

VINYL POLYMERIZATION

VI. Dilute Solution Properties of 1 : 1 Poly (Styrene-Co-Ethylmethacrylate)

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ABSTRACT

1:1 Poly (styrene-co-ethylmethacrylate) (PSEM) was prepared by bulk polymerization and fractionated using methylethyl ketone/petroleum ether system. IR and NMR analyses of the copolymer substantiated the composition kinetically expected. As the composition heterogeneity of the copolymer was narrow, the characterization of the copolymer was effected in a single solvent by light scattering as well as viscosity measurements at 35° C. The molecular weight dependence of $[\eta]$, the limiting viscosity number; $(\bar{r}^2)_w^{1/2}$, the *rms* end to end distance and A_2 the second virial coefficient were established. The solvent ethylacetate was found to be thermodynamically more ideal for PSEM, than for polyethylmethacrylate. In an attempt to evaluate K , the Flory's constant, application of various methods appeared to give almost similar values. In order to explain the low value of Φ , the Flory's universal parameter, rough estimates of $(\bar{r}_0^2)^{1/2}$, the unperturbed *rms* end to end distance; b , the statistical chain element; q , the persistence length and $\bar{r}_0^2/l\bar{r}_{\max}$, the semiflexibility parameter were also made.

INTRODUCTION

VERY few investigations on the dilute solution properties of copolymers are reported in the literature.¹⁻⁴ The theory of lightscattering by copolymers, constituting mass as well as composition heterogeneity was developed independently by Stockmayer *et al.*¹ and Benoit *et al.*,² for the estimation of true molecular weight and mean square radius of gyration of a copolymer by carrying out lightscattering measurements in different solvents which gave different refractive index increments, dn/dc . However, when molecular weight as well as composition heterogeneities were narrow the lightscattering measurement in a single solvent (of fairly high dn/dc value) was enough for the characterization of the copolymers in solution.

Dilute solution properties of random copolymer of styrene and methylmethacrylate in butanone were investigated by Stockmayer *et al.*,¹ while Sonja Krause² studied the solution properties of both fractionated and unfractionated block copolymer of styrene and methylmethacrylate in various solvents. Kotera *et al.*³ on the other hand investigated the effect of varying the copolymer composition on Mark-Houwink equation for poly (methylacrylate-co-methylmethacrylate)/butanone system. The solution properties of poly (styrene-co-ethylmethacrylate) (PSEM) of fixed composition (1:1) were investigated in the present work. The equations relating the molecular weight \bar{M}_w , and (a) $[\eta]$, the limiting viscosity number (b) $(\bar{r}^2)_w^{\frac{1}{2}}$ the root mean square end to end distance and (c) A_2 , the second virial coefficient were established. The evaluation of K (of Fox-Flory equation $[\eta] = KM^{\frac{1}{2}}a^3$) and $(\bar{r}_0^2)^{\frac{1}{2}}$, the unperturbed dimension, were also made.

The parameters $[\eta]$, (\bar{S}^2) and A_2 the second virial coefficient, for random copolymer of styrene and methylmethacrylate in butanone are higher than those for the component homopolymers,¹ but the block copolymer of styrene—and methylmethacrylate exhibited an opposite behaviour.³

These parameters of random poly (styrene-co-ethylmethacrylate) in ethyl acetate, however, are lower than those obtained for PEM in ethylacetate.

EXPERIMENTAL

(a) *Solvents* : Ethylacetate (BDH A.R) methylethylketone (BDH LR) petroleum ether (60–80° C., Burmah Shell Company) methanol, etc., were purified by standard procedures.

(b) *Monomers* : Ethylmethacrylate (Rohm and Haas) and styrene (Kopps) were washed thrice with NaOH (5%) followed by distilled water, dried over anhydrous Na_2SO_4 and distilled under reduced pressure (< 25 mm. of Hg) in an atmosphere of pure dry nitrogen.

(c) *Polymerization*.—Bulk copolymerization of styrene and ethylmethacrylate monomers (41.8 ml. of styrene and 68.2 ml. of ethyl methacrylate calculated from their respective reactivity ratios⁵ $r_1 = 0.65$ and $r_2 = 0.29$ for getting 1:1 copolymer) was carried out with Benzoyl peroxide (0.05–0.1 gm.) as initiator under deaerated conditions to a conversion < 10% at $72 \pm 0.1^\circ \text{C}$. The reaction mixture was taken up with methylethylketone; methanol was added; the polymer precipitated was

purified by dissolution and reprecipitation. The negligible probability of homopolymer formation was confirmed by fractional precipitation data. The volume fractions of methanol for the incipient-complete precipitation from 1% solution of various polymeric and copolymeric species (of similar molecular weight) in methylethyl ketone at 30° C. were initially found out:

Sample	Volume fraction of methanol for precipitation	
	Commencement	Completion
Poly (styrene)	0.11	0.22
Poly (ethylmethacrylate)	0.85	0.95
Poly (styrene-co-ethylmethacrylate)	0.46	0.56

A (1:1) mixture of two homopolymers was found to precipitate separately at the corresponding volume fraction of the precipitant, *i.e.*, at 0.11-0.22 and 0.85-0.95 respectively.

The copolymer was subjected to fractionation and refractionation by fractional precipitation technique using methyl ethyl ketone/petroleum ether. From fractions (10 Nos.) only 6-fractions were selected for investigation.

(*d*) *Viscosity*.—Viscosity measurements were made on filtered solvent and polymer solutions (six concentrations in the range 3×10^{-3} to 5×10^{-4} gm./ml.) with a suspended level dilution viscometer (PCL cat. No. D. 445 46T. Colchester Instruments Ltd., U.K.) at $35 \pm 0.01^\circ \text{C}$. in a constant temperature viscometer bath (Kreb's Elec. Mfg. Co., Inc., New York). The kinetic energy correction, though small, were applied to the measured flow times. The limiting viscosity number, $[\eta]$, was obtained as a mean of three $[\eta]$'s from the plots according to equations:

$$\frac{\eta_{sp.}}{C} = [\eta] + k_1 [\eta]^2 C \quad (1)$$

$$\frac{(\ln \eta_{rel.})}{C} = [\eta] - k_2 [\eta]^2 C \quad (2)$$

$$\frac{\eta_{sp.}}{C} = [\eta] + k_3 [\eta] \eta_{sp.} \quad (3)$$

(e) *Lightscattering*.—Lightscattering measurements were carried out in a Brice-Phoenix Universal lightscattering Photometer⁶ (1,000 series, Phoenix Precision Instruments Company, Philadelphia) at $35 \pm 0.5^\circ \text{C}$. using unpolarized light ($\lambda = 4356 \text{ \AA}$) with solvent or solutions centrifuged, filtered and then refiltered direct into the circular cell through pyrex sintered glass crucible (G_3 porosity 1.4μ) at various angles ($45\text{--}135^\circ$). dn/dc for PSEM/ethyl acetate system measured by means of Brice-Phoenix differential refractometer⁷ (Phoenix Precision Instruments Co., Philadelphia) was found to be $0.164, \pm 0.002$ at $\lambda = 4356 \text{ \AA}$.

The lightscattering data were treated according to Zimm.⁸ Plots of HC/τ vs. $\sin^2(\theta/2) + 1,000 C$ were made and extrapolated to get $(HC/\tau)_{c=0}$ for various angles. An estimate of \bar{M}_w/\bar{M}_n for one of the copolymer fractions was made by measuring the \bar{M}_n (2.8×10^5) in an Osmometer (Pinner-Stabin, Colchester Instruments Ltd., U.K.) and found to be 1.16. Hence the value of $h = 4$ was assumed without much error. The plot of $(HC/\tau)_{c=0}$ vs. $\sin^2(\theta/2)$ was first smoothly extrapolated and then corrected for molecular weight heterogeneity according to Zimm⁸ (Table X in Ref. 8). The molecular weight \bar{M}_w and the Z' average mean square radius of gyration $(\bar{S}^2)_{Z'}$, were then obtained from the reciprocal of the intercept on the ordinate, and the ratio of initial slope to intercept of the corrected $(HC/\tau)_{c=0}$ vs. $\sin^2(\theta/2)$ plot respectively. The translation of Z' average mean square radius of gyration $(\bar{S}^2)_{Z'}$ into $(\bar{r}^2)_w$ was effected⁹ by

$$(\bar{r}^2)_w = (\bar{S}^2)_{Z'} \frac{(h+1)}{(h+2+\beta)} \cdot (3+\beta)(2+\beta) \quad (4)$$

where: $h = 1/[(\bar{M}_w/\bar{M}_n) - 1]$ and $3 = (2a - 1)/3$ (a = molecular weight exponent in the Mark-Houwink equation $[\eta] = (K^1 M^a)$).

(f) *Analysis of the copolymer*.—The composition of the copolymer was estimated from IR measurements (Perkin Elmer IR spectrophotometer) on 2% solution of the polymer in chloroform using KCl crystal, and NMR analysis of the copolymer in CHCl_3 using Tetramethylsilane as an internal standard (Figs. 1 and 2).

RESULTS AND DISCUSSION

Composition of the copolymer.—From the copolymerization kinetics, the composition of instantaneous copolymer is given¹⁰ by

$$\frac{m_1}{m_2} = \left(\frac{M_1}{M_2}\right) \frac{M_1 r_1 + M_2}{M_2 r_2 + M_1} \quad (5)$$

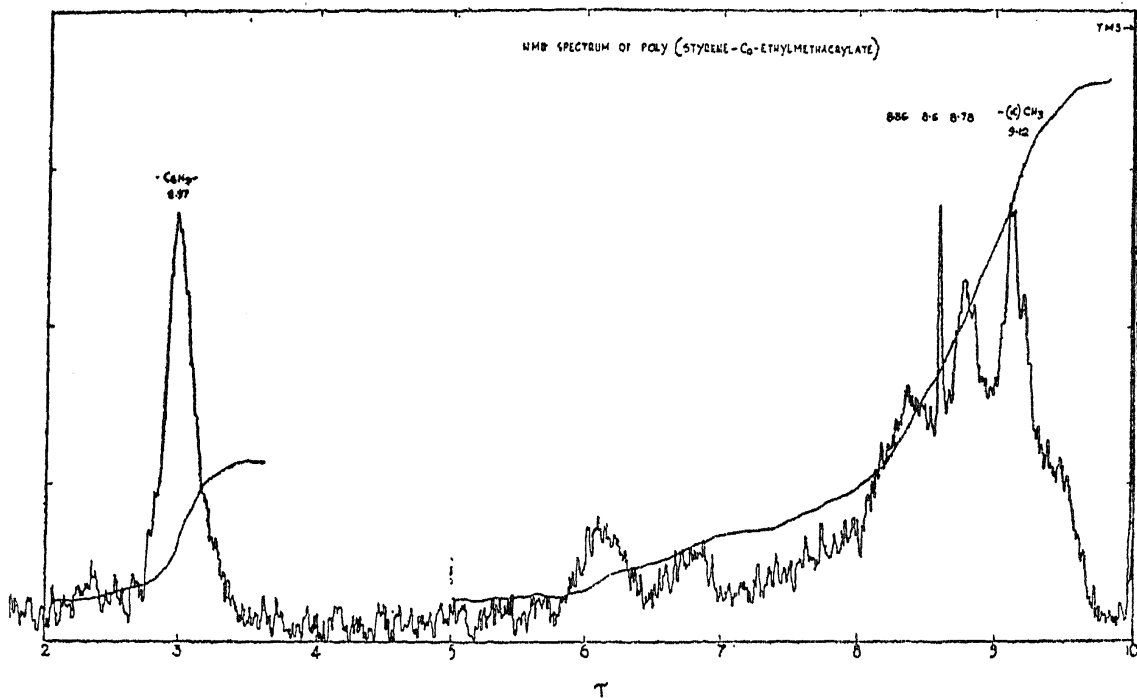


FIG. 1. NMR spectrum of (1:1) poly (styrene-co-ethylmethacrylate).

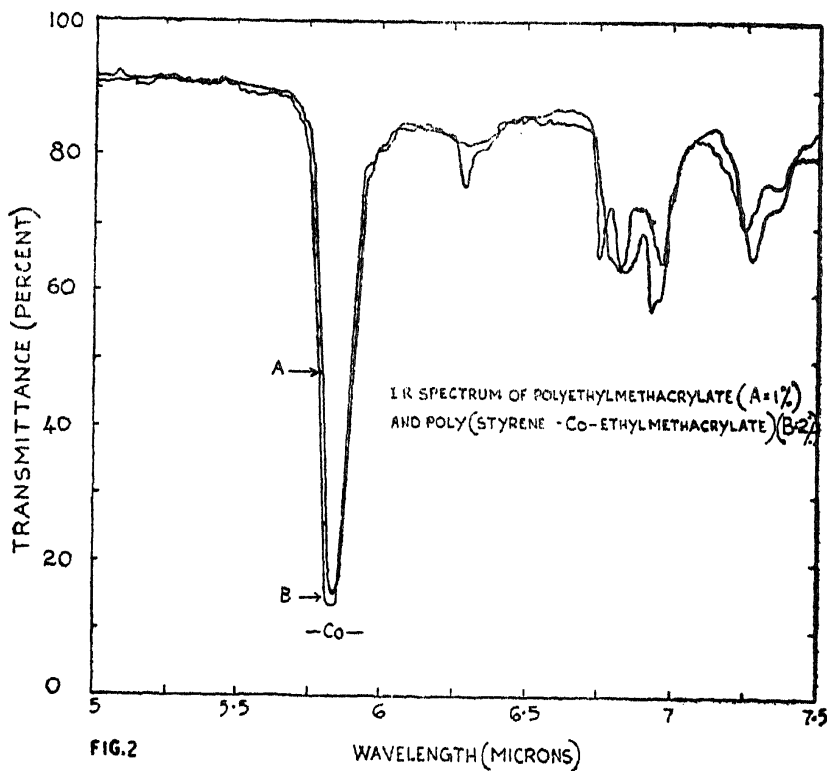


FIG. 2. IR spectra of polyethylmethacrylate (1%) and (1:1) poly (styrene-co-ethylmethacrylate) (2%).

where m_1/m_2 is the ratio of monomer units present in the copolymer, and M_1 and M_2 are the initial concentration of monomers with respective reactivity ratio r_1 and r_2 . Since the conversion was only less than 10%, justifying the use of equation 5, the value of m_1/m_2 with known M_1 M_2 .

r_1 and r_2 , was obtained to be = 1. The NMR¹¹ and IR analyses of the copolymer were performed with a view to ascertain the composition as well as the microstructure of the copolymer. The NMR spectrum of one of the samples showed the phenyl proton peak at 2.97 τ and the $-\text{C}-\text{CH}_2-$ proton peak at 6.11 τ and 6.65–6.9 τ . The relative areas of these peaks showed a higher percentage of styrene units ($\approx 60\%$) in the copolymer than expected (50%). But the estimation of α -methyl proton peak area was not possible due to poor resolution of the spectrum. However the NMR spectrum of PSEM gave an insight into the microstructure of the copolymer, as the phenyl proton peak at 2.97 τ showed no shoulder at 3.11 to 3.3 τ which is characteristic of orthoproton effect¹¹ when the sequence length of styrene units exceed 5, proving, thereby, the sequence length of styrene units to be < 5 , i.e., nearly alternating nature of the copolymer. IR spectra of a 2% solution of the copolymer, and 1% solution of poly (ethylmethacrylate) in CHCl_3 were recorded on the same paper (Fig. 2). A perfect overlap of the $> \text{C} = \text{O}$ absorption peak at 5.75 μ indicated the composition of the copolymer to be 1:1. Being a low conversion copolymer, the solution properties of the copolymer were characterized only in a single solvent of fairly high dn/dc .

Solution properties. : (i) $[\eta]$ (67.7 to 105.7 ml gm.⁻¹) for PSEM/ethyl acetate at 35° C. obtained as the mean of $[\eta]$'s from equations (1), (2) and (3) are given in Table 1, along with the Huggins's constant k_1 (0.29 ± 0.06) and the value of $(k_1 - k_2)$ was found to be 60.49 ± 0.015 as expected (Table I).

TABLE I

Polymer : Poly (styrene-co-ethylmethacrylate)
Solvent : ethylacetate
Temperature : 35° C.

$dn/dc = 0.164 \pm 0.002$
 $\lambda = 4356 \text{ \AA}$

Fraction	$[\eta]$ ml. gm. ⁻¹	k_1	M_w $\times 10^{-5}$	$(\bar{r}^2)_w^{\frac{1}{2}}$ \AA	$(\bar{r}_0^2)^{\frac{1}{2}}$ \AA	α	Φ $\times 10^{-23}$	$A_2 \times 10^4$ c.c. mole gm. ⁻²
PSEM ₁	.. 67.7	0.35	2.872	0.81
PSEM ₂	.. 69.4	0.25	3.256	602	578	1.041	1.11	0.95
PSEM ₃	.. 72.2	0.22	4.019	632	610	1.036	1.13	0.72
PSEM ₄	.. 77.8	0.27	4.312	650	632	1.044	1.13	0.65
PSEM ₅	.. 85.3	0.33	4.763	707	657	1.076	1.15	0.34
PSEM ₆	.. 105.7	0.29	6.226	750	696	1.077	1.55	0.61

(ii) The molecular weight \bar{M}_w , $(\bar{r}^2)_w^{\frac{1}{2}}$, and A_2 the second virial coefficient obtained from light scattering are given in Table I. The following relationships for PSEM/ethyl acetate at 35° C in the molecular weight range ($M_w = 2.8 \times 10^5$ to 6.2×10^5) were established (Fig. 3):

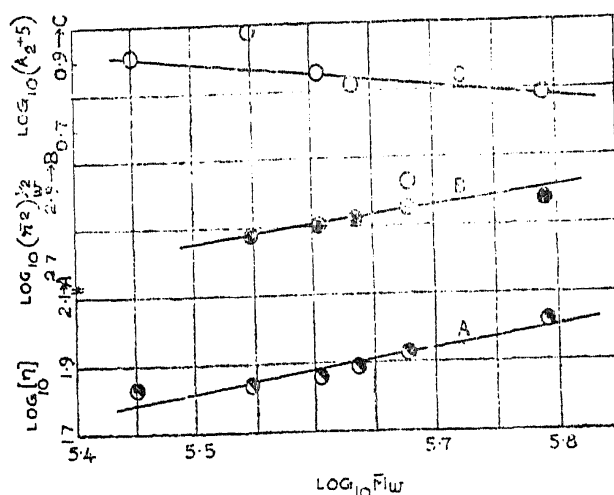


FIG. 3. (A) Plot of $\log_{10} [\eta]$ vs. $\log_{10} \bar{M}_w$, (B) Plot of $\log_{10} (\bar{r}^2)_w^{\frac{1}{2}}$ vs. $\log_{10} \bar{M}_w$, (C) Plot of $\log_{10} A_2$ vs. $\log_{10} \bar{M}_w$.

$$(i) \quad [\eta] = 3.25 \times 10^{-2} \bar{M}_w^{0.59} \quad (5)$$

$$(ii) \quad (\bar{r}^2)_w^{\frac{1}{2}} = 0.33 \bar{M}_w^{0.54} \quad (6)$$

The low values of the exponent of \bar{M}_w [Equations (5) and (6)] for the copolymer compared to those (0.71 and 0.56) for poly (ethylmethacrylate)/ethylacetate system¹² at 35° C. indicated the reduced thermodynamic interaction between PSEM chain and ethyl acetate. The value of A_2 was low because of the more ideal nature of ethylacetate towards PSEM, than one of its component homopolymer, *i.e.*, poly (ethylmethacrylate).

(iii) The molecular weight dependence of A_2 was given by,

$$A_2 = 0.84 \times 10^{-3} \bar{M}_w^{-0.38}.$$

(iv) Evaluation of Flory constant K was effected as for homo polymers by three methods based on (a) Flory-Fox,¹³ (b) Kurata-Stockmayer¹⁴ and (c) Stockmayer and Fixman¹⁵ expressions. The value of K obtained by the methods (b) and (c) were fairly in good agreement (10.2×10^{-2} and 9.9×10^{-2}) while that from (a) was slightly higher (11.9×10^{-2}); For the calculation of unperturbed dimension, however, a mean value of K (10.67×10^{-2}) was employed. The high value of K (10.67×10^{-2})

for PSEM/ethylacetate at 35° C. compared to that for the component homopolymers at this temperature [poly (styrene)¹⁶ 7×10^{-2} and poly (ethyl methacrylate)¹² 5.6×10^{-2}] pointed to the extension of the polymeric chain (PSEM) mainly as a result of steric effects.

(v) The value of the unperturbed dimension $(\bar{r}_0^2)^{\frac{1}{2}}$ of the co-polymer was found out from K and Φ values from the relation

$$K = \Phi (\bar{r}_0^2/M)^{3/2}.$$

Use of the accepted value of Φ (2.1×10^{23}) would yield a low value for this dimension and consequently a high value of α , (linear expansion factor) which is inconsistent with the observed low value of A_2 . Hence Φ (1.11×10^{23} to 1.55×10^{23}) obtained in this investigation were used and a rough estimate of $(\bar{r}_0^2)^{\frac{1}{2}}$ and α , were obtained. Low values of the universal parameter, Φ , were reported in the studies on block copolymer of styrene and methylmethacrylate,³ and also in some homopolymer systems.¹⁷ This may probably be due to the composition heterogeneity present in the copolymer. The extension of polymeric chain due to long range as well as steric effects $(\bar{r}^2)^{\frac{1}{2}} (\bar{r}_f^2)^{\frac{1}{2}}$ (3.35–3.48), the extension of the chain due to steric effect alone, $(r_0^{-2}/\bar{r}_f^2)^{\frac{1}{2}}$ (3.25), the statistical chain element, b (7.1 Å) obtained from the slope of $(\bar{r}_0^2)^{\frac{1}{2}}$ vs. $(2DP)^{\frac{1}{2}}$ ($DP =$ degree of polymerization), the parameter $\bar{r}_0^2/i r_{max}$ (4.86) calculated from the semi-flexible chain treatment of Flory¹⁸ and the persistence length 'q' of Kratky and Porod¹⁹ (23.4 Å) evaluated from Benoits' equation,²⁰ indicated that the coil of PSEM was considerably stiff.

The higher values of these parameters being partly due to composition heterogeneity cannot be altogether neglected.

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