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Conformational Changes of Methacrylonitrile-Styrene Copolymers in Diluted Solutions

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Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

Conformational changes of methacrylonitrile - styrene random copolymers, at different temperatures and in various solvents (dimethylformamide, dioxane and methyl ethyl ketone), have been studied by light scattering measurements.

INTRODUCTION

Conformational studies of copolymers in diluted solutions were approached by both theoretical and experimental papers (DONDOS et al., 1967; DANON and JOZEFONVICZ, 1970; DONDOS et al., 1972). The observed conformational changes were proved to depend on copolymer configuration and molecular weight, on the nature of the solvent and on temperature.
The present paper is dealing with conformational changes occuring in the particular case of methacrylonitrile - styrene copolymers of different compositions, in various solvents and at different temperatures; light scattering method was used as experimental technique.

EXPERIMENTAL

Methacrylonitrile (MAN, M_1) - styrene (S, M_2) copolymers were obtained by plasma-induced copolymerization; their synthesis as well as some microstructural aspects were previously presented (SIMIONESCU et al., 1981). ^{1}H-NMR studies confirmed the statistic character of the copolymers.
Light scattering measurements were performed on a PCL Peaker apparatus, at 4360 Å, in the 25°C - 60°C temperature range; the solvents used were dimethylformamide (DMF), dioxane (D) and methyl ethyl ketone (MEK).

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RESULTS AND DISCUSSION

The composition and the probability of occurence of each type of contact ($M_1 - M_1$ (f_{11}), $M_1 - M_2$ and $M_2 - M_1$ ($f_{12} + f_{21}$), and $M_2 - M_2$ (f_{22}))) of the studied copolymers are given in Table 1.

TABLE 1
Structural characteristics of the copolymers

Sample	Composition MAN (%)	Composition S (%)	Contact type (probability) f_{11}	$f_{12}+f_{21}$	f_{22}
1	70.33	29.67	0.419	0.570	0.014
2	47.65	52.35	0.083	0.787	0.133
3	32.43	67.57	0.009	0.630	0.361

Conformational changes, appearing under the influence of temperature and in different solvents, were studied observing c/R_Θ ratio variation, extrapolated to zero concentration (c - concentration, R_Θ - Rayleigh intensity). These changes, as well as the appearance of some conformational transitions, were explained on the base of copolymer structure and on the modification of the existing interactions in the system under the influence of both temperature and the nature of the solvent.

In a copolymer chain, the interaction parameter Z is a linear combination of three terms:

$$Z = f_{11}Z_{11} + f_{22}Z_{22} + f_{12}Z_{12} \qquad (1)$$

where Z_{11}, Z_{22} and Z_{12} are proportional to the interaction energy for each type of contact in the given solvent, and f_{11}, f_{22} and f_{12} are the probabilities of occurence of each type of contact.

The interaction parameters determine the expansion of the macromolecular chain, according to the equations:

$$\alpha_1^2 = 1 + (134/105)Z_{11} + \ldots\ldots\ldots \qquad (2)$$

with

$$Z_{11} = (3/2\pi b^2)^{3/2}\ N^{1/2}\ 2V_S\ (1/2 - \chi_{1,S}) \qquad (3)$$

where α_1 is the expansion factor of homopolymer 1 in a solvent S, b is the length of a statistical segment, N the number of segments, V_S the specific volume of the solvent.

The heterocontact interactions are characterized by the parameter Z_{12}, given by the expression:

$$Z_{12} = (3/2\pi b^2)^{3/2}\ N^{1/2}\ 2V_S\ (1/2 - (\chi_{1S}+\chi_{2S}-\chi_{12})/2)$$

The increase of Z_{11} and Z_{22} proves the existence of weak interactions between each of the two comonomers and the solvent (small values of χ_{1S} and χ_{2S}) and the decrease of the expansion of the macromolecular chain. Z_{12} increases when χ_{12} increses; this demonstrates that, with the increase of the number of heterocontacts in the copolymer chain, the incompatibility also increases and consequently the expansion of the chain increases too. The variation of temperature to higher values results in a diminishing of incompatibility, thus determining a corresponding decrease of the expansion of the random copolymer chain in a given solvent.

As concerns copolymer 1 (high MAN content), the conformational changes appearing under the influence of temperature will be determined by Z_{11} and Z_{12}; as shown in Table 1, the probability of occurence of 11 and 12 type contacts in this copolymer is high. The increase of the temperature implies, on the one hand, the increase of the expansion of the chain due to monomer 1 - DMF interactions (Figure 1), and, on the other hand, the decrease of chain expansion due to the decrease of components incompatibility.

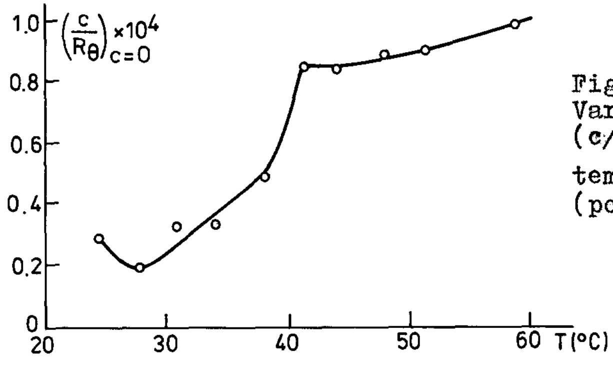

Fig. 1. Variation of $(c/R_\theta)_{c=0}$ against temperature (poly MAN, DMF).

It has to be mentioned that DMF is a θ solvent for poly MAN, at 29.2°C (BANKS et al., 1970) and manifests hydrogen bonds with the polymer; MEK and D are non-solvents for this homopolymer.

The global effect of conformational changes for copolymer 1 is pointed out by the appearance of conformational transitions varying with the nature of the solvent (Figure 2). The values of χ_{12} increase with solvent selectivity and decrease with temperature; the decrease is more pronounced as the solvent is more selective.

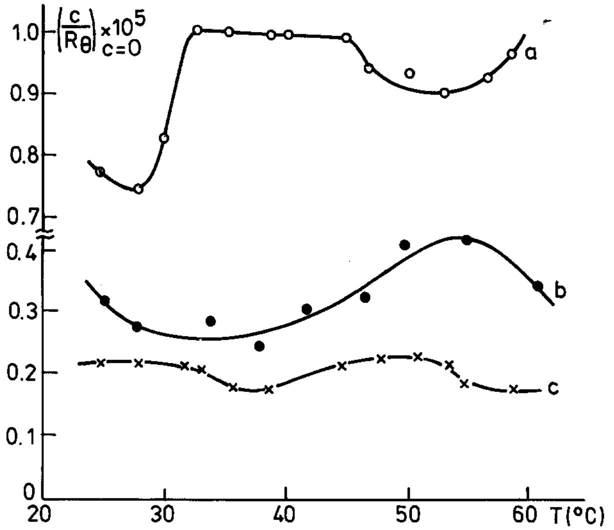

Fig. 2. Variation of $(c/R_\theta)_{c=0}$ against temperature for copolymer 1.
a - DMF
b - D
c - MEK

As concerns copolymer 3 (high S content), 12 and 22 type interactions predominate (Table 1); these interactions are the ones determining the conformational changes appearing with temperature. The increase of the temperature has a small influence on the conformation of poly S (Figure 3), no matter the solvent.

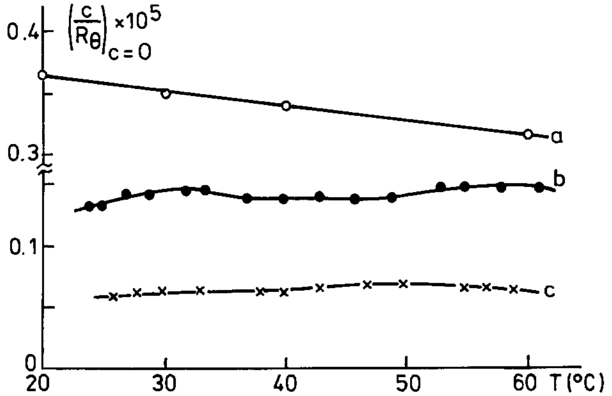

Fig. 3. Variation of $(c/R_\theta)_{c=0}$ against temperature (poly S).
a - D (from DONDOS et al., 1972)
b - DMF
c - MEK

As for copolymer 3, the increase of the temperature diminishes the expansion of the chain due to the increase of the compatibility of the two components. The importance of the existing interactions explains the appearance of transitions (Figure 4) as the result of the modification of the energetic equilibrium. The nature of the solvent influences the temperature of appearance of the mentioned transitions - the phenomenon is noticed at a smaller temperature in D and at a higher one in DMF.

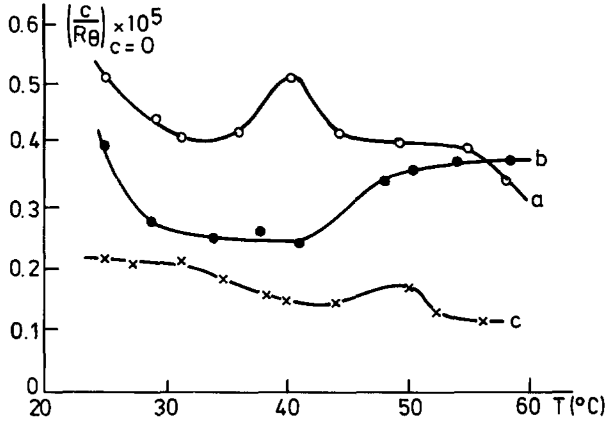

Fig. 4. Variation of $(c/R_\theta)_{c=0}$ against temperature for copolymer 3.
a - D
b - DMF
c - MEK

Copolymer 2 has a pronounced alternating character. The observed conformational changes are not of much importance (Figure 5). This comportment is quite normal, the interactions of the two comonomers with the solvent having opposite conformational results.

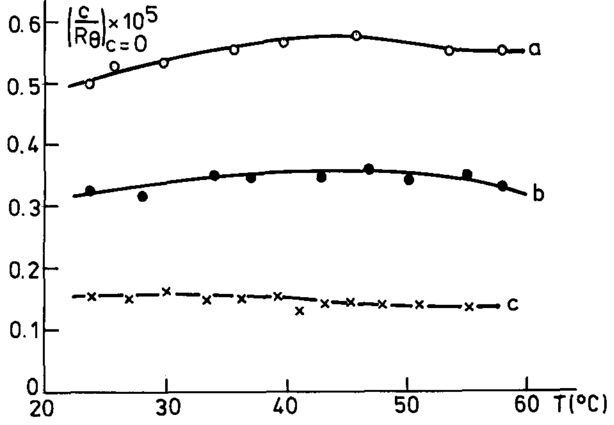

Fig. 5. Variation of $(c/R_\theta)_{c=0}$ against temperature for copolymer 2.
a - DMF
b - D
c - MEK

It has to be mentioned that, according to the given equations, in studying such aspects of polymer mobility in solution, one has to consider the existence of different effects, whose influence is changing function of many parameters.

CONCLUSIONS

Light scattering measurements were proved to be usefull in observing conformational changes of MAN - S random copolymers in different solvents.

The mentioned conformational changes are more pronounced for copolymers with high MAN or S content and less important for an about 1:1 composition copolymer having a very high probability of occurence of 12 + 21 type contacts.

The solvent has a strong influence on the conformational changes, this influence being directly related to solvent selectivity for one or the other of the two components. The changes are more spectacular in DMF, in which poly MAN has its Θ temperature; in MEK and D, non-solvents for poly MAN, the appearing conformational changes are due, on the one hand, to a micellation (aggregation) tendency of the copolymers, and, on the other hand, to the increase of the compatibility with temperature.

Certainly, the molecular weight of the copolymers has to play an important role on the transition temperature; this aspect will be discussed in the near future.

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