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# Plasma-Induced Polymerization
## 8. On 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 compositional polydispersity of plasma copolymers.

## 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 $\nu_A$, $\nu_B$ and $\nu$ are the refractive index increments of polystyrene, poly(methacrylonitrile) and of the co-

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polymer, respectively;
$P = \sum_i \gamma_i M_i \delta x_i \qquad Q = \sum_i \gamma_i M_i \delta x_i^2$
where $\gamma_i$ 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 the compositional heterogeneity of the macromolecular chain.

TABLE 1
Characteristics of the copolymers

| Sample | Copolymer composition (%) MAN | S | Yield (%) |
|---|---|---|---|
| 1 | 70.33 | 29.67 | 5.25 |
| 2 | 54.75 | 45.25 | 7.12 |
| 3 | 47.65 | 52.35 | 7.06 |
| 4 | 40.83 | 59.17 | 6.15 |
| 5 | 32.43 | 67.57 | 12.63 |

The refractive index 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 the 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 the 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.

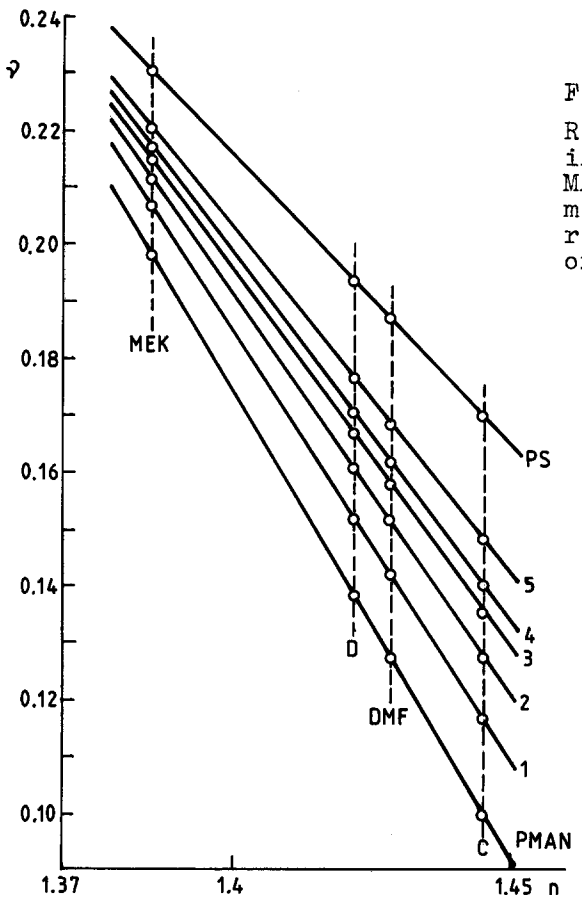


Figure 1.

Refractive index increments of MAN - S copolymers against the refractive index 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.

It can be seen, from Table 3, that both P and Q vary between the admissible limits

$$-xM_W \leqslant P \leqslant (1-x)M_W$$
$$0 \leqslant Q \leqslant M_W(1 - x(1-x))$$

The compositional heterogeneity, given by $Q/Q_{max.}$ ratio, where $Q_{max.}$ is obtained for the mixture of

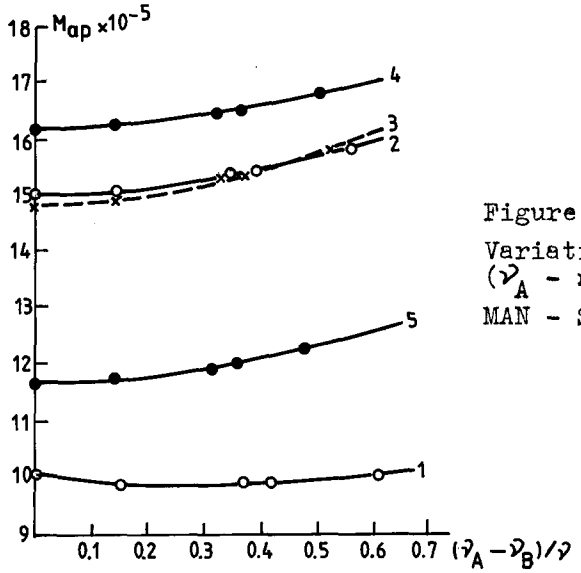


Figure 2.
Variation of Map vs. $(\nu_A - \nu_B)/\nu$ for MAN - S copolymers

the two homopolymers and results from $x(1-x)M_w$, is shown in Table 4.

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 | 1.525 | 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 |

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 compositional heterogeneity 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.
It also appears from Table 4 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 ultrahigh molecular weight 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.

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