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Electronic absorption spectroscopy of liquid systems containing polystyrene and polyacrylonitrile

1. Individual polymer solutions

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Summary

Individual polystyrene (PS) and polyacrylonitrile (PAN) solutions in N,N-dimethylformamide (DMF) were studied by electronic absorption spectroscopy. Upon increasing the polymer concentration in the PS-DMF binary system a bathochromic shift of the band at about 260 nm was found. This spectral effect could be explained by an association of PS phenyl groups and/or by a complex formation between DMF and PS. The UV spectrum of PAN in DMF solution was interpreted in terms of the variety of possible donor-acceptor complex formations. The specific intermolecular interactions in the investigated binary liquid systems were discussed on the basis of the spectral data.

Introduction

In our previous papers (1-3), concerning the polystyrene (PS) - polyacrylonitrile (PAN) - N,N-dimethylformamide (DMF) ternary system, we have assumed that intermolecular interactions of its constituents (complex formation, association) exist and supposed what the character of these interactions could be. To clarify the question, additional investigations were necessary. Spectral methods are known as suitable for this purpose. That is why investigations using some of them were carried out. A parallel consideration of the three-constituent system mentioned and PS-DMF and PAN-DMF two-constituent systems was quite logical (naturally, priority was given to the former).

With the exception of electronic and infrared spectral investigations of PAN-DMF binary systems, no other study on individual and mixed PS and PAN solutions in DMF by electronic and vibrational spectroscopy was found in the literature.

The aim of the present work, which is the first part of our investigations on solutions of the two polymers by electronic absorption (UV) spectroscopy, is to study the character of intermolecular interactions in PS-DMF and PAN-DMF binary systems.

Experimental

To carry out the investigations, the following materials were employed: PS-5 ($\overline{M}_w$ = $8,06.10^5$ g/mol in DMF) - synthesized via radical emulsion polymerization described earlier (1), PAN ($\overline{M}_w$ = $1,03.10^5$ g/mol in DMF) - an industrial scale product, type “Bulana”, and DMF for UV spectroscopy (“Fluka”). The individual polymer solutions in DMF were prepared to cover a wide range of concentrations of the polymer constituent (0,05 - 7,5 g/100 ml for PS and 0,05 - 5,0 g/100 ml for PAN). The spectra were recorded on a Perkin-Elmer double-beam UV/VIS spectrophotometer, “Lambda 3”.

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The photometric accuracy of this spectrometer was ±0,5 %, the photometric reproducibility ±0,2 %, and the wavelength reproducibility ±0,2 nm. The feasible photometric measuring range had an optical density, D = -0,3 ÷ 3,0, and the scan speed was 60 nm/min. In the absorption maxima region the D value was recorded at each nanometer. This enabled us to determine precisely λ_{max} and to plot D as a function of the polymer concentration in the respective binary liquid system at certain wavelengths. Quartz cells of 1-mm path length were used for all measurements.

Results and discussion

The electronic absorption spectrum of PS in DMF solution at various polymer concentrations is shown in Figure 1. Two bands are observed - at about 260 nm and at 268 nm. The absorption of PS at about 260 nm in solutions of different solvents (cyclohexane, dioxane, THF, $CHCl_3$, CCl_4) or in the form of films prepared from solution is well-known in the literature (4-9). This absorption maximum is attributed to the $\pi \rightarrow \pi^*$ electronic transition of the phenyl groups (8-10). The 268 nm band is part of the fine vibrational structure of the band centered around 260 nm (10,11).

Upon increasing the polymer content in the PS-DMF binary system a shift of the first absorption maximum towards the longer wavelengths (bathochromic effect) is observed. From 258 nm (at the lowest concentration) λ_{max} increases gradually and reaches the value of 265 nm (Figure 2).

This bathochromic shift of the band at about 260 nm indicates a decrease in the excitation energy of the $\pi \rightarrow \pi^*$ transition and probably is due to a more favourable mutual position of the adjacent aromatic rings at a higher PS concentration in the solution leading to an overlap of their π-electron clouds and formation of associates of phenyl groups (8,12). A suitable steric arrangement of these groups of PS macromolecules causing a maximum interaction between their aromatic rings has been assumed by other authors as well (13-15).

On the other hand, the role of DMF as a strong electron donor should be considered too. In principle, the shift of absorption

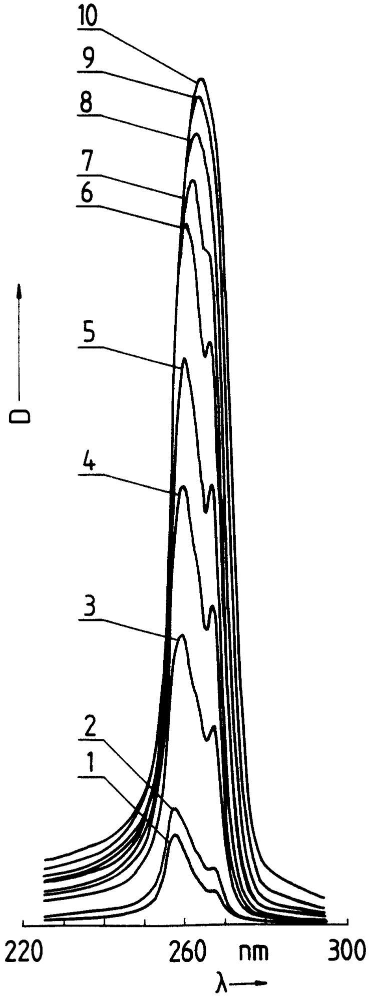

Figure 1. Electronic absorption spectra of PS in DMF solutions. 1 to 10 - polymer concentrations of: 0,05; 0,1; 0,4; 0,7; 1,0; 1,5; 2,0; 3,0; 5,0 and 7,5 g/100 ml, respectively.

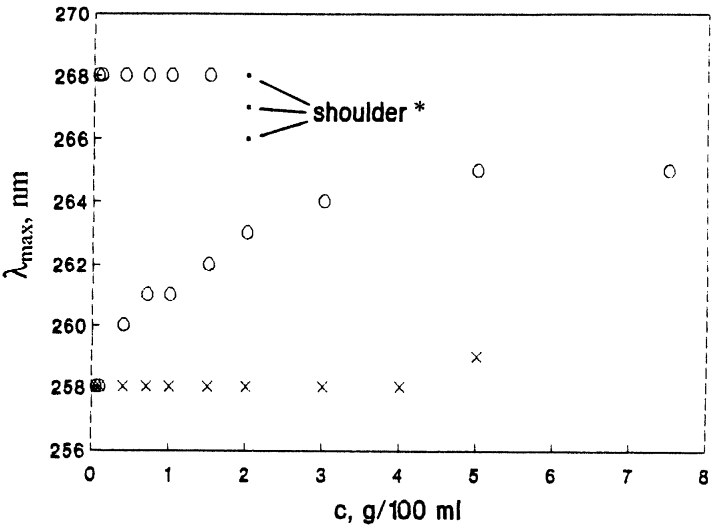

Figure 2. λ_{max} vs. polymer concentration **c** in the binary liquid systems. o, • - PS; x - PAN.
* No maximum at 268 nm but a shoulder in the 266-268 nm range appears in the spectrum of PS at **c** = 2,0 g/100 ml.

bands can be caused by any increase in the interactions of atomic groups and/or solvents with the chromophore units (16). Story et al. (6) have noted that a shift of the UV spectrum of dissolved PS is possible, when there is an interaction between the solvent and the polymer. The authors have illustrated their statement by comparing the spectra of PS dissolved in the non-polar cyclohexane and in CCl_4, respectively. The molecules of the second solvent form complexes with the PS aromatic rings.

Thus, a donor-acceptor interaction of the system of free electron pairs in DMF molecules with the π-electron sextet of the aromatic nuclei in PS macromolecules may occur in the individual PS solution in DMF investigated in this work. The conclusions in some papers concerning the properties of N,N-dialkylamides (incl. DMF) - aromatic hydrocarbon (benzene, toluene) binary liquid systems support our understanding. The presence of specific interactions, respectively the complex formation between the amide (electron donor) and the hydrocarbon (electron acceptor) has been proved by NMR spectroscopy (17,18), thermoanalytical measurements (19), and ultrasonic and densitometric studies (20). Moreover, Hatton et al. (17,18) have assumed that the nitrogen atom of DMF is situated above or below the plane of the aromatic ring.

In our opinion, the π electrons of the phenyl groups in PS can interact not only with the free s-electron pair of the nitrogen atoms, but also with those (*s* and *p*) of the oxygen atoms in DMF molecules.

Probably, with the complex formation discussed in the PS-DMF system, the $\pi \rightarrow \pi^*$ transition is influenced and the excited electron level of the polymer molecules is lowered in relation to their ground state; as a result, the bathochromic effect mentioned for the band at about 260 nm is observed.

Unfortunately, the nature of the binary system studied does not allow to determine unambiguously the reason for this shift. It may be due to the one or simultaneously to both types of interactions (association of PS phenyl groups, complex formation between DMF and PS).

The pronounced absorption maximum at 268 nm is observed up to a polymer concentration of 2,0 g/100 ml when it is modified into a shoulder (Figure 1, spectrum 7). At a higher concentration the two closely situated bands overlap (the absorption maximum at 268 nm is no more observable) because of the bathochromic shift of the band around 260 nm. Obviously, under these conditions, the vibrational state of PS molecules is no more manifested in the electronic spectrum. As seen from Figure 1, the 268 nm band does not shift on changing the polymer concentration in the range where it is observable - its λ_{max} value remains constant (Figure 2).

The UV spectrum of PAN in DMF solution at various polymer concentrations is given in Figure 3. This spectrum differs considerably in shape and intensity from that of the PS-DMF binary system. A relatively weak absorption maximum at 258 nm and appearance of a diffuse shoulder in the 260-300 nm region, which trends to form a broad maximum on increasing the polymer concentration, are noticed. Interestingly, UV spectra of a similar shape have been obtained by other authors (21) but they refer to thermally treated films prepared from PAN solutions in DMF.

A band at about 270 nm has been observed in the UV spectral studies of PAN in the form of films (22,23) and in solution (23). In accordance with the latter reference, it corresponds to the $\pi \rightarrow \pi^*$ electronic transition of the nitrile groups and is assigned to the absorption of complicated associates consisting of three nitrile groups. According to the authors, the strong dipole-dipole interaction between these groups belonging to different macromolecules causes the formation of associates, hence the $\pi \rightarrow \pi^*$ transition band is bathochromically shifted with respect to its position corresponding to non-associated molecules or to binary associates (associates of two nitrile groups). Furthermore, it is supposed that in PAN solutions in DMF or in dimethyl sulfoxide the binary associates are destroyed but the ternary ones are remarkable for their high stability.

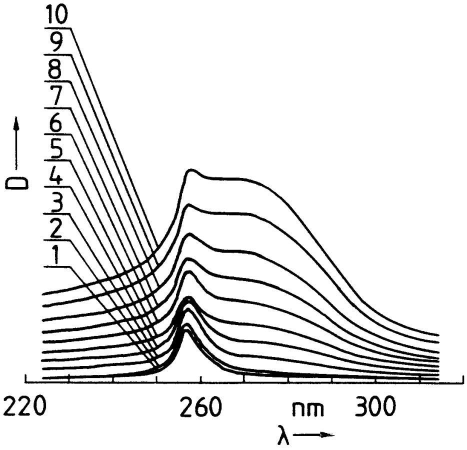

Figure 3. Electronic absorption spectra of PAN in DMF solutions. 1 to 10 - polymer concentrations of: 0,05; 0,1; 0,4; 0,7; 1,0; 1,5; 2,0; 3,0; 4,0 and 5,0 g/100 ml, respectively.

We are inclined to interpret the appearance of the above-mentioned diffuse wing of the spectrum in the 260-300 nm region also by the formation of higher order associates (e.g. of three nitrile groups). In general, it can be assumed that in this large range the maximum D value is at about 270 nm. However, the spectrum shape does not provide a possibility for exact determination of the λ_{max} value in the region indicated. So it is not possible to draw a conclusion about the shift of this broad band on increasing the polymer content in PAN-DMF binary systems. Nevertheless, a realization of a more favourable mutual position and interaction of nitrile groups at a higher PAN concentration in the solution, like the phenyl groups in PS, might be possible.

On varying the PAN concentration in the range investigated, the absorption maximum at 258 nm almost does not change its position - the λ_{max} value remains practically constant (Figures 2 and 3). However, because of the specific nature of the system studied which consists of a strongly polar polymer and a bipolar solvent, the interpretation of this band is a complicated task. Without claiming an explicit and unambiguous assignment, we assume that the absorption may be due to interactions of the free electron pairs and the hydrogen atom in DMF molecules with the π electrons of the nitrile groups in PAN and the free electron pairs of their nitrogen atoms, respectively. It should be mentioned that the free electron pairs of the oxygen and nitrogen atoms in the molecules of DMF impart electron donor properties to the latter with regard to the electron acceptor nitrile groups of PAN.

On the other hand, fluorescent and IR spectral investigations of PAN which had been dissolved and subsequently isolated from its solution in DMF (24) have shown that a cyclization leading to a helical conformation of the macromolecules is realized along the polymer chains. This process occurs under the influence and with the immediate participation of DMF molecules. Two cyclization mechanisms via formation of hydrogen bonds have been supposed: in the absence of water in both polymer and solvent hydrogen bridges are formed between a nitrile group and the hydrogen atom of a tertiary carbon of the PAN chain; in the presence of water hydrogen bonds are formed between the nitrile groups of the polymer. Naturally, in the second case besides DMF molecules the bridges would contain water molecules as well. It has been assumed that actually both types of cyclization of the polymer chains are realized.

Berlin et al. (25) have also paid attention to the possible interaction of PAN with DMF. On the ground of the differences in the IR spectra of PAN which had been dissolved and subsequently isolated from its solution in DMF and of original PAN, the authors have assumed a complex formation between the polymer and the solvent. However, the structure of the complex has not been defined.

Based on the nature of the binary system under study, we think that the dipole-dipole interaction between the carbonyl groups in DMF molecules and the nitrile groups of PAN should be also manifested in the UV spectrum. As known (26), DMF can form dipole-dipole associates with these groups of the polymer. Actually, in this way a solvation of the macromolecules via orientational forces of the interaction between $C\equiv O$ and $C\equiv N$ dipoles is realized.

Thus, the variety of possible donor-acceptor complex formations in PAN-DMF binary system does not enable us to attribute the 258 nm band to a definite type of interaction. These complex formations are likely to affect the spectrum in the 260-300 nm region as well.

Figure 4 presents the optical density as a function of PS or PAN concentration in

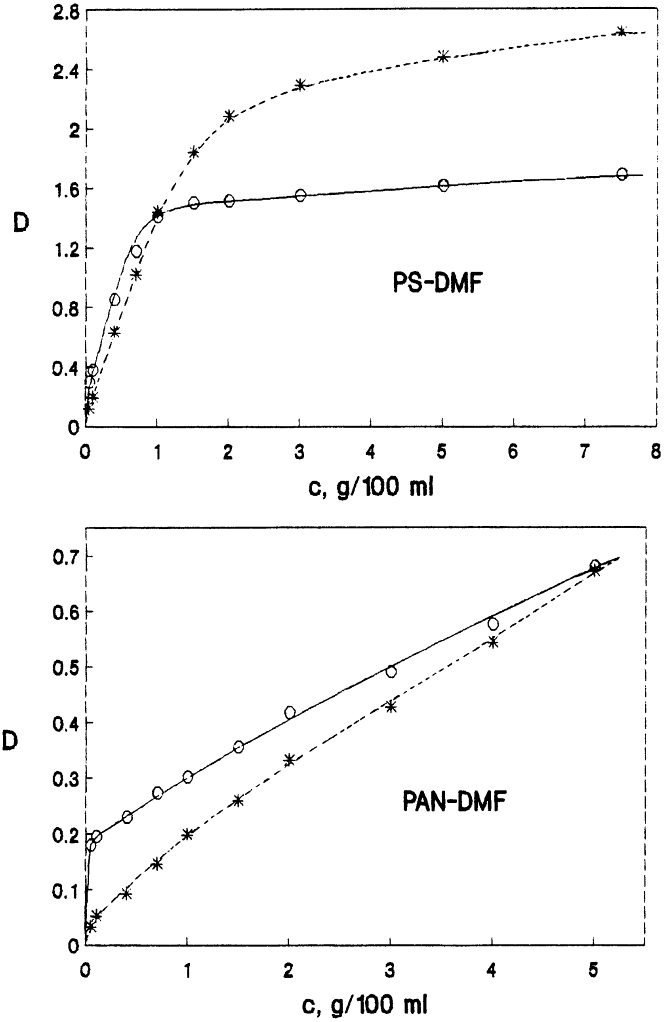

Figure 4. Optical density, D, vs. polymer concentration, **c**, in PS-DMF and PAN-DMF binary systems at λ = 258 nm (o) and λ = 268 nm (*).

the respective binary liquid system at 258 and 268 nm, the two characteristic polymer wavelengths. In the wide concentration range applied, the D curves of the PAN-DMF system are notable for a small curvature, and those of the PS-DMF system have a bend while their other parts are also slightly curved or represent straight sections.

As a conclusion, it is worth noting that in the binary liquid systems studied, specific intermolecular interactions (complex formations) exist, mainly of the electron donor-acceptor type.

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