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; \((\bar{r}^2)_0^{\frac{1}{2}}\), 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 \(\Phi\), the Flory’s universal parameter, rough estimates of \((\bar{r}_0^2)^\frac{1}{2}\), the unperturbed \(rms\) end to end distance; \(b\), the statistical chain element; \(q\), the persistence length and \(\bar{r}_0^2/\bar{r}_{max}\), the semiflexibility parameter were also made.

INTRODUCTION

Very few investigations on the dilute solution properties of copolymers are reported in the literature.\(^1\)-\(^3\) 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 Krause\(^2\) 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 (methacrylate-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) \((r^2)_w\) 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 \([\eta] = KM^4_{\infty} a^3\)) and \((r^2)_w\), the unperturbed dimension, were also made.

The parameters \([\eta]\), \((S^2)\) 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 AR) methylethylketone (BDH LR) petroleum ethyl (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\(_2\)SO\(_4\) 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 ratios\(^5\) \(r_1 = 0.65\) 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 ± 0.1°C. The reaction mixture was taken up with methylethylketone; methanol was added; the polymer precipitated was
purified by dissolution and precipitation. 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:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fraction of methanol for precipitation</th>
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</thead>
<tbody>
<tr>
<td>Poly (styrene)</td>
<td>Commencement: 0.11 Completion: 0.22</td>
</tr>
<tr>
<td>Poly (ethylmethacrylate)</td>
<td>Commencement: 0.85 Completion: 0.95</td>
</tr>
<tr>
<td>Poly (styrene-co-ethylmethacrylate)</td>
<td>Commencement: 0.46 Completion: 0.56</td>
</tr>
</tbody>
</table>

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 methylethyl 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 $3 \times 10^{-3}$ to $5 \times 10^{-4}$ gm./ml.) with a suspended level dilution viscometer (PCL cat. No. D. 445 46T. Colchester Instruments Ltd., U.K.) at 35 ± 0.01°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, $\eta_1$, was obtained as a mean of three $\eta_1$'s from the plots according to equations:

$$\eta_{sp.} = \frac{\eta}{C} + k_1 \frac{\eta^2}{C}$$  \hspace{1cm} (1)

$$\ln \left( \frac{\eta}{C} \right) = \frac{\eta}{C} - k_2 \frac{\eta^2}{C}$$ \hspace{1cm} (2)

$$\frac{\eta_{sp.}}{C} = \frac{\eta}{C} + k_2 \frac{\eta^2}{C}$$ \hspace{1cm} (3)
(e) Lightscattering.—Lightscattering measurements were carried out in a Brice-Phoenix Universal lightscattering Photometer (1,000 series, Phoenix Precision Instruments Company, Philadelphia) at 35 ± 0.5°C using unpolarized light (λ = 4356 Å) with solvent or solutions centrifuged, filtered and then refiltered directly into the circular cell through pyrex sintered glass crucible (G, porosity 1.4 µ) at various angles (45-135°). dn/dc for PSEM/ethyl acetate system measured by means of Brice-Phoenix differential refractometer (Phoenix Precision Instruments Co., Philadelphia) was found to be 0.164, ± 0.002 at λ = 4356 Å.

The lightscattering data were treated according to Zimm. Plots of HC/τ vs. sin²(θ/2) + 1,000 C were made and extrapolated to get (HC/τ)∞ 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 × 10⁶) 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/τ)∞ vs. sin²(θ/2) was first smoothly extrapolated and then corrected for molecular weight heterogeneity according to Zimm (Table X in Ref. 8).

The molecular weight \( \bar{M}_w \) and the \( Z' \) average mean square radius of gyration (\( \bar{S}^2 \)) were then obtained from the reciprocal of the intercept on the ordinate, and the ratio of initial slope to intercept of the corrected (HC/τ)∞ vs. sin²(θ/2) plot respectively. The translation of \( Z' \) average mean square radius of gyration (\( \bar{S}^2 \)) into (\( \bar{P}^2 \)) was effected by

\[
(\bar{P})_w = (\bar{S}^2)_w \frac{(h + 1)}{(h + 2 + \beta)(3 + \beta)(2 + \beta)}
\]

where \( h = 1.1[(\bar{M}_w/\bar{M}_n) - 1] \) and \( \beta = (2a - 1), 3(a = \text{molecular weight exponent in the Mark-Houwink equation} [\eta] = (K\bar{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 CHCl₃ 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 given by

\[
\frac{m_1}{m_2} = \left( \frac{M_1}{M_2} \right) \frac{M_1r_1 + M_2}{M_2r_2 + \bar{M}_1}
\]
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 $M_1$, $M_2$, 

**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%).
and \( r_2 \) were obtained to be \( = 1 \). The NMR\(^{11} \) 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\( \tau \) and the -C-CH\(_2\)-proton peak at 6.11\( \tau \) and 6.65-6.9\( \tau \). 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 \( \alpha \)-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\( \tau \) showed no shoulder at 3.11 to 3.3\( \tau \) which is characteristic of orthoproton effect\(^{11} \) 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 > C = O absorption peak at 5.75\( \mu \) 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\(^\circ\) 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 \( \pm \) 0.06) and the value of \( (k_1 - k_2) \) was found to be 60.49 \( \pm \) 0.015 as expected (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Polymer : Poly (styrene-co-ethylmethacrylate)</th>
<th>Solvent : ethylacetate</th>
<th>( dn/dc = 0.164 \pm 0.002 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature : 35(^\circ) C.</td>
<td>( \lambda = 4356 \AA )</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction</th>
<th>([\eta] ) ml. gm(^{-1})</th>
<th>( k_1 \times 10^{-5} )</th>
<th>( (\rho^2)^{1/2} \times 10^{-5} )</th>
<th>( (\rho_0^2)^{1/2} \times 10^{-28} )</th>
<th>( \alpha )</th>
<th>( \Phi \times 10^4 ) c.c. mole gm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSEM(_1)</td>
<td>67.7</td>
<td>0.35</td>
<td>2.872</td>
<td></td>
<td></td>
<td>0.81</td>
</tr>
<tr>
<td>PSEM(_2)</td>
<td>69.4</td>
<td>0.25</td>
<td>3.256</td>
<td>602</td>
<td>578</td>
<td>1.041</td>
</tr>
<tr>
<td>PSEM(_3)</td>
<td>72.2</td>
<td>0.22</td>
<td>4.019</td>
<td>632</td>
<td>610</td>
<td>1.036</td>
</tr>
<tr>
<td>PSEM(_4)</td>
<td>77.8</td>
<td>0.27</td>
<td>4.312</td>
<td>650</td>
<td>632</td>
<td>1.044</td>
</tr>
<tr>
<td>PSEM(_5)</td>
<td>85.3</td>
<td>0.33</td>
<td>4.763</td>
<td>707</td>
<td>657</td>
<td>1.076</td>
</tr>
<tr>
<td>PSEM(_6)</td>
<td>105.7</td>
<td>0.29</td>
<td>6.226</td>
<td>750</td>
<td>696</td>
<td>1.077</td>
</tr>
</tbody>
</table>
(ii) The molecular weight $\bar{M}_w$, $(\bar{\rho}^2)_w$, 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 $(M_w = 2.8 \times 10^5 \ldots 6.2 \times 10^5)$ were established (Fig. 3):

$$[\eta] = 3.25 \times 10^{-2} \bar{M}_w^{0.59}$$  \hspace{1cm} (5)

$$A_2 = 0.33 \bar{M}_w^{0.54}$$  \hspace{1cm} (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 system 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 ($10.2 \times 10^{-2}$ and $9.9 \times 10^{-2}$) while that from (a) was slightly higher ($10.9 \times 10^{-2}$); For the calculation of unperturbed dimension, however, a mean value of $K (10.67 \times 10^{-2})$ was employed. The high value of $K (10.67 \times 10^{-2})$
for PSEM/ethylacetate at 35°C, compared to that for the component homopolymers at this temperature [poly (styrene) \(16 \times 10^{-2}\) and poly (ethyl methacrylate) \(5.6 \times 10^{-2}\)] pointed to the extension of the polymeric chain (PSEM) mainly as a result of steric effects.

(v) The value of the unperturbed dimension \((\bar{r}_0)^d\) of the co-polymer was found out from \(K\) and \(\Phi\) values from the relation

\[
K = \frac{1}{\Phi} \frac{(\bar{r}_0)^d}{M} \frac{1}{r_{\text{max}}^2}
\]

Use of the accepted value of \(\Phi (2.1 \times 10^{28})\) would yield a low value for this dimension and consequently a high value of \(\alpha\) (linear expansion factor) which is inconsistent with the observed low value of \(A_2\). Hence \(\Phi (1.11 \times 10^{28} \text{ to } 1.55 \times 10^{28})\) obtained in this investigation were used and a rough estimate of \((\bar{r}_0)^d\) and \(\alpha\) were obtained. Low values of the universal parameter, \(\Phi\), were reported in the studies on block copolymer of styrene and methylmethacrylate, and also in some homopolymer systems. 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 \((\bar{r}_0)^d (\bar{r}_f)^d (3.35-3.48)\), the extension of the chain due to steric effect alone, \((r_0^{-2}/\bar{r}_f^{-2})^{\frac{1}{3}} (3.25)\), the statistical chain element, \(b (7.1 \text{ Å})\) obtained from the slope of \((\bar{r}_0)^d\) vs. (2DP)\(^{\frac{1}{2}}\) (DP = degree of polymerization), the parameter \(\bar{r}_0^{-2}/r_{\text{max}}^2 (4.86)\) calculated from the semi-flexible chain treatment of Flory\(^{18}\) and the persistence length ‘\(q\)’ of Kratky and Porod\(^{19}\) (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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REFERENCES


Moore, L. D., Jr., Fixman, M. and Epstein, B. N.
Vinyl Polymerization—VI

2. (a) Bushuk, W. and Benoit, H. 
   (b) Leng, M. and Benoit, H. 
   J. Polymer Sci., 1962, 57, 263.

3. (a) Sonja Krause 
   (b) ———— 
   Ibid., 1964, 68, 1948.

4. Kotera, A., Saito, T., Watanabe, Y. and Ohama, M. 

5. Young, J. 


7. ——— and Speiser, R. 
   Ibid., 1946, 36, 363.

8. Zimm, B. H. 

9. Cleland, R. L. 
   J. Polymer Sci., 1953, 27, 249.

10. Alfrey, T., Bohrer, J. and Mark, H. 
    Copolymerisation, High Polymer Series, Interscience, N.Y. 
    1952, p. 10.

11. (a) Bovey, F. A., Tiers, G. V. D. and Fillipovich, G. 
    J. Polymer Sci., 1959, 38, 73.
   (b) Ito, K. and Yamashita, Y. 
    Ibid., 1965, B 3, 625.

12. Karunakaran, K. and Santappa, M. 

13. Flory, P. J. and Fox, T. G., Jr. 


15. Stockmayer, W. H. and Fixman, M. 
    J. Polymer Sci., 1963, C 1, 137.

    Ibid., 1956, 22, 527.

17. (a) Trementozzi, Q. A. 
    Ibid., 1959, 36, 113.
   (b) Jennings, B. R. and Jerrard, H. G. 
    Ibid., 1964, A 2, 4517.

18. Flory, P. J. 

19. (a) Kratky and Porod, G. 
   (b) Porod, G. 
    Monatsch. Chem., 1949, 80, 251.

20. Benoit, H. and Doty, P. 