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SOLUTION PROPERTIES OF STYRENE-*p*-METHOXYSTYRENE RANDOM COPOLYMERS—II

VISCOSITY, OSMOTIC PRESSURE AND LIGHT SCATTERING STUDIES

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Abstract—Molecular weight determinations by light scattering and osmometry and also measurements of intrinsic viscosity were made in toluene for fractions of styrene-*p*-methoxystyrene "random" copolymers with different compositions. Relationships between intrinsic viscosity and molecular weight thus established are compared with those of the parent homopolymers.

The values of the Flory constant (K_θ) and the polymer-solvent interaction parameter (B) have been evaluated applying the theories of Kurata–Stockmayer–Roig, Stockmayer–Fixman and Berry.

On the basis of the experimental data, it was found that the unperturbed dimensions for copolymers are larger than those for homopolymers and that the copolymer of about equimolecular composition shows peculiar behaviour in comparison with copolymers of other compositions.

INTRODUCTION

The aim of this paper is a physicochemical investigation of a series of styrene and *p*-methoxystyrene random copolymers in solution. The monomers were selected in order to ensure a high "randomness" of distribution of monomer units along the polymeric chains; the monomer reactivity ratios for the system are well-known and their product is near unity.

The first paper(1) of this series gave a description of the preparation and fractionation of a number of random copolymers with a good degree of homogeneity of composition. In this work, we present the results of an examination of the viscosity, osmometry and light scattering behaviour of these polymers.

Mark–Houwink relationships and equations relating $\bar{M}_w$ to the second virial coefficient A_2 and to the root mean square of statistical radius $\sqrt{(\bar{\rho})_z{}^2}$ are established for each available composition.

The parameter K_θ is evaluated from the Kurata–Stockmayer–Roig,(2) Stockmayer–Fixman,(3) Berry(4) and Krigbaum(5) expressions.

EXPERIMENTAL AND RESULTS

p-*Methoxystyrene* (*p*MOS) was prepared by decarboxylation(6) of *p*-methoxycinnamic acid(7) and rectified under nitrogen at reduced pressure (b.p. 69° at 3 mm Hg) prior to use.

Styrene, a commercial product, was used immediately after distillation.

Copolymerization runs with different monomer feeds were carried out at 60° under nitrogen; benzoyl peroxide was used as initiator. Six copolymer samples of (three) different compositions were obtained, coded thus:

Sample	*p*-Methoxystyrene (mol %)
Co-1	26·4
Co-1′	26·0
Co-2	53·0
Co-2′	53·8
Co-3	75·6
Co-3′	75·6

Each copolymer sample (6–8 g) was divided into 14–17 fractions at 25° by the column elution technique: methylethylketone and ethanol were selected as the solvent–non-solvent system. More details on copolymer preparation and fractionation are given elsewhere.(1)

TABLE 1. CHARACTERIZATION OF COPOLYMERS BY OSMOMETRY AND VISCOMETRY IN TOLUENE AT 25°.

Sample	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-3}$	$A_2 \times 10^4$ ($cm^3 mol\ g^{-2}$)
Co-1′			
C_3–5	0·315	53·0	
C_4–5	0·346	71·0	5·0
C_3–7	0·434	86·0	5·6
C_4–7	0·545	105	4·6
C_4–8	0·600	137	4·3
C_3–9	0·660	171	4·3
C_4–10	0·860	245	
C_4–11	1·100	308	3·8
C_3–13	1·413	350	3·0
Co-2′			
D_3-3	0·200	35·5	4·1
D_3-4	0·250	50·5	5·2
D_3-5	0·300	60·0	4·2
D_4-4	0·320	72·0	3·6
D_3-6	0·380	94·0	4·0
D_3-7	0·463	115	
D_4-6	0·476	100	3·6
D_3-8	0·500	121	3·5
D_4-7	0·600	154	3·2
D_4-9	0·864	234	4·2
D_4-11	1·314	400	3·8
D_3-13	1·640	660	3·9
D_3-14	1·870	701	3·2
Co-3′			
F_1-3	0·233	44·0	5·9
F_1-4	0·270	61·0	5·4
F_1-5	0·354	85·0	
F_1-6	0·466	119	4·1
F_1-7	0·564	169	3·9
F_2-8	0·594	187	4·2
F_2-10	0·794	232	3·2
F_2-11	0·965	294	3·0
F_1-12	1·214	421	3·5

The chemical compositions of fractions and unfractionated samples were found spectrophotometrically measuring the absorption of chloroform solutions according to Melville and Valentine.(8) The analysis of the fractions showed negligible fluctuation of composition.

Intrinsic viscosity measurements were carried out in toluene solutions using Bischoff dilution viscometers at 25·0 ± 0·1°. Toluene was dried over sodium and fractionated through an efficient column.

Osmometry

The osmotic pressure measurements were made at 25·00 ± 0·02° by Hellfritz osmometers with toluene as solvent. Ultracellafilter grade feinst or allerfeinst properly conditioned membranes were used. Tests for polymer diffusion through membranes were always negative. The osmotic pressure plots for all the fractions were linear allowing direct extrapolation to zero concentration according to the relationship:

$$\pi/c = RT\,(1/\bar{M}_n + A_2c + \ldots\ldots).$$

The number-average molecular weights $\bar{M}_n$ thus obtained, together with the corresponding second virial coefficients A_2 and the intrinsic viscosities $[\eta]$, are shown in Table 1. There is a tendency for A_2 to decrease as the size of the molecule is increased, but the points are subject to too much scattering to deduce any quantitative relationship.

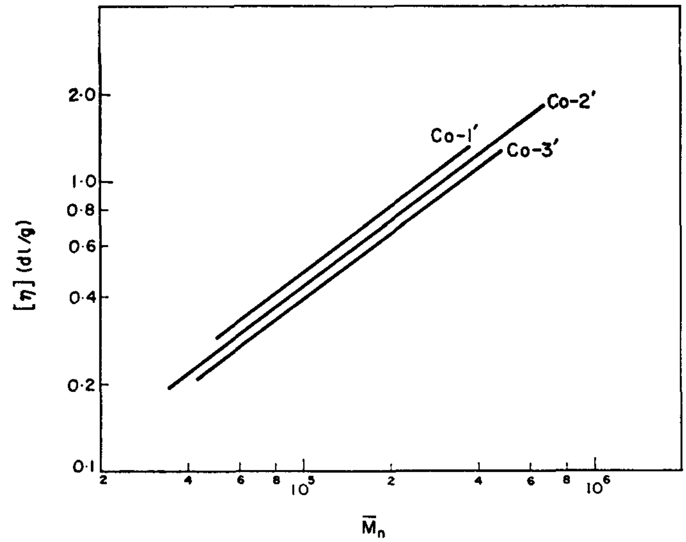

FIG. 1. Double logarithmic plots of $[\eta]$ vs. $\bar{M}_n$ for ST-*p*MOS copolymers in toluene at 25°.

The log-log plots of the intrinsic viscosity against $\bar{M}_n$ are shown in Fig. 1. The values of K and a, calculated according to the Mark-Houwink equation $[\eta] = K\,\bar{M}^a$, are listed in Table 2 for each copolymer together with the corresponding values for the homopolymers. From these values, we can see that the viscometric behaviour of copolymers lies between those of the parent homopolymers: there is a small decrease

TABLE 2. MARK–HOUWINK RELATIONSHIPS FOR THREE COPOLYMER SAMPLES AND PARENT HOMOPOLYMERS IN TOLUENE AT 25°

Sample	*p*MOS (mol %)	Mol wt. range ($\bar{M}_n \times 10^{-3}$)	Number of fractions	Parameters of the Mark–Houwink rel. $K \times 10^4$	a
PolyST*	0	70–1500		1·34	0·71
Co-1′	26·0	53–350	9	0·82	0·755
Co-2′	53·8	35–700	13	0·73	0·755
Co-3′	75·6	44–420	9	0·70	0·75
Poly*p*MOS†	100	34–400	12	0·63	0·75

* C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin, *Trans. Faraday Soc.* **46**, 1107 (1950).
† See ref. (9).

of K with increasing *p*MOS content from sample Co-1′ to sample Co-3′ but the exponent a is unchanged.

Light scattering

A SOFICA photometer (mod. 42000) was used to measure the intensities of scattered light in toluene solutions at 25°. The angular variation of the scattered intensity was determined with cylindrical cells in the angular range 30–150°, with incident light of $\lambda = 546$ nm. Solutions and solvent were freed from dust by 2 hr centrifugation at 25,000 g.

Specific refractive index increments (d*n*/d*c*) were measured at $\lambda = 546$ nm with a Brice–Phoenix differential refractometer, calibrated using aqueous potassium chloride solutions. The values of (d*n*/d*c*) obtained were 0·111, 0·107 and 0·104 (ml/g) for Co-1, Co-2 and Co-3, respectively.

Light scattering data were treated using the following equation:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w}\left(1 + \frac{16\pi^2}{3\lambda^2}\,(\overline{\rho^2})_z\,\mathrm{sen}^2\,\frac{\theta}{2}\right) + 2\,A_2 c$$

where

$$K = \frac{2\pi^2 n^2}{N_A \lambda_0{}^4}\,(\mathrm{d}n/\mathrm{d}c)^2.$$

Extrapolations to c and $\theta = 0$ were carried out by Zimm procedure, to obtain the weight-average molecular weight $\bar{M}_w$, the second virial coefficient A_2 and the root mean square of statistical radius $\sqrt{(\overline{\rho^2})_z}$. Results are listed in Table 3.

It is well-known that light scattering measurements on a heterogeneous copolymer give only an apparent molecular weight which depends on the refractive index of the solvent; measurements in solvents with different refractive indices are needed to obtain the true molecular weight. The present copolymer fractions, however, were uniform in composition, so the observed value can be regarded as the true molecular weight.

The assumption of chemical homogeneity of fractions was supported by additional experiments in a solvent (methylethylketone) with a different specific refractive index increment (d*n*/d*c* range: 0·210–0·220 ml/g).

TABLE 3. CHARACTERIZATION OF COPOLYMERS BY LIGHT SCATTERING AND VISCOMETRY IN TOLUENE AT 25°

Sample	[η] (dl/g)	$\bar{M}_w \times 10^{-3}$	$A_2 \times 10^4$ (cm³mol g⁻²)	$(\overline{\rho^2})_z^{1/2}$ (Å)	$\phi \times 10^{-21}$
Co-1					
C_5-5	0·338	61·0	$5\cdot3_4$		
C_5-6	0·461	93·0	$5\cdot6_2$		
C_5-7	0·553	131	$5\cdot5_4$		
C_5-9	0·721	200	$4\cdot9_9$	178	2·2
C_5-10	0·869	245	$4\cdot6_4$	221	1·7
C_6-9	0·932	285	$4\cdot6_9$	248	1·6
C_5-11	1·070	348	$4\cdot6_7$	284	1·5
C_5-12	1·271	420	$4\cdot4_9$	317	1·6
C_6-14	1·736	665	$4\cdot2_9$	394	1·7
Co-2					
D_5-4	0·332	66·0	$5\cdot4_6$		
D_5-6	0·456	104	$5\cdot3_3$		
D_5-8	0·622	168	$4\cdot6_8$		
D_6-8	0·803	269	$4\cdot2_6$	238	1·4
D_5-9	0·829	292	$4\cdot2_2$	212	2·2
D_6-10	1·123	446	$3\cdot9_7$	305	1·6
D_5-11	1·230	564	$3\cdot9_8$	355	1·5
D_6-11	1·409	642	$3\cdot8_6$	391	1·5
D_5-13	1·737	920	$3\cdot8_2$	474	1·5
D_5-14	2·091	1346	$3\cdot8_1$	604	1·3
D_6-15	2·630	1783	$3\cdot4_1$	715	1·3
Co-3					
F_3-4	0·342	79·0	$4\cdot5_4$		
F_3-5	0·403	118	$4\cdot5_0$		
F_3-7	0·620	184	$3\cdot9_2$	179	1·7
F_3-8	0·781	279	$3\cdot7_2$	214	1·9
F_3-9	1·058	431	$3\cdot5_5$	298	1·6
F_3-11	1·520	730	$3\cdot3_0$	411	1·6
F_3-13	1·983	1149	$3\cdot0_5$	568	1·3
F_3-15	2·612	1717	$3\cdot0_0$	745	1·2

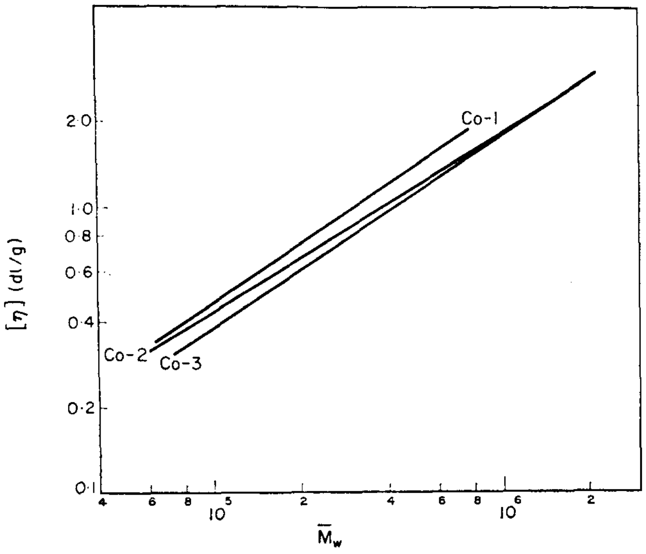

FIG. 2. Double logarithmic plots of [η] vs. $\bar{M}_w$ for ST-*p*MOS copolymers in toluene at 25°.

The molecular weights of the copolymer fractions measured in the two solvents were in good agreement, confirming the composition heterogeneity to be narrow; the characterization of copolymers was therefore carried out in a single solvent.

The viscosity–molecular weight relationships are shown in Fig. 2 and the values of the constants K and a in the Mark–Houwink equation from such plots are given in Table 4. The viscometric behaviour of the three samples lies between parent homopolymers although there is not a gradual change with composition, as seen before from $[\eta]$–$\bar{M}_n$ relationships. The sample at about equimolecular composition shows in fact peculiar behaviour in comparison with the others.

TABLE 4. MARK–HOUWINK RELATIONSHIPS FOR THREE COPOLYMER SAMPLES AND PARENT HOMOPOLYMERS IN TOLUENE AT 25°

Sample	*p*MOS (mol %)	Mol. wt. range ($\bar{M}_w \times 10^{-3}$)	Number of fractions	Parameters of the Mark–Houwink rel. $K \times 10^4$	a
PolyST*	0	170–1800	9	1·05	0·73
Co-1	26·4	61–700	9	1·86	0·68
Co-2	53·0	66–1800	11	3·7	0·615
Co-3	75·6	79–1700	8	1·69	0·67
Poly*p*MOS†	100	60–1600	12	1·05	0·70

* W. Breitenbach and G. Olay, *Makromolek. Chem.* **81**, 32 (1965).
† See ref. (9).

A_2–$\bar{M}_w$ *relationship*

The virial coefficients from light scattering measurements show the same trend as those obtained by osmotic pressure measurements, in that A_2 values increase slightly with decreasing molecular weight.

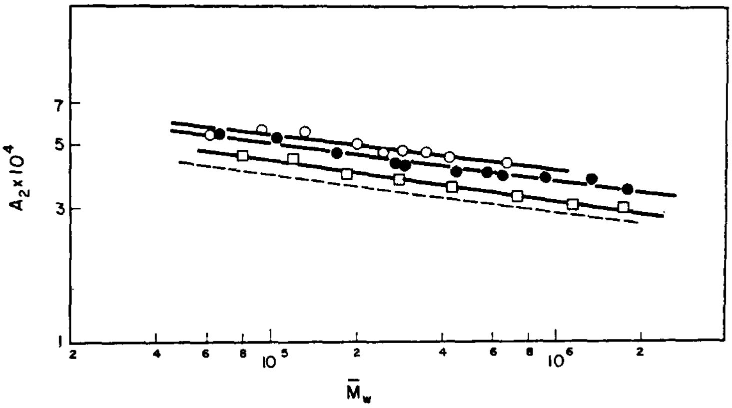

FIG. 3. Double logarithmic plots of A_2 vs. $\bar{M}_w$: ○ Co-1; ● Co-2; □ Co-3; ---- poly*p*MOS.

From the double log plot of A_2 versus $\bar{M}_w$ for the three copolymer samples (see Fig. 3) the corresponding relationships were established by the least squares method:

Copolymer 1 $A_2 = 2{\cdot}0 \times 10^{-3}\,\bar{M}_w^{-0{\cdot}11_5}$

Copolymer 2 $A_2 = 2{\cdot}4 \times 10^{-3}\,\bar{M}_w^{-0{\cdot}13_5}$

Copolymer 3 $A_2 = 2{\cdot}3 \times 10^{-3}\,\bar{M}_w^{-0{\cdot}14_5}$

In Fig. 3 the molecular weight dependence of A_2 is also given for poly-*p*MOS;(9) the plots show that the values for copolymers are greater than for poly-*p*MOS indicating that toluene is a better solvent for the copolymers than for the homopolymer.

Relationship between chain extension and molecular weight

The log–log plot of the root mean square of statistical radius against $\bar{M}_w$ is given in Fig. 4. The figure shows that a single equation is sufficient to represent the experimental points for all copolymer samples:

$$\sqrt{(\overline{\rho^2})_z} = 0{\cdot}09\,\bar{M}_w^{0.62}.$$

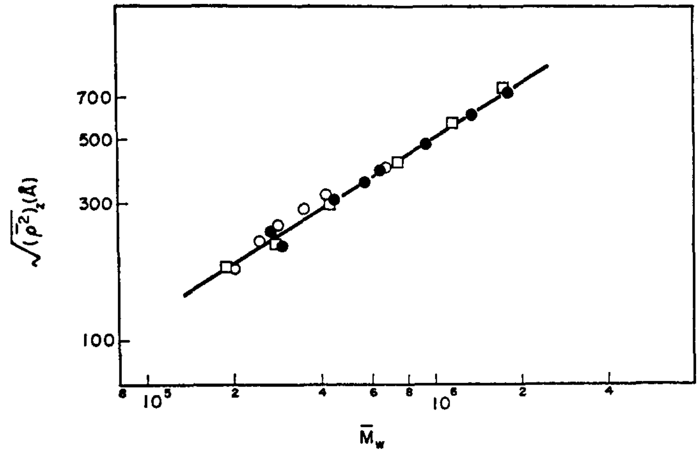

FIG. 4. Double logarithmic plots of $\sqrt{(\overline{\rho^2})_z}$ vs. $\bar{M}_w$: ○ Co-1; ● Co-2; □ Co-3.

The universal parameter ϕ

The Flory–Fox viscosity constant ϕ(10) was calculated as:

$$\phi = \frac{[\eta]\,\bar{M}_w}{[6(\overline{\rho^2})_w]^{3/2}}.$$

The weight-average mean square statistical radius was obtained by the equation:

$$(\overline{\rho^2})_w = (\overline{\rho^2})_z \frac{h+1}{h+2}$$

where

$$h = \left[\frac{\bar{M}_w}{\bar{M}_n} - 1\right]^{-1}$$

in the Schulz–Zimm distribution function ($\bar{M}_w/\bar{M}_n$ values, previously obtained for comparable copolymer fractions, were in the range 1·2–1·5).

The last column in Table 3 shows that ϕ values do not depend on the *p*MOS content and range from $1 \cdot 2 \times 10^{21}$ to $2 \cdot 2 \times 10^{21}$ (the individual values would increase by about 10–20 per cent if the residual heterogeneity is taken into account).

These values are low compared with the experimentally determined average(10) of $2 \cdot 1 \times 10^{21}$ for homopolymers; the origin of such a discrepancy is not clear. Similar low values, however, have been observed by some authors both for copolymers(11,12) and for homopolymers.(13)

Unperturbed dimensions of copolymers

In order to calculate the unperturbed dimensions, the data on viscosity–molecular weight relations were subjected to the graphical extrapolation procedures of Kurata–Stockmayer–Roig(2) (K–S–R), Stockmayer–Fixman(3) (S–F) and Berry(4)(B).

The extrapolations, shown in Figs. 5–7, were drawn according to:

$$\text{K–S–R} \qquad \frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0 \cdot 363\, \phi\, B\, g(\alpha_\eta)\, \frac{M^{2/3}}{[\eta]^{1/3}}$$

$$\text{S–F} \qquad \frac{[\eta]}{M^{1/2}} = K_\theta + 0 \cdot 51\, \phi\, B\, M^{1/2}$$

$$\text{B} \qquad \frac{[\eta]^{1/2}}{M^{1/4}} = K_\theta^{1/2}\left(1 + 0 \cdot 42\, \phi\, B\, \frac{M}{[\eta]}\right)$$

where K_θ is the Flory constant, related to the unperturbed dimensions, and B is the polymer–solvent interaction parameter.

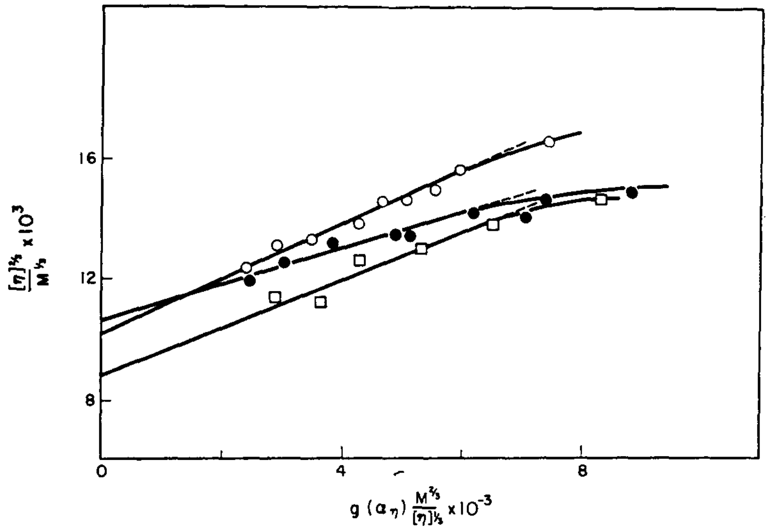

FIG. 5. Kurata–Stockmayer–Roig plots for ST–*p*MOS copolymers in toluene at 25°: ○ Co-1; ● Co-2; □ Co-3.

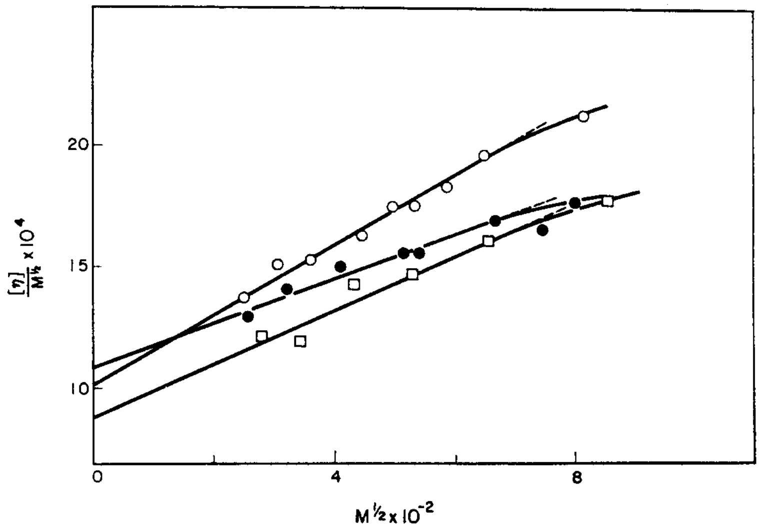

FIG. 6. Stockmayer–Fixman plots for ST–*p*MOS copolymers in toluene at 25°: ○ Co-1; ● Co-2; □ Co-3.

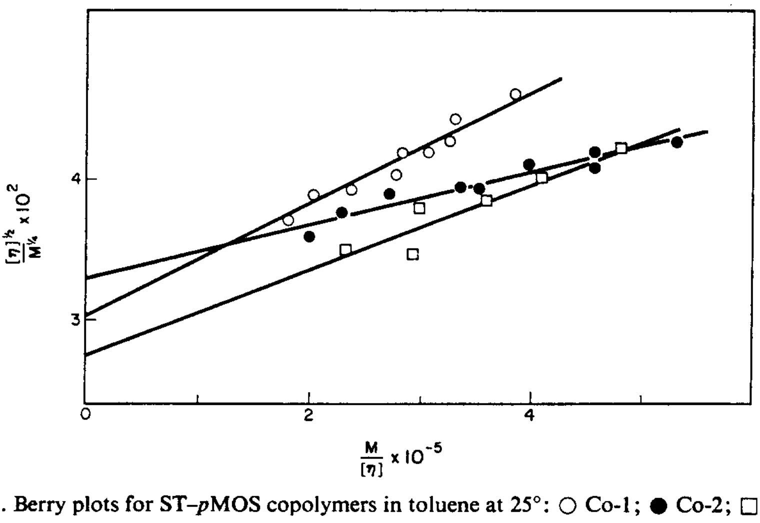

FIG. 7. Berry plots for ST–*p*MOS copolymers in toluene at 25°: ○ Co-1; ● Co-2; □ Co-3.

As pointed out by many authors,$^{(13-15)}$ the plots according to K–S–R and S–F are not linear over the whole molecular weight range and bend towards the abscissa in the region of higher molecular weight, especially when the weight average molecular weight is considered. A fairly accurate extrapolation can however be effected neglecting the high molecular weight region. K_θ and B values so obtained are summarized in Table 5. An estimate of K_θ was also made according to Krigbaum,$^{(5)}$ who takes into account the dependence of A_2 on $\bar{M}_w$. The values obtained were $9 \cdot 0 \times 10^{-4}$, $11 \cdot 1 \times 10^{-4}$ and $7 \cdot 8 \times 10^{-4}$ for Co-1, Co-2 and Co-3 samples, respectively, in good agreement with the mean values of Table 5.

TABLE 5. COMPARATIVE DATA FOR K_θ AND B MEAN VALUES

Sample	$\bar{K}_\theta \times 10^4$	$\bar{B} \times 10^{28}$
Co-1	9·8	10·6
Co-2	10·9	6·0
Co-3	8·1	9·0
PolypMOS†	6·9	7·6*

* Unpublished results.
† See ref. (9).

It can be seen that the K_θ values of copolymers are greater than the "ideal" values evaluated on the basis of the additivity rule from the unperturbed dimensions of corresponding homopolymers (K_θ of polystyrene $= 7 \cdot 9 \times 10^{-4}$). Similar results have earlier been reported for different systems: *p*-chlorostyrene–methylmethacrylate,(12) styrene–methylacrylate(11) and styrene–methylmethacrylate(16) copolymers. In the last case Dondos and Benoit observed that K_θ values were not only quite different from "ideal" values but also solvent and temperature dependent.

The copolymer unperturbed dimensions cannot be calculated unambiguously from K_θ values of Table 5, owing to the uncertainty in the value of ϕ; these dimensions however are greater for copolymers than for homopolymers.

This result might be due to overestimate of K_θ, values for which were obtained from $[\eta]$ data in a good solvent, and/or to extra short-range interactions between unlike monomeric units.

Next we examine $\bar{B}$ values of Table 5. Neglecting the absolute values, we can note that the interaction parameter increases on decreasing *p*MOS content, except for Co-2 sample for which the value is lower than in the other cases (clearly related to the low *a* value in Table 4).

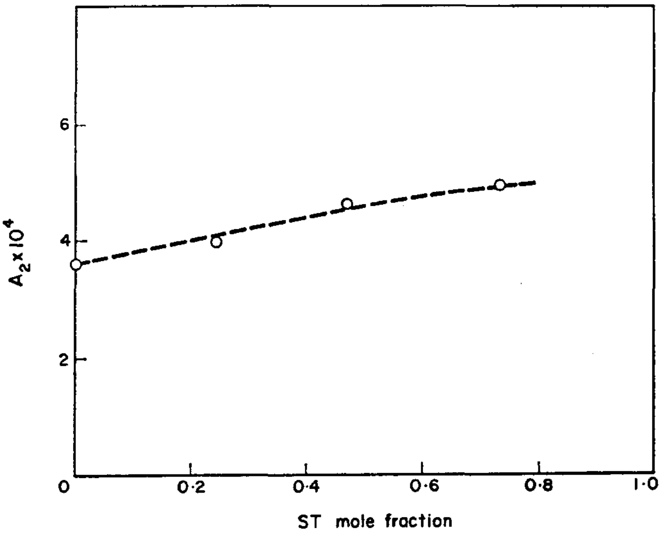

FIG. 8. Composition dependence of A_2 by light scattering in toluene at 25°. The molecular weight is taken as $2 \cdot 0 \times 10^5$.

This peculiarity contrasts with the dependence of A_2 on the composition: in fact, from light scattering measurements in toluene, we noted a gradual decrease of A_2 with increasing *p*MOS content. In Fig. 8 this change of A_2 for each composition is evident; the values are taken at a molecular weight of $2 \cdot 0 \times 10^5$.

In order to clarify the behaviour of ST-*p*MOS copolymers in more detail, more comprehensive experiments are in progress with other solvents.

Acknowledgement—We thank Professor G. Smerano for helpful discussions during this work.

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Résumé—On a effectué dans le toluène des déterminations de poids moléculaire par diffusion de la lumière et par osmométrie ainsi que des mesures de viscosité intrinsèque pour des fractions de copolymères statistiques styrène-*p*-méthoxystyrène de différentes compositions. On a comparé les relations ainsi établies entre la viscosité intrinsèque et le poids moléculaire avec celles des homopolymères parents.

On a évalué les valeurs de la constante de Flory (K_θ) et du paramètre d'interaction polymère–solvant (B) en appliquant les théories de Kurata–Stockmayer–Roig, Stockmayer–Fixman et Berry.

A partir des résultats expérimentaux, on a trouvé que les dimensions non perturbées des copolymères sont plus grandes que celles des homopolymères et que le copolymère de composition sensiblement équimoléculaire présente un comportement particulier par comparaison aux copolymères de composition différente.

Sommario—Su diverse frazioni di copolimeri "random" stirene-*p*-metossistirene a diversa composizione sono state effettuate determinazioni di peso molecolare con il metodo osmotico e di diffusione della luce e misure di viscosità in toluene.

Le relazioni $[\eta]$-M così ottenute vengono confrontate con quelle dei rispettivi omopolimeri.

Applicando le teorie di Kurata–Stockmayer–Roig, Stockmayer–Fixman e Berry sono stati calcolati i valori della costante di Flory (K_θ) e del parametro di interazione polimero–solvente (B).

In base ai dati sperimentali si è trovato che le dimensioni non perturbate dei copolimeri sono maggiori di quelle degli omopolimeri e che il copolimero a composizione intermedia mostra un comportamento particolare rispetto agli altri.

Zusammenfassung—An Fraktionen von Styrol-*p*-Methoxystyrol "statistischen" Copolymeren verschiedener Zusammensetzung wurden Molekulargewichtsbestimmungen durch Lichtstreuung und Osmometrie sowie Viskositätsmessungen in Toluol durchgeführt. Dir Viskositäts-Molekulargewichtsbeziehungen wurden aufgestellt und mit denen der entsprechenden Homopolymeren verglichen.

Die Werte für die Flory Konstante (K_θ) und der Parameter der Polymer–Lösungsmittel Wechselwirkung (B) wurden bestimmt unter Anwendung der Theorien von Kurata–Stockmayer–Roig, Stockmayer–Fixman und Berry.

Aus den experimentellen Daten ergibt sich, daß die ungestörten Dimensionen für die Copolymeren größer sind als die für die Homopolymeren und daß ein Copolymeres mit äquimolekularer Zusammensetzung im Vergleich mit Copolymeren anderer Zusammensetzung ein spezielles Verhalten zeigt.