The study of the structure of solutions of the H-complexes of diesters of tetracarboxylic acids with diamines by the light scattering method

2.* Investigation of the H-complex of dimethyl of benzophenonetetracarboxylate with diaminodiphenylmethane

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The process of structurization in solutions of H-complexes of dimethyl 3,3′,4,4′-benzophenonetetracarboxylate with 4,4′-diaminodiphenylmethane has been investigated in 90 % aqueous methanol in the concentration range 6 to 0.2 g L^{-1}. Structural instability of the solutions has been found in the concentration range from 1.2 to 2 g L^{-1}. The addition of an ionogenic substance stabilizes the solution and results in monotonic changes in the structural parameters as solution is diluted. A tendency toward variation of the extemum in the mean correlation radius of the polarizability fluctuation has been found in the concentration range 0.6—1 g L^{-1}, which had been observed previously for polymer systems.

Key words: polyimides; diesters of 3,3′,4,4′-benzophenonetetracarboxylic acid; 4,4′-diaminodiphenylmethane; H-complexes.

One of the promising two-stage methods for preparing polyimides is based on the interaction of diesters of aromatic tetracarboxylic acids with aliphatic, aromatic, and heterocyclic diamines.[2] It has been shown[3] that complexes of diamines and acidic diesters with hydrogen bonds (H-complexes) are formed in the first stage of the reaction as the diamines and diesters dissolve in absolute or aqueous alcohol. For the preparation of polyimidic materials, for example, elastic foams, H-complexes are isolated from the solution and treated thermally in the second stage of the reaction.[4] The study of H-complexes in solutions is of interest because not only the H-bonds but also the pseudo-polymeric structure formed in the alcohol solution are retained after the removal of the solvent.[5]

Previously[1] the scattering of polarized light was used to study the structure of solutions of H-complexes based on dimethyl 3,3′,4,4′-benzophenonetetracarboxylate (BPT) and 1,6-hexamethylenediamine (HMDA) in absolute and aqueous methanol. The present work is devoted to the study of the structure of solutions of H-complexes based on BPT and 4,4′-diaminodiphenylmethane (DADPM).

Experimental

BPT was prepared by refluxing benzophenonetetracarboxylic dianhydride (m.p. 225 °C) with 90 % aqueous methanol under the conditions described previously,[3] and the BPT · DADPM H-complex was prepared by dissolving DADPM in a BPT solution with stirring at room temperature.

The structure of the water-alcohol solutions of the H-complexes was studied by measuring the scattering of polarized light using a FIS-3M instrument with a photoelectric system for registering the intensity of the light scattered for angles of 40—140°.

The parameters of the hypermolecular structure were determined by the known procedure:[6] the mean square of the density of the polarizability fluctuation $<\bar{\eta}^2>$ and the mean correlation radius of the polarizability fluctuation a_{V_V}.

The concentration dependences of the statistical structural parameters of the system were found by measuring the light scattering for consecutive dilutions of the same concentrated solution with 90 % aqueous methanol from 6 to 0.2 g L^{-1}.

IR spectra were recorded on a Perkin Elmer-580B spectrometer, and ^{1}H NMR spectra were recorded on a JEOL C-60 HL spectrometer (60 MHz).

Results and Discussion

The dependences of a_{V_v} and $<\bar{\eta}^2>$ on the concentrations of solutions of H-complexes of BPT · DADPM are presented in Fig. 1. The tendency of the position of the maximum in the parameter a_{V_v} to change is observed in the range of low (≤1 g L^{-1}) concentrations (see Fig. 1, curves *1, 2*). A similar effect for a_{V_v} was observed previously[1] for H-complexes of BPT · HMDA. It should be emphasized that similar extremum dependences are general for a wide class of polymer solutions[7] and are explained by two factors: an increase in associative

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* For Part 1, see Ref. 1.

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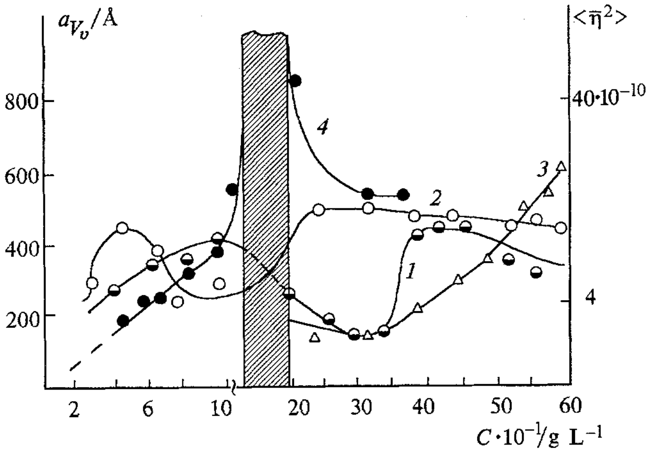

Fig. 1. Dependences of the correlation radius of the polarizability fluctuation (*1, 2, 3*) and the mean square of density of the polarizability fluctuation (*4*) on the concentration of water—methanol solutions (methanol—water, 9 : 1) of the H-complexes BPT · DADPM (*1, 4*) and the same solutions with the addition of ionogenic (*2*) and nonionogenic (*3*) substances.

phenomena due to the growth of the fluctuating polymeric mass, and a decrease in the size of the associates caused by the previously established increase in molecular sizes as the concentration increases.[8] Therefore, the maximum of the concentration dependence of a_{V_v} for the H-complexes of BPT · HMDA is attributed to the occurrence of anisotropic packing of the H-complexes in the fluctuation associates. It has been found that the H-complexes in these associates behave like units of a flexible chain macromolecule. Analogous dependences for solutions of H-complexes of BPT · DADPM (see Fig. 1, curves *1, 2*) allow one to say that they, like the H-complexes of BPT · HMDA,[1] form pseudo-polymeric structures in solution. Naturally, the positions of the a_{V_v} maxima for the solutions of H-complexes lie at higher concentrations than those for the solutions of high-molecular polymers.[7]

It should be mentioned that the solution was found to be unstable in the concentration range 1.2—2 g L^{-1} (see Fig. 1, curve *1*). This manifests itself in the lamination of the solution over time. The study of the upper and lower layers of the system by IR and ^{1}H NMR spectroscopy showed that the solutions contain substances identical in chemical composition to H-complexes of BPT · DADPM. The bands at 1708 and 1220 cm^{-1} (C=O and C—O of carboxyl groups) are absent in the IR spectra, the absorption intensity decreases in the range of stretching vibrations of NH_2 groups (3300—3400 cm^{-1}),[4] and the frequency and shape of these bands change. Absorption is observed in the range 1560—1590 and 1370 cm^{-1} caused by the asymmetric and symmetric vibrations of a partly deprotonated carboxyl group.

In the ^{1}H NMR spectrum, the signal of aromatic protons of DADPM (6.75 ppm, H arom., AA'BB' type spectrum) shifts down field and is transformed to a singlet at 7.04 ppm, which attests to the decrease in the electron density at the nitrogen atom of the amino group of DADPM that occurs during the formation of the H-bond with BPT.

The concentration of H-complexes of BPT · DADPM was higher in the lower layer, which was smaller in volume. No precipitate was formed when the solution was kept for several days at room temperature.

It is known[9] that the transition to the development of critical phenomena in solutions, lamination in this case, is accompanied by an increase in the level of fluctuation of the polymer concentration in the system and, as a consequence, by a sharp increase in the scattering intensity. In our case, a similar effect is distinctly observed in the curve of the $<\bar{\eta}^2>$ dependence on the concentration (see Fig. 1, curve *4*): $<\bar{\eta}^2>$ values approach infinity in the concentration range 1.2—2 g L^{-1}. The lamination is probably caused by the fact that the decrease in viscosity caused by the dilution of the highly concentrated solution results in an increase in the mobility of the associates of H-complexes, and the largest of them drop down but do not precipitate. The system becomes stable again after it diluted to the concentrations of 1 g L^{-1} or lower due to the improvement of the thermodynamic quality of the solution. A qualitative change in the composition of the solvate shells of the pseudo-polymeric H-complexes is likely to occur in this process. One may suggest that the first layer of the solvate shell of a pseudo-polymeric H-complex consists of water molecules and only the second layer has a mixed methanol—water composition due to strong dilution by the methanol—water mixture. Taking into account the fact that the polarity of water is higher than that of methanol, the formation of the hydrate layer may be considered as the reason for the increase in the dielectric permeability of the solvate shell around the pseudo-polymeric complexes, which favors the stable existence of the pseudo-polymeric complexes in the solution.

Lamination of the solution was also observed in the experiments with absolute methanol in the concentration range 1.2—2 g L^{-1} but H-complexes were not found in the upper layer. The fact that H-complexes were found in the upper layer in the experiment with aqueous methanol (1 : 9) may also testify that a small amount of water may increase the stability of solutions of H-complexes. The validity of the suggestion that the stability of H-complex solutions in the presence of water is caused by an increase in the polarity of the solvate shell of the pseudo-polymeric H-complex can be checked by an indirect method. For this purpose, an ionogenic substance capable of forming aggregates with pseudo-polymeric H-complexes to endow them with an integer charge was added to the solutions studied. It was suggested that this should enhance the stability of the system over the whole concentration range.

N-3-[*N,N*-Dimethyl-*N*-(2-hydroxyethyl)ammonio]propyl perfluoroheptanamide chloride was introduced as an ionogenic substance. *N*-3-(*N,N*-Dimethylamino)propyl perfluoroheptanamide with almost the same chemical structure but without ionogenic properties was used for comparison. The absence of a stabilization effect when a non-ionogenic substance with a similar structure is used would confirm that it is the charge effects that favor the stabilization of the solution.

The experimental data (see Fig. 1, curve *2*) show that the ionogenic additive has almost no effect on the size of the hypermolecular formations of the pseudo-polymeric H-complexes but significantly stabilizes the solution in the range of moderate concentrations (1.2—2 g L^{-1}). The minimum in the curve of the concentration dependence of a_{V_v} shifts to lower concentrations. Lamination of the solution does not occur.

The behavior of the solution in the range of moderate concentrations after the addition of the nonionogenic substance is exactly the same as without its addition (see Fig. 1, curves *1, 3*), *i.e.,* lamination is observed in the concentration range 1.2—2 g L^{-1}, and the concentration ~3 g L^{-1} corresponds to the minimum values of a_{V_v}. However, in the case of addition of the ionogenic substance, the system becomes thermodynamically unstable at high concentrations, as indicated by the monotonic decrease in a_{V_v} from the first point at 6 g L^{-1} to the minimum values at ~3 g L^{-1}.

It should be mentioned that the solutions of H-complexes of BPT · HMDA in 90 % aqueous methanol studied previously[1] were stable in the concentration range 6—0.2 g L^{-1}. Taking into account that the H-complexes of BPT · HMDA have an ionic structure,[3] the stability of these solutions may be explained by the charge effects. Thus, it should be considered that the charge effects play a considerable role in the stabilization of solutions of pseudo-polymeric H-complexes.

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