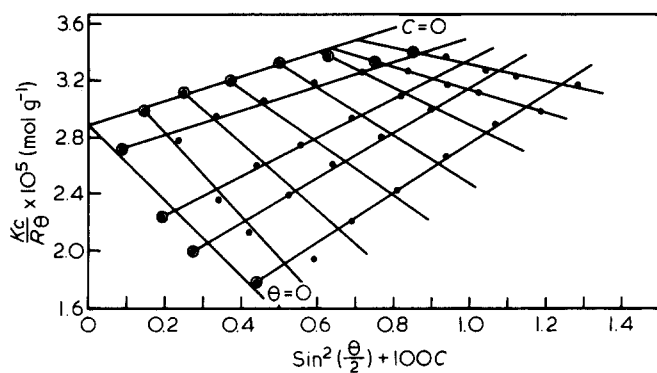


Figure 2 Zimm plot for PS-PEO-PS copolymer 4 in carbon tetrachloride

utilized for homopolymer solutions were also adopted for the copolymeric samples in various solvents. This time, however, the molecular weights and the radii of gyration from Zimm plots yielded the apparent values. Hence, the real molecular weight, M_w , and the heterogeneity parameters, P and Q , were calculated from the following relation:

$$M_{app} = M_w + 2P \left(\frac{v_A - v_B}{v} \right) + Q \left(\frac{v_A - v_B}{v} \right)^2 \quad (2)$$

where v , v_A and v_B are the dn/dc values as indicated before. The quantity P describes the variation in chemical composition as a function of molecular weight, whereas Q is a measure of the total compositional heterogeneity in the copolymer systems^{1,16}. The apparent molecular weights, M_{app} , were determined in benzene, carbon tetrachloride and cyclohexane for samples 1-7, and in benzene, carbon tetrachloride and chloroform for samples 8-10, and are given in Table 3. This Table also includes the calculated values of real molecular weights, M_w , relative heterogeneities, M_{app}/M_w , and heterogeneity indices, HI , which is obtained from g.p.c. measurements.

The number-average molecular weights of the central blocks in both types of copolymers were measured experimentally and are included in Table 1. The molecular weights of the side blocks, however, could not be measured in these systems. They were calculated by using the following arguments. The ratio of the molecular weight of block A to the sum of the molecular weights of blocks A and B is equal to the composition by weight of component A:

$$W_A = M_w^A / (M_w^A + M_w^B) \quad (3)$$

Since W_A and M_w^B (the molecular weight of the central

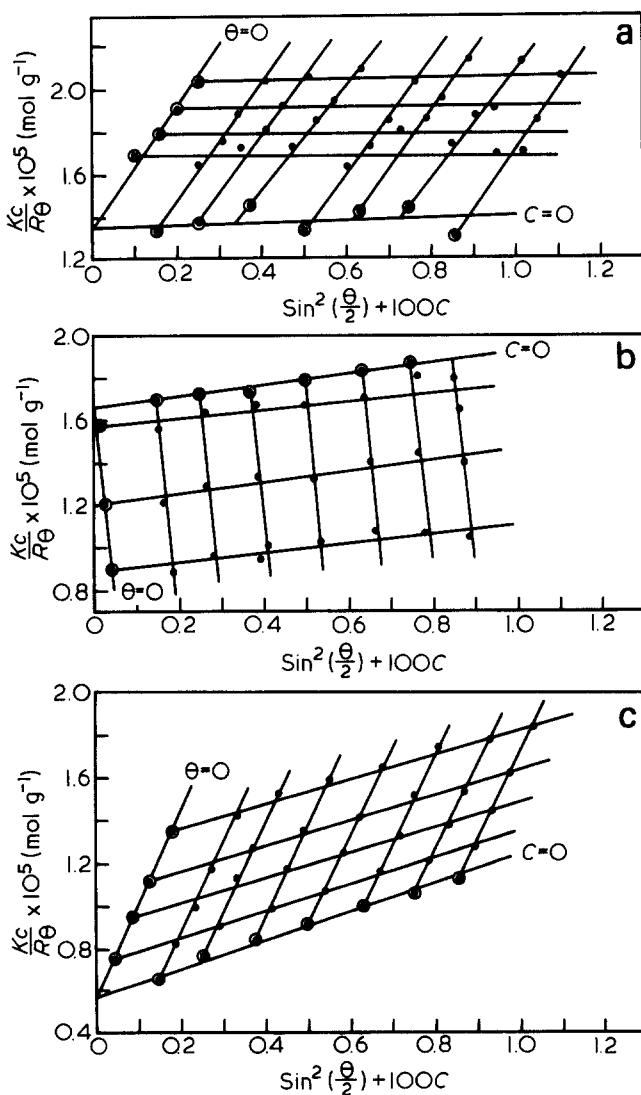


Figure 3 Zimm plots for PMMA-PS-PMMA copolymer 8 in (a) benzene, (b) carbon tetrachloride, and (c) chloroform

Table 3 Summary of M_{app} , M_w , P , Q and HI results for the copolymers

Copolymer no.	$M_{app} \times 10^{-5}$				$M_w \times 10^{-5}$	M_{app}/M_w				HI	$-P \times 10^{-5}$	$Q \times 10^{-5}$
	S_1^*	S_2	S_3	S_4		S_1	S_2	S_3	S_4			
1	1.2	1.3	1.0	—	1.45	0.8	0.9	0.7	—	1.84	0.13	0.03
2	0.4	0.5	0.4	—	0.62	0.6	0.7	0.6	—	2.14	0.14	0.07
3	0.4	0.4	0.3	—	0.23	1.8	1.6	1.2	—	1.93	-0.14	-0.11
4	0.4	0.4	0.5	—	0.36	1.0	1.0	1.3	—	2.59	0.01	0.02
5	0.4	0.4	0.3	—	0.49	0.7	0.9	0.6	—	2.36	0.05	0.01
6	4.2	3.3	10.1	—	11.10	0.4	0.3	0.9	—	3.36	7.73	6.72
7	5.3	2.3	16.7	—	13.51	0.4	0.2	1.2	—	3.45	12.35	13.03
8	0.7	0.6	—	1.8	7.65	0.1	0.1	—	0.2	4.37	4.07	2.28
9	1.1	0.9	—	1.5	8.83	0.1	0.1	—	0.2	4.91	5.66	4.01
10	1.1	1.3	—	1.4	1.93	0.6	0.7	—	0.7	2.56	0.36	0.11

* Solvents as in Table 2

blocks) were determined experimentally, the M_w^A (molecular weight of the side blocks) value of the copolymers could be calculated from the above relation.

Another method for this purpose is based on the evaluation of the following expressions¹⁶:

$$2P = (1 - W_A)(M_w - M_w^B) - W_A(M_w - M_w^A) \quad (4)$$

$$Q = W_A(1 - W_A)(M_w^A + M_w^B - M_w) \quad (5)$$

The quantities P and Q are calculated from equation (2) for each copolymeric sample and are included in Table 3.

In addition, the molecular weight of the side blocks, M_w^A , can be calculated from the following relation based on the refractive-index increments and M_{app} values determined in selected solvents:

Table 4 Calculated values of the molecular weight of the side blocks in the copolymers

Copolymer no.	$M_w^A \times 10^{-5}$			$M_w^A \times 10^{-5}$ (Eq.(6))			
	Eq.(3)	Eq.(4)	Eq.(5)	S_1^*	S_2	S_3	S_4
1	0.9	1.1	2.0	1.2	1.2	1.2	—
2	6.6	0.3	1.5	0.4	0.4	0.5	—
3	5.3	0.6	—	0.4	0.4	0.2	—
4	2.9	0.4	0.1	0.3	0.4	0.3	—
5	4.9	0.4	0.2	0.4	0.4	0.4	—
6	2.3	27.0	85.0	5.4	0.4	9.9	—
7	3.5	39.0	220.0	7.0	2.9	15.0	—
8	1.0	18.0	16.0	20.0	17.0	—	5.5
9	1.0	24.0	24.0	28.0	23.0	—	26.0
10	0.6	2.5	1.3	20.0	5.5	—	3.1

* Solvents as in Table 2

Table 5 The calculated values of A_2 and $\langle S_{app}^2 \rangle^{1/2}$ in the selected solvents

Copolymer no.	$A_2 \times 10^3$ (cm ³ mol g ⁻²)				$\langle S_{app}^2 \rangle^{1/2}$ (Å)			
	S_1^*	S_2	S_3	S_4	S_1	S_2	S_3	S_4
1	1.3	1.0	-3.3	—	180	210	80	—
2	1.5	1.5	-1.0	—	(-) 80	110	(-) 100	—
3	1.9	1.8	-1.5	—	45	50	(-) 100	—
4	1.4	-1.4	-0.4	—	80	220	(-) 110	—
5	1.4	0.9	-2.4	—	60	150	(-) 100	—
6	1.4	1.1	-1.0	—	400	440	1500	—
7	1.5	-0.5	-0.06	—	530	420	2300	—
8	1.5	-12.2	—	2.2	120	140	—	460
9	0.7	-5.6	—	1.4	150	180	—	290
10	0.7	1.0	—	1.8	160	160	—	310

* Solvents as in Table 2

$$M_{app} = (\nu_A \nu_B / \nu^2) M_w + [\nu_A (\nu_A - \nu_B) / \nu^2] M_w^A W_A + [\nu_B (\nu_B - \nu_A) / \nu^2] (1 - W_A) M_w^B \quad (6)$$

The data for the molecular weights of the side groups of the copolymeric samples is given in Table 4 using equations (3)–(6).

The apparent mean square radii of gyration, $\langle S_{app}^2 \rangle$, and the second virial coefficients, A_2 , are calculated from the Zimm plots for each copolymeric sample in various solvents and are listed in Table 5.

DISCUSSIONS AND CONCLUSIONS

The dn/dc values for parent homopolymers, namely PS and PMMA as given in Table 2, are in good agreement with the literature data^{18,19}. The dn/dc values for PEO residue (in peroxy-carbamate form), which is the other component of our copolymers (samples 1–7), do not exist in the literature. Our results also indicate that there is a variation of dn/dc values of PEO in benzene and cyclohexane with molecular weight. The dn/dc values are independent of molecular weight, however, for carbon tetrachloride solutions for this range.

For long copolymeric chains, the apparent molecular weights show a dependence on the solvent as indicated in Table 3. The ratio M_{app}/M_w for all samples indicates that most of the copolymers are rather homogeneous in composition^{6,16,20}.

The heterogeneity indices (HI) of copolymers obtained from g.p.c. measurements are also given in Table 3. It can be seen that the copolymers with higher molecular weights indicate rather inhomogeneous molecular-weight distributions.

In this study almost all of the 10 copolymers are characterized by $P < 0$, which confirms that with an increase in molecular weight the copolymer molecules are enriched with PS or PMMA units in PS-PEO-PS and PMMA-PS-PMMA copolymers respectively²¹. Only sample 3 has a positive value of P , which may suggest a different structure for this copolymer²². In addition, this copolymer sample has a negative Q value, which is physically impossible²³. Since the preparation of this copolymeric sample is identical with samples 2-5, these discrepancies can be attributed to the accumulation of experimental error in calculations^{22,24,25}.

Although samples are left to attain complete dissolution for up to a week, especially in poor solvents such as cyclohexane and carbon tetrachloride as suggested in the literature²⁶, high P and Q values are observed for the copolymers, especially for those which have high molecular weights and high HI values. This may be due to the presence of some sequence of PS homopolymers along with the copolymers which could not be removed completely¹³. Examination of the data presented in Table 4 for the length of the side blocks (A) of copolymeric samples support this suggestion related to those systems for molecular weights higher than about 10^5 , since M_w^A values calculated from equations (4)-(6) are larger than the expected theoretical value based on equation (3). In addition, the presence of aggregates when working with poor solvents can lead to overestimated values of P and Q .

The dependence of A_2 values on the solvent for a homopolymer or a copolymer is a very good guide to the extent of interaction between solvent and polymer molecules. The calculated values of A_2 given in Table 5 show that, for PS-PEO-PS copolymers, benzene is a good solvent but cyclohexane is a poor solvent, whereas carbon tetrachloride is in between these two. On the other hand, for PMMA-PS-PMMA copolymers, chloroform is a better solvent than benzene, whereas carbon tetrachloride acts as a good solvent if PS content of the copolymer is over 50%.

The $\langle S_{app}^2 \rangle^{1/2}$ values of copolymers, which are also given in Table 5, increase for good solvents. Negative values are obtained for poor solvents for low-molecular-weight samples. This can happen when the dn/dc values of two parent homopolymers have opposite values in sign¹.

The polydispersity of copolymeric systems is attempted by Leng and Benoit²⁷ by studying the product of the apparent mean square radius and the apparent molecular weight, $M_{app} \langle S_{app}^2 \rangle$. According to their discussions, the structure of copolymers can be determined by the direction of parabola-bending for the variation of the above product with $W_A v_A/v$. We have applied our data for M_{app} and $\langle S_{app}^2 \rangle$, given in Tables 3 and 5 respectively, to the above theory and obtained the bending conditions of the parabola for all of our copolymeric samples. For this purpose, a computer program is developed and downward-bending parabolae are obtained for all samples except samples 4 and 10. The upward bending observed for these two samples may indicate the presence of homopolymers in the copolymeric samples. Figure 4

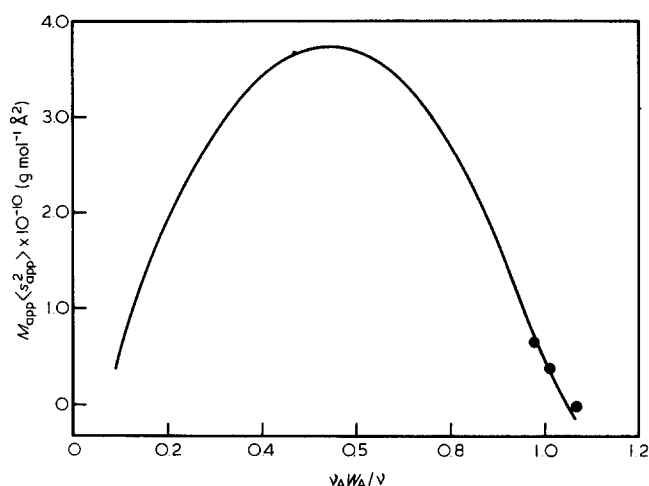


Figure 4 Variation of $M_{app} \langle S_{app}^2 \rangle$ with $v_A W_A/v$ for copolymer 1

shows a typical parabola obtained from these calculations. These results confirm the block structure of our copolymeric samples.

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