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Fluorescence Measurements of Critical Concentration of Styrene and Methyl Methacrylate Copolymers in Solution

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SUMMARY

It is shown that the critical concentration of statistical copolymers in solution may be determined from fluorescence spectra. For styrene-methyl methacrylate copolymers the critical concentration varies from 2.5 kg m^{-3} for polystyrene to 12.0 kg m^{-3} for the copolymer with 0.75 molar fraction styrene.

INTRODUCTION

Critical concentration (c_{crit}) of macromolecules in a solution maybe defined as that at which the concentration dependence of a measured physical quantity is changed by altering its power law dependence (ROOTS and NYSTROM, 1979).

Several experimental methods have been applied when investigating critical concentration: gel-permeation chromatography, X-ray, light and neutron scattering, osmotic pressure, diffusion and excimer fluorescence (KOK and RUDIN, 1982). ROOTS and NYSTROM (1979) determined c_{crit} for polystyrene with different molecular mass based on the concentration measurements of excimer fluorescence. The base of this method has been described by FRANK et al. (1981). Concentration investigations of fluorescence spectra may be also carried out in order to determine c_{crit} of statistical copolymers, which will be shown in this paper. The method has been illustrated for statistical styrene and methyl methacrylate copolymers (S-co-MMA).

EXPERIMENTAL

Particulars of the synthesis, determination of the copolymer

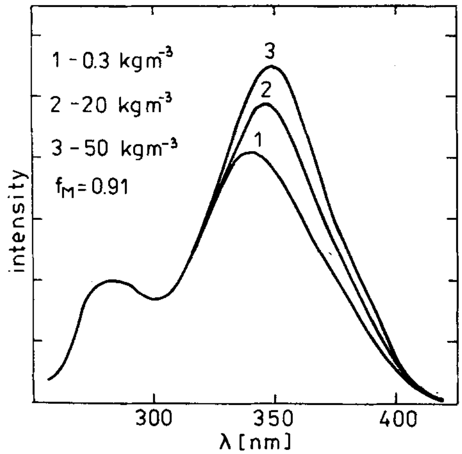

Fig.1 Fluorescence spectra of S-co-MMA depending on concentration.

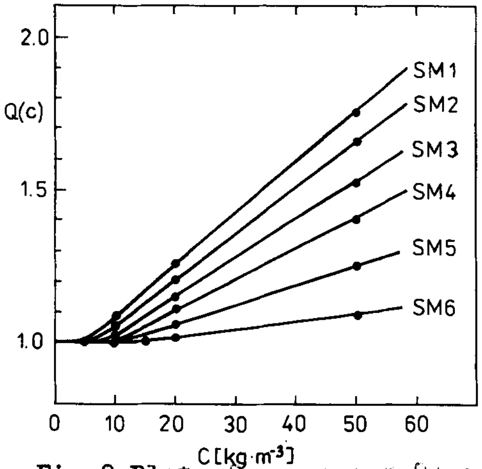

Fig.2 Plot of parameter Q(c) as a function of concentration c.

composition and the description of the measuring equipment have been given separately (SIENICKI and BOJARSKI, 1983). The measurements were carried out in dioxane (Serva, for fluorescence spectroscopy) at 293 K.

RESULTS AND DISCUSSION

Figure 1 shows typical changes in the fluorescence spectra of S-co-MMA as a function of the copolymer concentration in dioxane at fixed styrene content ($f_M = 0.91$). The band at 285 nm is identified from monomer fluorescence (MF), whereas that occurring at 340 nm arises from excimer fluorescence (EF). The spectra were normalized at the maximum intensity of the MF for a concentration of 0.3 kg m^{-3}. The increase in the copolymer concentration in a solution results in the enhancement of the EF intensity and the red shift of its maximum. These effects may be due to (i) the increase of the viscosity of the solution, (ii) the change of the refractive index, (iii) the reabsorption and (iv) the formation of intermolecular excimers. A simple analysis of the factors mentioned leads to the conclusion that three of them are negligible as compared to the last one.

Figure 2 shows the coefficient $Q(c) = (I_D/I_M)_c / (I_D/I_M)_{c=0}$ (I_D and I_M are the intensities of the MF and

Tab. 1. Critical concentrations for S-co-MMA in dioxane.

Sample	f_M	c_{crit} [kg m^{-3}]
SM1	1.00	2.5
SM2	0.95	5.5
SM3	0.91	7.0
SM4	0.87	9.5
SM5	0.80	11.0
SM6	0.75	12.0

EF, respectively) as a function of concentration (c) of the copolymer. The increase in Q(c) results from the occurrence of interactions between the copolymer chains, leading to the formation of intermolecular excimers (for $Q(c) > 1$). Therefore, the copolymer concentration in the solution, at which forming of intermolecular excimers begins, is considered c_{crit}. The values of c_{crit} determined from Fig. 2 are summarized in Table 1. As is seen, c_{crit} depends on the copolymer composition (f_M) and decreases with growing f_M, attaining a value of 2.5 kg m^{-3} for polystyrene. It is also worth mentioning that plotting of equation $\log c_{crit} = f(f_M)$ leads to relation $c_{crit} \sim f_M^{-1.66}$. The method of determining c_{crit} may be also applied to other aromatic copolymers.

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