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Plasma-Induced Polymerization

8. The Heterogeneity of Chain Composition of Methacrylonitrile-Styrene Copolymers

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SUMMARY

Light scattering method was used to study the heterogeneity of chain composition of statistical methacrylonitrile - styrene copolymers obtained by plasma-induced copolymerization.

INTRODUCTION

In a previously published paper (IOAN et al., 1981), the influence of solvent and temperature on conformational changes of methacrylonitrile - styrene copolymers obtained by plasma-induced copolymerization was presented. The homopolymers behave differently in the same solvent, this comportment affecting the solution properties of the copolymers.
The present paper is dealing with the influence of the solvent on the apparent molecular weight, as well as with the influence of copolymer composition on the heterogeneity of the macromolecular chains, in order to obtain some data concerning the polydispersity of plasma polymers.

EXPERIMENTAL

The synthesis and the microstructural aspects of the copolymers were previously described (SIMIONESCU et al., 1981); some data are given in Table 1.
Light scattering studies were performed on a P.C.L. Peaker apparatus, at 25°C and 4360 Å, using measurements ranging from 40 to 140°. Average apparent molecular weights (M_{ap}) were determined by means of Zimm plots; weight average molecular weights (M_w) were obtained from M_{ap}, in a series of solvents (methyl ethyl ketone (MEK), dioxane (D), dimethylformamide (DMF) and chloroform (C)), according to the equation

$$M_{ap} = M_w + 2P(\nu_A/\nu - \nu_B/\nu) + Q(\nu_A/\nu - \nu_B/\nu)^2 \qquad (1)$$

where ν_A, ν_B and ν are the indexes of refraction increments of polystyrene, poly(methacrylonitrile) and

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of the copolymer, respectively;

$P = \sum_i \gamma_i M_i \delta x_i \qquad Q = \sum_i \gamma_i M_i \delta x_i^2$

where γ_i is defined as the relative concentration of molecules of composition x_i, and $\delta x_i = x_i - x$ is the difference between the composition of molecule "i" and the average composition. One can see that P and Q parameters are function of macromolecular chain compositional heterogeneity.

TABLE 1
Characteristics of the copolymers

Sample	Copolymer composition (%) MAN	S	Yield (%)
1	70.33	29.67	5.35
2	54.75	45.25	7.12
3	47.65	52.35	7.06
4	40.83	24.16	6.15
5	32.43	67.57	12.63

The indexes of refraction increments were determined on a Zeiss interferometer; the experimental data were verified according to the equation

$$\nu = x\nu_A + (1 - x)\nu_B \qquad (2)$$

where x and (1 - x) are weight fractions of components A (styrene) and B (methacrylonitrile). Equation (2) was used to calculate the refractive index increments of poly(methacrylonitrile) in MEK and D.

RESULTS AND DISCUSSION

The data used to calculate true weight average molecular weights and P and Q parameters, according to equation (1), are given in Table 2 and Figure 1.

TABLE 2
Molecular weights of copolymers

Sample	$M_{ap} \cdot 10^{-5}$ MEK	D	DMF	C	Inherent visc. (C, 24°)
1	10,000	9,981	9,987	10,050	1.414
2	15,063	15,392	15,482	15,883	2.054
3	14,985	15,334	15,428	15,818	2.106
4	16,282	16,509	16,579	16,837	2.306
5	11,792	12,022	12,080	12,292	1.689

The apparent molecular weight dependence on solvent is presented in Figure 2, where M_{ap} is plotted against $(\nu_A - \nu_B)/\nu$. For all compositions, M_{ap} is slightly dependent on solvent.

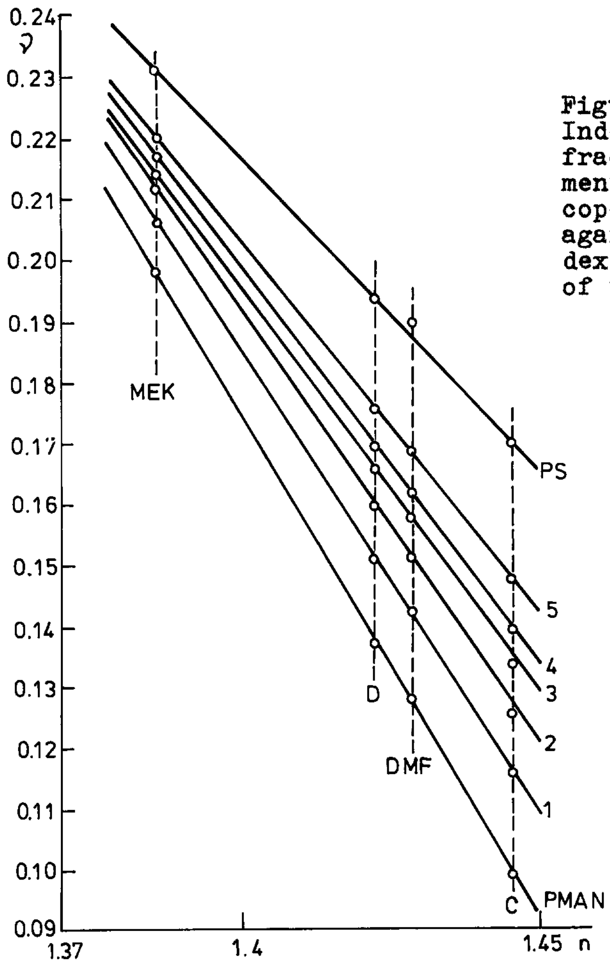

Figure 1.
Indexes of refraction increments of MAN - S copolymers against the index of refraction of the solvent.

The molecular weight of the components, M_A and M_B, was determined by using the equations

$$Q = x(1-x)(M_A + M_B - M_w)$$
$$2P = (1-x)(M_w - M_B) - x(M_w - M_A) \qquad (3)$$

Their sum differs from the molecular weight of the copolymer (Table 3), this indicating the existence of a compositional heterogeneity of the macromolecular chain.
From Table 3 it can be seen that both P and Q vary between the admissible limits

$$-xM_w \leq P \leq (1-x)M_w$$
$$0 \leq Q \leq M_w(1 - x(1-x))$$

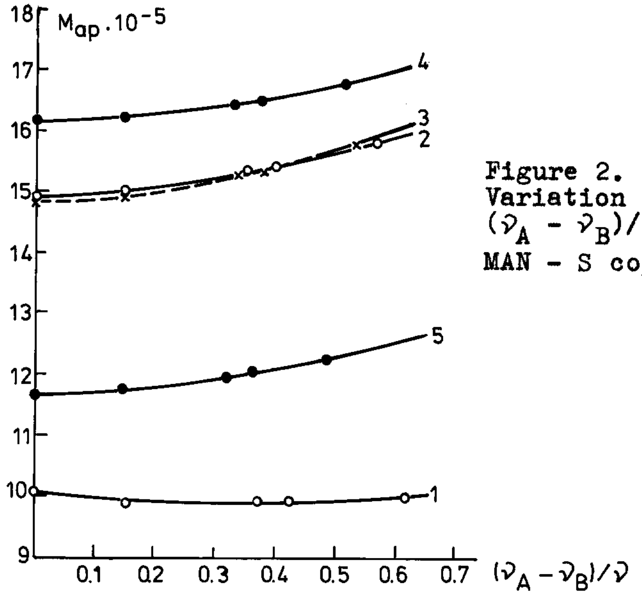

Figure 2. Variation of $(\nu_A - \nu_B)/\nu$ for MAN - S copolymers.

TABLE 3
Heterogeneity parameters and true weight average molecular weights

Sample	$M_w \cdot 10^{-5}$	$P \cdot 10^{-5}$	$Q \cdot 10^{-5}$	$M_A \cdot 10^{-5}$	$M_B \cdot 10^{-5}$
1	10,060	-0.255	0.801	5,174	8,724
2	14,894	0.438	1.524	10,978	10,068
3	14,795	0.513	1.668	11,958	9,525
4	16,173	0.247	1.575	12,725	9,966
5	11,645	0.428	1.000	10,205	6,005

Compositional heterogeneity, given by Q/Q_{max} ratio, where Q_{max} is obtained for the mixture of the two homopolymers and results from $x(1-x)M_w$, is shown in Table 4.

TABLE 4
Compositional heterogeneity data

Sample	Q_{max}/M_w	Q/M_w	Q/Q_{max}
1	0.2087	0.0796	0.381
2	0.2477	0.1023	0.413
3	0.2494	0.1127	0.452
4	0.2416	0.0974	0.403
5	0.2191	0.0859	0.392

Q/Q_{max} may be defined as a quantitative measure of the polydispersity and its maximum value is 1. According to the data presented in Table 4, the copolymers under study have a small compositional heterogeneity.

Even if for high molecular weight copolymers the compositional fluctuations may be undetectable (REMPP and BENOIT, 1968), considering that our products are low conversion copolymers (Table 1), this conclusion seems to be a real one.

From Table 4 it also appears that compositional heterogeneity reaches its maximum value for an about 1:1 composition and decreases with the decrease or with the increase of styrene content in the copolymer. Certainly, the compositional heterogeneity of the macromolecular chain can play an important role on conformational changes of copolymers in diluted solutions. However, in the particular case of high molecular weight methacrylonitrile - styrene copolymers, this parameter has a limited influence on the conformation of the macromolecular chain (IOAN et al., 1981).

CONCLUSIONS

Light scattering measurements were used to determine the true weight average molecular weights of methacrylonitrile - styrene copolymers. The quantitative values of compositional heterogeneity (Q/Q_{max}) are relatively small and depend on copolymer composition, being less important for extreme compositions. Considering, in addition, our previous results (IOAN et al., 1981), one can conclude that compositional heterogeneity has a limited influence on the conformation of methacrylonitrile - styrene copolymers in various solvents and at different temperatures.

REFERENCES

IOAN,S., SIMIONESCU,B.C. and SIMIONESCU,C.I.: Polym. Bull., submitted (1981)

REMPP,P. and BENOIT,H.: Rubber Chem. and Technol. 41, 245 (1968)

SIMIONESCU,B.C., NATANSOHN,A., LEANCA,M., ANANIESCU,C. and SIMIONESCU,C.I.: Polym.Bull. 4, 569 (1981)

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