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Plasma-Induced Polymerization

10. On the Heterogeneity and Excluded-Volume Effect of Methyl Methacrylate-Styrene Copolymers

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SUMMARY

Light scattering method was used to study the heterogeneity of chain composition and the polydispersity of 50:50 ultrahigh molecular weight random methyl methacrylate - styrene copolymers obtained by plasma-induced copolymerization.

INTRODUCTION

In a previously published paper, the synthesis of ultrahigh molecular weight methyl methacrylate - styrene 50:50 random copolymers by plasma-induced copolymerization was reported (SIMIONESCU et al., 1982). The present communication is concerned with the characterization of the obtained copolymers by light scattering technique. The heterogeneity of chain composition was studied based on the data concerning the influence of the solvent on the molecular weight of the copolymer.

It is well known that the light scattering method operates with the so-called particle scattering function $P(\theta)$ which depends on both particle size and shape, and on the scattering angle θ. According to the Debye theory (STACEY, 1956), the analysis of the $P(\theta)$ function (calculated from experimental results) allows the evaluation of the polydispersity of the studied polymer. So, for a linear gaussian chain, the $P(\theta)$ function is given by (1)

$$yu^2 = (2/A^2)\int_0^\infty \frac{f(M)}{M}\, e^{-AuM}\, dM - (2/A^2)\int_0^\infty \frac{f(M)}{M}\, dM + \frac{2}{A}\, u$$

where

$$y = \bar{M}_w\, P(\theta) = (R_\theta/Kc)_{c=0} \qquad (2)$$

$$u = (4\pi/\lambda)^2 \sin^2(\theta/2) \qquad (3)$$

$$A = \langle S_0^2\rangle/M \qquad (4)$$

and $f(M)$ is the weight distribution of molecular weights in the sample, θ is the scattering angle, λ is

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the wavelength of incident light in the solution, $\langle S_o^2 \rangle$ is the unperturbed mean-square radius of gyration of a monodisperse sample with molecular weight M, so that A is a constant for the polymer under consideration.

For high-average molecular weights, the first term on the right-hand side of equation (1) may be neglected in comparison with the remaining two terms when the values of u are sufficiently large, and

$$yu^2 = \frac{-2}{A^2 \bar{M}_n} + \frac{2}{A} u \qquad (5)$$

where $\bar{M}_n$ is the number-average molecular weight, given by

$$\bar{M}_n = 1/(\int_0^\infty \frac{f(M)}{M} dM)$$

These equations were used to estimate the polydispersity ($\bar{M}_w/\bar{M}_n$) of two samples.

The excluded-volume effect was discussed in terms of the two-parameter theory.

EXPERIMENTAL

Six 50:50 random methyl methacrylate - styrene copolymer samples were studied in dioxane (D), methyl ethyl ketone (MEK) and cyclohexanol (C), on a P.C.L. Peaker apparatus, at 20°C (D and MEK solutions) and 68.6°C (C solutions), using measurements ranging from 40 to 140° at 4360 Å.

The indexes of refraction increments were determined on a Zeiss interferometer, for the same wavelengths and temperatures.

The experimental precision in the determination of weight-average molecular weights was ± 10%, and in the determination of refractive index increments, ± 1.5%.

RESULTS AND DISCUSSION

1. Heterogeneity of chain composition

Weight-average molecular weights ($\bar{M}_w$), obtained in D, MEK and C, were determined by using Zimm plots and according to BERRY's method (1966).

Figure 1 presents the angular dependence of reciprocal square root of reduced scattering intensity for sample 1 (Table 1), at four copolymer concentrations, in D, at 20°C. Figure 2 shows the reciprocal square root of reduced scattering intensity as a function of polymer concentration (sample 1, D, 20°C) at fixed scattering angles. These plots allow a better estimation of the weight-average molecular weights, of the second virial coefficient and of the radius of gyration.

Table 1 presents the $\bar{M}_w$ values of the studied samples. One can see that plasma-induced copolymerization method led to ultrahigh molecular weight copolymers; it

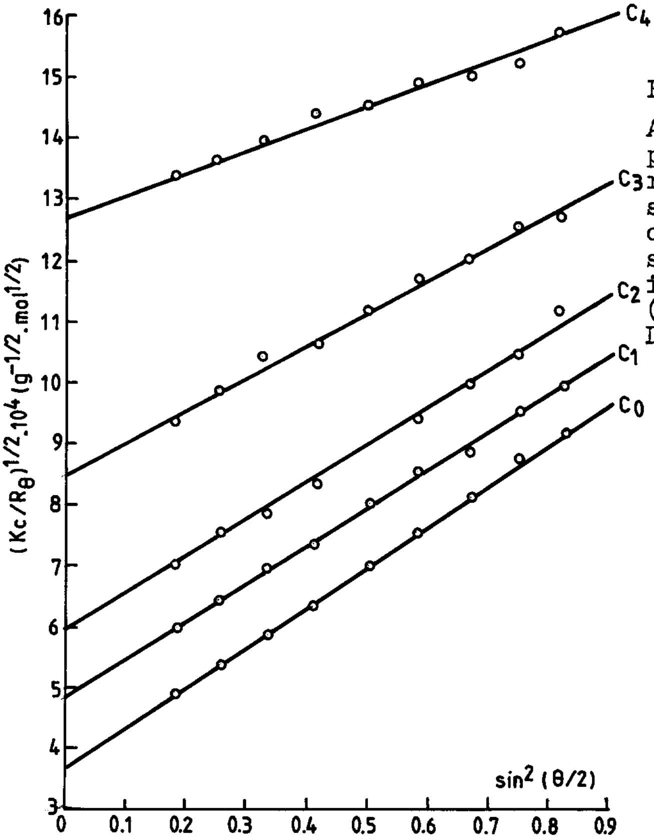


Figure 1. Angular dependence of reciprocal square root of reduced scattering intensity (sample 1, D, 20°C)

TABLE 1

Weight-average molecular weights of the copolymers

Sample	$\overline{M}_w$ $(x10^{-6})$ D	 MEK	 C
1	7.370	7.323	
2	18.423	17.974	18.321
3	20.470	20.175	
4	36.846	39.544	37.250
5	55.269	57.668	
6	67.551	65.966	

also appears that, for the same sample, only small differences are noted (within the experimental errors) for the molecular weights determined in the three solvents. Considering, in addition, that the copolymerization yields were lower than 3%, one can conclude that the copolymers have a very small compositional hetero-

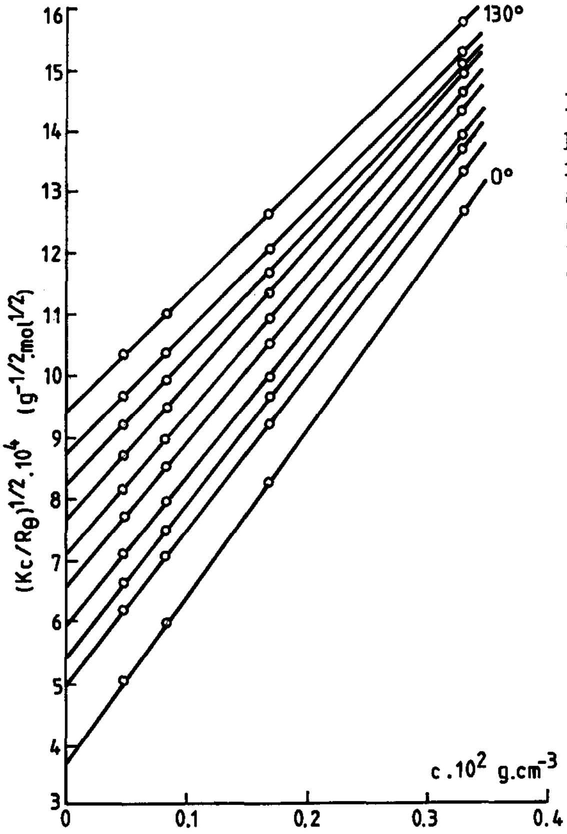


Figure 2.
Reciprocal square root of reduced scattering intensity as a function of copolymer concentration (sample 1, D, 20°C)

geneity, as observed for methacrylonitrile - - styrene copolymers obtained in similar conditions (IOAN et al., 1982). Detailed results concerning this aspect of copolymers obtained by plasma-induced polymerization will be described in a later paper

2. Molecular weight heterogeneity

To obtain some data on the polydispersity of methyl methacrylate - styrene copolymers, samples 2 and 4 were studied in cyclohexanol, at 68.6°C, temperature which corresponds to the unperturbed state.
Figure 3, which illustrates the reciprocal square root of reduced scattering intensity at zero scattering angle as a function of concentration for the two copolymers, in D and MEK at 20°C, and in C at 68.6°C, shows that the second virial coefficient is 0 in this solvent, at the mentioned temperature.
To estimate the number-average molecular weight of the studied copolymers, as well as the unperturbed radius of gyration, yu^2 was represented as $yu^2 = f(u)$ (Figure 4), according to equation 5.
The values of $\overline{M}_n$, A, $\overline{M}_w/\overline{M}_n$ and $\langle S_o^2\rangle^{1/2}$ for all methyl methacrylate - styrene copolymers, obtained in cyclohexanol, at θ temperature (68.6°C), are given in Table 2. Part of $\langle S_o^2\rangle^{1/2}$ values were obtained by using the average value of A.

TABLE 2

$\overline{M}_n$, A, $\langle S_o^2\rangle^{1/2}$ and $\overline{M}_w/\overline{M}_n$ values obtained for the studied copolymers, in C, at 68.6°C

Sample	$\overline{M}_n$ ($\times 10^{-6}$)	A (cm^2) ($\times 10^{18}$)	$\langle S_o^2\rangle^{1/2}$ (Å)	$\overline{M}_w/\overline{M}_n$
1			749*	
2	11.268	7.692	1187	1.626
3			1244*	
4	24.890	7.576	1680	1.497
5			2068*	
6			2244*	
average value of A =		7.634		

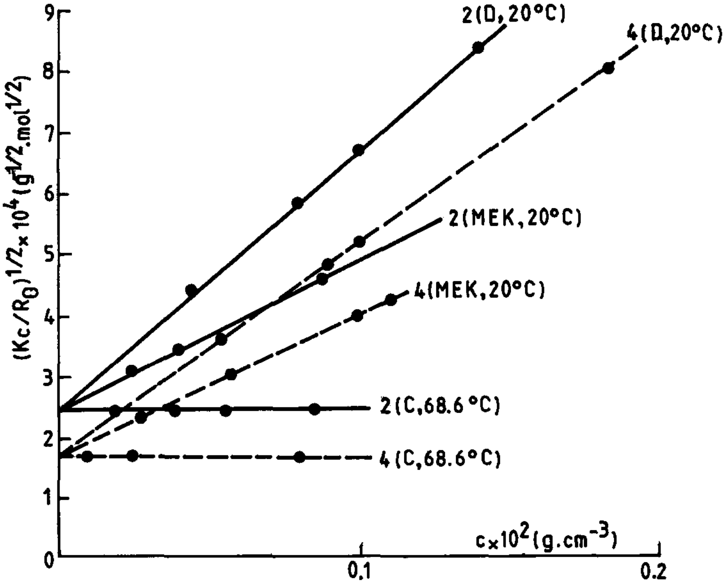
* - data obtained from the average value of A

The values obtained for $\overline{M}_w/\overline{M}_n$ ratio indicate a quite narrow polydispersity of the copolymers obtained by plasma-induced polymerization.

Further results will prove that this new method of polymer synthesis may be used to obtain uniform molecular weight ("monodisperse") polymers and copolymers.

Figure 3.

Reciprocal square root of reduced scattering intensity at zero scattering angle as a function of concentration, for samples 2 (——) and 4 (– –), in the three solvents



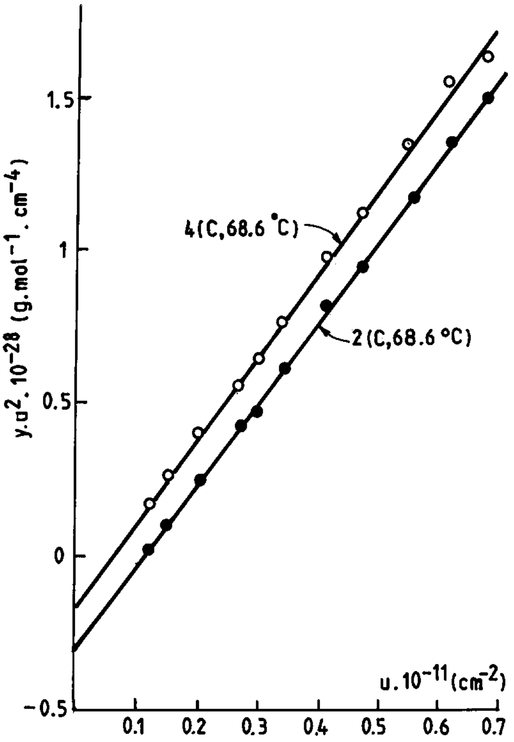


Figure 4.
Plots of yu^2 vs. u for samples 2 and 4 in cyclohexanol, at 68.6°C

3. Excluded-volume effect

The excluded-volume effect in diluted polymer solutions is generally discussed in terms of the expansion factor α_s^2 and of the interpenetration function ψ (YAMAKAWA, 1971):

$$\alpha_s^2 = \langle S^2\rangle/\langle S_o^2\rangle \tag{6}$$

$$\psi = A_2M^2/4\ {}^{3/2}N_A\langle S^2\rangle^{(3/2)} \tag{7}$$

where A_2 is the second virial coefficient, S^2 is the perturbed mean-square radius of gyration, N_A is the Avogadro number. According to the two-parameter theory, α_s^2 and ψ are dependent of the excluded-volume parameter, Z, defined by

$$Z = (1/4\pi)^{3/2}(B/A^{3/2})M^{1/2} \tag{8}$$

where $B = \beta/M_o$, β is the binary cluster integral for interaction at great distance, and M_o is the molar weight of a repeat unit of the polymer.
Theoretical investigations established some equations giving the dependence of the expansion factor on the excluded-volume parameter, equations which were used in many papers (FLORY, 1949; YAMAKAWA and TANAKA, 1967; DOMB and BARRETT, 1967). In our studies, we exa-

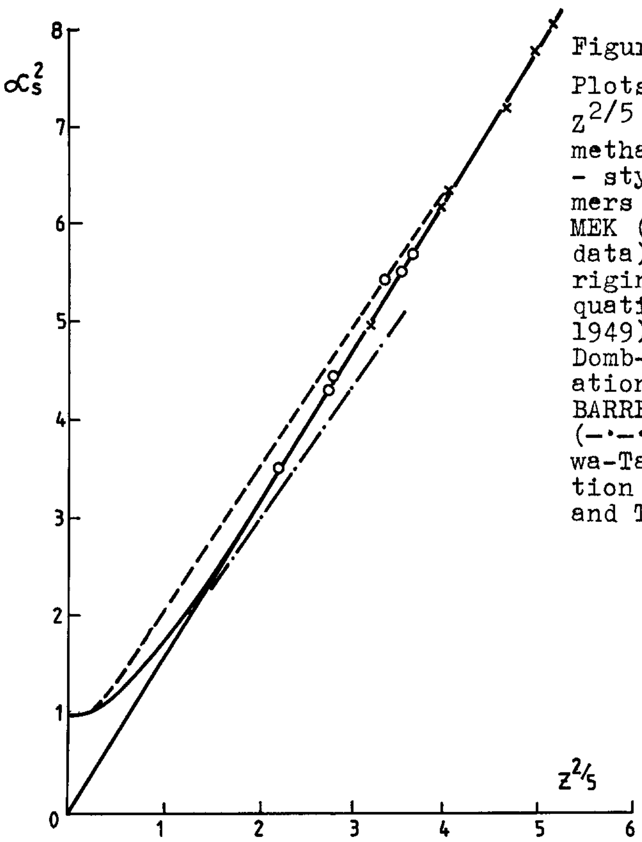


Figure 5.
Plots of α_s^2 vs. $z^{2/5}$ for methyl methacrylate - - styrene copolymers in D (o) and MEK (x) (present data); (- - -) original Flory equation (FLORY, 1949); (———), Domb-Barrett equation (DOMB and BARRETT, 1967); (—·—·—·), Yamakawa-Tanaka equation (YAMAKAWA and TANAKA, 1967)

mined these dependence according the relation of DOMB and BARRETT (1967):

$$\alpha_s^2 = (1.53 \pm 0.01)z^{2/5}$$

using the unperturbed dimensions determined in C. The results are presented in Table 3.

TABLE 3

$\langle S^2\rangle^{1/2}$ and α_s^2 values obtained in D and in MEK

	$\langle S^2\rangle^{1/2}$ (Å)		α_s^2	
Sample	D	MEK	D	MEK
1	1414	1675	3.5	5.0
2	2498	2956	4.4	6.2
3	2638	3147	4.5	6.4
4	3831	4507	5.2	7.2
5	4872	5775	5.5	7.8
6	5357	6346	5.7	8.0

To verify the theoretical foresights (YAMAKAWA, 1971) the values of Z were calculated from equation 9. Figure 5 collects the data in the form of α_S^2 plotted against $Z^{2/5}$, also including literature data (MIYAKI et al., 1978).
By using equation 8, the interaction parameter at great distance was calculated. The value obtained for the binary cluster integral, in D, $\beta = 30 \cdot 10^{-24}$ cm^3, is in good agreement with literature data.
To conclude, light scattering data showed that the copolymers present a small compositional and molecular weight polydispersity. The values of β, Z and $\langle S_0^2 \rangle^{1/2}$ were determined and proved to correspond to the theory of linear flexible polymers.

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