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Single phase polystyrene – polyacrylonitrile – dimethylformamide system studied by light scattering

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Summary

The single phase system consisting of polystyrene and polyacrylonitrile in a mass ratio of 3:1 and dimethylformamide as a low-molecular weight solvent was studied by the light scattering method. The dependence of the ratio between the experimentally found and calculated intensities of scattered light on the scattering angle, θ, and on the total polymer concentration was followed. It was established that the concentration of the beginning of association of macromolecules could be determined by light scattering at various angles. The method of dissymmetry and the Zimm method were applied for determination of the root-mean-square dimensions of coils, weight-average molecular weight, second virial coefficient and specific volume of macromolecules. The values of macromolecular parameters of the system studied were compared with the corresponding values of the individual polymer solutions. On the basis of the data obtained, it was shown that in the mixed solution occur contraction and association of the macromolecules.

Introduction

In our previous papers (1,2) we have studied polystyrene (PS) - polyacrylonitrile (PAN) - dimethylformamide (DMF) three-component systems in two phase and single phase state. A typical behaviour of the system containing PS and PAN in a mass ratio of 3:1 was found. Viscometry and light scattering method were used in studying the behaviour of the system mentioned in single phase state (2). The pronounced enhancement of the experimentally found intensity of light scattered at an angle of 90°, $(I^m_{90^o})_{exp}$, on increasing total concentration of the two polymers, c, up to the concentration of the single phase/two phase transition, c_2, was attributed to the formation of associates of macromolecules in the mixed solution. This assumption was in agreement with the viscosimetric data as well. The concentration where $(I^m_{90^o})_{exp}$ becomes equal to the corresponding additively calculated value, $(I^m_{90^o})_{calc}$, was supposed as a concentration of the beginning of association of macromolecules, c_1, determined by light scattering.

In this paper, the results from light scattering study of the system mentioned at various angles - θ, are presented,

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and the characteristic concentration c_1, dimensions and some other parameters of the macromolecular coils in solution are determined. These quantities are discussed from the point of view of the assumed contraction and association of macromolecules in the three-component system studied (2).

Experimental

The components of the system investigated were the same as in our previous papers (1,2): PS-1 - prepared synthetically in the laboratory via radical emulsion polymerization, PAN - an industrial scale product, type "Bulana", and analytical grade DMF.

Before the measurements of intensity of scattered light, I, the solutions with definite concentrations had been centrifuged directly in light scattering cells at 15000 rpm for 1 hr. The intensities were determined at 11 scattering angles over the range 30 to 150° with a photogoniodiffusometer Sofica at 25°C and with a wavelength, λ, of 546,1 nm. At the same temperature and λ, the refractive index increments were measured by the use of a Brice-Phoenix, model BP-2000-V, differential refractometer.

The light scattering data for the individual (binary) PS and PAN solutions in DMF were also taken under consideration with the calculations and discussion of results.

Results and Discussion

The calibration curves of I vs. concentrations of PS and PAN, respectively, in their individual solutions were plotted for each scattering angle. At concentrations equal to the corresponding polymer partial concentrations in the common solution ($c^{PS} + c^{PAN} = c$), $(I_\theta^{PS})_{c^{PS}}$ and $(I_\theta^{PAN})_{c^{PAN}}$ were determined from these curves. The equation

$$(I_\theta^m)_{calc} = (I_\theta^{PS})_{c^{PS}} + (I_\theta^{PAN})_{c^{PAN}} \qquad /1/$$

applied in our previous paper (2) for $\theta = 90°$, was used to evaluate $(I_\theta^m)_{calc}$ at various total concentrations of both polymers in the ternary system which are the same as the concentrations where the corresponding $(I_\theta^m)_{exp}$ were measured.

The dependence of the $(I_\theta^m)_{exp}/(I_\theta^m)_{calc}$ ratio on θ and c is illustrated in three-dimensional coordinates in Fig. 1. It can be noticed that this ratio enhances on increasing concentration up to c_2 (2,20 g of PS and PAN per 100 ml) and on decreasing θ from 150° down to 30°. The ratio mentioned takes quite large values at $c = c_2$ and small scattering angles (the effective range of apparatus proved to be insufficient for the intensity measurements at $\theta = 30$; 37,5 and 45°, and $c = c_2$). However, a concentration exists, at and below which the ratio $(I_\theta^m)_{exp}/(I_\theta^m)_{calc}$ becomes equal to 1, i.e. $(I_\theta^m)_{exp} = (I_\theta^m)_{calc}$.

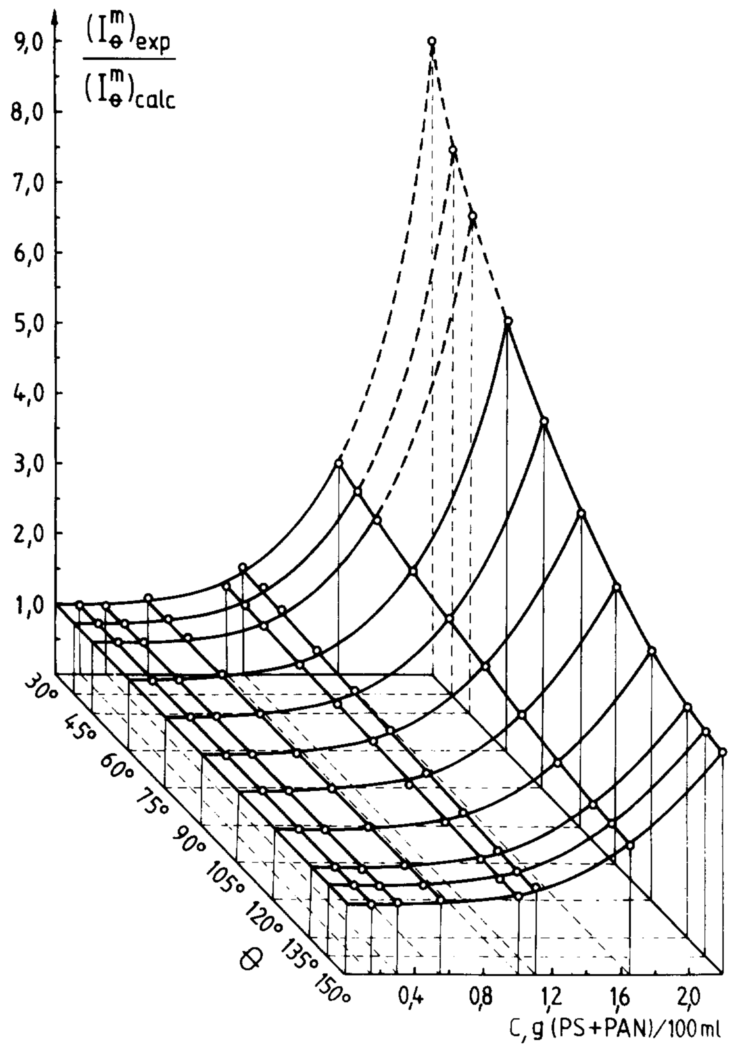

Fig. 1: Dependence of the ratio between the experimentally determined and calculated intensities of scattered light, $(I_\theta^m)_{exp}/(I_\theta^m)_{calc}$, of the system containing PS and PAN in a mass ratio of 3:1 on the scattering angle, θ, and on the total polymer concentration, c.

Interestingly, the concentration mentioned, which we have admitted earlier (2) for the concentration of the beginning of association of macromolecules and designated as c_1, is approximately one and the same at all scattering angles - about 0,30 g of PS and PAN per 100 ml. That fact allows to be claimed more confidently that the macromolecular coils in the system investigated are in isolated state below c_1. The increase of the ratio $(I_\theta^m)_{exp}/(I_\theta^m)_{calc}$ at $c > c_1$, at 90° as well as at the other angles is of course determined by the formation of macromolecular associates.

Determination of some macromolecular parameters of the three-component system studied and their comparison with the corresponding parameters of the individual polymer solutions were of interest too. It is known that for the scattering particles with dimensions larger than $0{,}05\lambda$ - $0{,}1\lambda$ (as it was assumed for the macromolecules in the solutions investigated) two methods can be used for that purpose - the method of dissymmetry (Debye method) and the method of double extrapolation (Zimm method).

At first we applied the method of dissymmetry (3) for determination of the root-mean-square dimensions of macromolecules in the individual PS and PAN solutions as well as in the three-component system. From the light scattering data at $\theta = 45^\circ$ and $\theta = 135^\circ$ and various concentrations, we calculated the scattering dissymmetry, z, by:

$$z = I_{45^\circ}/I_{135^\circ} \qquad /2/$$

where $I_\theta = I_\theta^{solution} - I_\theta^{solvent}$. In order to eliminate the influence of concentration on z, $1/(z-1)$ was extrapolated to $c = 0$, and so the intrinsic dissymmetry, $[z]$, was found (4). We assumed that the PS and PAN macromolecules in their individual solutions and in the ternary system take a coil form (this assumption is reasonable, taking into account that PS and PAN are flexible chain polymers and the solutions investigated are sufficiently diluted). This macromolecular form corresponds to a certain theoretical model (Gaussian coils) (3).

The root-mean-square end-to-end distance, $\langle h^2\rangle^{1/2}$, was determined from a table (5) representing the relationship between $\langle h^2\rangle^{1/2}/\lambda'$ and $[z]$ ($\lambda' = \lambda/n_0$, where n_0 is the refractive index of DMF), according to the mentioned model.

Besides by the Debye method, $\langle h^2\rangle^{1/2}$ was also found using the following equation (6):

$$[z] = 1 + 6{,}556\langle h^2\rangle/\lambda'^2 \qquad /3/$$

The values of $\langle h^2\rangle^{1/2}$ determined by the two methods were approximately equal or the same.

The radius of gyration of macromolecules, $\langle R_G^2\rangle^{1/2}$, was calculated from the correlation

$$\langle R_G^2\rangle = \langle h^2\rangle/6 \qquad /4/$$

valid for Gaussian coils (7).

As a comparison to the experimentally found values $\langle h^{m2}\rangle_{exp}^{1/2}$ and $\langle R_G^{m2}\rangle_{exp}^{1/2}$ of the macromolecular coils in the ternary system, the corresponding additive values were calculated as mass averages of the parameters of the macromolecules in individual polymer solutions.

Table 1: Parameters determined by the method of dissymmetry

Parameter \ Macromolecules in	PS solution	PAN solution	Three-component system	
			exp	calc
[z]	1,500	1,166	1,606	-
$\langle h^2 \rangle^{1/2}.10^7$, cm	106	61	115	95
$\langle R_G^2 \rangle^{1/2}.10^7$, cm	43	25	47	39

The values of the parameters mentioned are given in Table 1. It could be noticed that the experimentally found mean dimensions of macromolecular coils in the mixed solution are larger than the dimensions of coils in both individual solutions. They are also approximately by 20% larger than the corresponding additively calculated values.

In order to determine some other macromolecular parameters of the system studied, we applied the Zimm method (8). On the basis of light scattering and refractive index increment data, the Zimm plots for individual polymer solutions and the three-component system were drawn. The weight-average molecular weight, $\bar{M}_w$, the second virial coefficient, A_2, and the radius of gyration of macromolecules, $\langle R_G^2 \rangle_z^{1/2}$, were found by double extrapolation to $\theta = 0$ and $c = 0$. The values of these parameters are given in Table 2. They are compared with the corresponding additive values for the mixed solution calculated in that case also as mass averages of the parameters of macromolecules in the individual polymer solutions. In this table it could be seen that the experimentally found values of $\bar{M}_w$ and $\langle R_G^2 \rangle_z^{1/2}$ for the mixed solution are practically

Table 2: Parameters determined by the Zimm method

Parameter \ Macromolecules in	PS solution	PAN solution	Three-component system	
			exp	calc
$\bar{M}_w.10^{-5}$	7,04	1,03	5,38	5,54
$A_2.10^4$, ml.g^{-2}.mole	1,9	18,3	0,0051	6,0
$\langle R_G^2 \rangle_z^{1/2}.10^7$, cm	43	25	38	39
$\langle R_G^2 \rangle_z^{3/2}/\bar{M}_w.10^{22}$, $cm^3.g^{-1}$.mole	1,2	1,5	1,0	1,3

equal to the corresponding additively calculated values. That fact is an indication that the macromolecular coils in the system studied are in isolated state under infinite dilution conditions and associates do not occur. However, the experimental value of A_2 is in 3 orders smaller than the calculated one. As A_2 is a parameter characterizing the thermodynamic affinity of a certain polymer and solvent, we could claim that DMF is much poorer solvent for the total polymer mixture in the ternary system than for PS and PAN in their individual solutions (as if the macromolecules in system are under θ-conditions, $(A_2^m)_{exp} \approx 0$).

It is known (9) that often the effect of the one polymer on the other polymer in a mixed solution is analogous to the adding of a low-molecular weight precipitant (nonsolvent). Therefore, also in our system, the solvent power of DMF decreases as a result of the presence of macromolecules of both types (A_2 decreases considerably). On the other hand, because of the relaxation in the polymer/solvent interaction, the interactions between macromolecules could be enhanced, which is a precondition for the formation of macromolecular associates.

The possibility to determine the mean dimensions of macromolecules without preliminary presumptions about their form in solution is an advantage of the Zimm method. If we compare the values of radius of gyration obtained by the method of dissymmetry (Table 1) with the corresponding values determined by the Zimm method (Table 2), we could verify whether our assumption is correct, i.e. that the PS and PAN macromolecules in their individual solutions and in the ternary system are in the form of Gaussian coils. Since the radii of gyration of PS and PAN, respectively, in their individual solutions, obtained by the two methods are equal, the additively calculated radius of gyration of macromolecules in the ternary system is one and the same. The experimental and theoretically calculated by the Zimm method values are approximately equal. However, the experimentally found by the two methods radii of gyration are different.

On the basis of this comparison and taking into account that the method of double extrapolation is more precise, we could claim that our assumption is correct for macromolecules in the individual solutions. However, in the mixed solution they probably do not keep the form mentioned, i.e. the preliminary supposed form (Gaussian coils) is not real ($\langle R_G^{m2}\rangle^{1/2}_{exp} \neq \langle R_G^{m2}\rangle^{1/2}_{z,exp}$). This fact is probably due to the rise of interactions between macromolecules (association) after mixing both polymers in a common solvent. Because of this the coils change their initial form.

We used the quantity $\langle R_G^2\rangle_z^{3/2}/\bar{M}_w$ as a measure of the specific volume, respectively, of the density of coils. It can be seen from Table 2 that the macromolecules in the ternary system are characterized by a smaller specific volume in comparison with the PS and PAN coils in their individual solutions. Therefore, the macromolecules are more contracted (tighter) in the mixed solution. Such a conclusion was made from our previous viscosimetric investigations (2) too. It is worth noting the very nice agreement in the specific volumes, respectively, in the densities of macromolecules in the ternary system determined by viscometry and light scattering.

In conclusion it can be pointed out that the light scattering study of the single phase PS - PAN - DMF system containing PS and PAN in a mass ratio of 3:1 confirms once more our assumption for certain changes of macromolecules in the mixed solution (contraction, association). On the other hand, it was shown that in this instance the concentration of the beginning of association of macromolecules could be found by light scattering measurements at single scattering angle.

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