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

3.* Characteristics of the hypermolecular order

O. V. Kallistov, N. A. Kalinina, I. G. Silinskaya, A. V. Sidorovich, V. N. Artem'eva,*
P. I. Chupans, and V. V. Kudryavtsev

Institute of Macromolecular Compounds, Russian Academy of Sciences,
31 Bol'shoi prosp., 199004 St. Petersburg, Russian Federation.
Fax: +7 (812) 218 6869

The parameters of the hypermolecular orientation order in H-complexes of the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic acid with 1,6-hexamethylenediamine (BPE · HMDA) and 4,4′-diaminodiphenylmethane (BPE · DADPM) in methanol and aqueous methanol have been investigated using the angular dependences of the isotropic and anisotropic components of scattered light. The radii of the inertias of the fluctuation domains and the factors of the orientation order of their scattering elements were determined. A model for the structure of the solutions of the complexes considered is presented. The experimental values of optical anisotropy have been compared with those calculated by the valence-optical scheme. The inversion of the calculated and experimental values of optical anisotropy is explained by the nature of the bonds fixing the ester and diamines in both complexes.

Key words: light scattering; diesters of 3,3′,4,4′-benzophenonetetracarboxylic acid, 1,6-hexamethylenediamine, 4,4′-diaminodiphenylmethane, H-complex; fluctuation domain, orientation order.

In the previous works[1,2] we have studied the hypermolecular structure of the solutions of H-complexes of dimethyl ethers of 3,3′,4,4′-benzophenonetetracarboxylic acid (BPE) with 1,6-hexamethylenediamine (BPE · HMDA) and with 4,4′-diaminodiphenylmethane (BPE · DADPM). In these studies we mostly used data from the measurements of the isotropic component of scattering and the total Rayleigh ratio. Based on these data, we concluded that, as the concentration of the solution increases, the H-complexes behave like units of a flexible-chain molecule and aggregate into pseudopolymeric structures. In the present communication we have studied the parameters of the hypermolecular orientation order obtained from the angular dependences of the anisotropic (R_{H_v}) and isotropic ($R_{V_v} - \frac{4}{3}R_{H_v}$) components of scattering. This allowed an additional evaluation of the degree of order of the H-complexes in these pseudopolymeric aggregates. The calculations were carried out by a new procedure[3] that makes it possible to determine the average cosine of the angle θ between the main optical axes of arbitrary (i and j) scattering units of an H-complex (Fig. 1) located within the range of the correlation radius of fluctuations of polarizability (a_v). Starting from the correlation radii of the fluctuations of polarizability a_v and orientation a_H, determined by the known method[4] from the angular dependence of the intensity (indicatrix) of the isotropic and anisotropic components of scattering, one can calculate the factor of orientation order (S_D):[3]

$$S_D = \left\langle \cos^2 \theta_{ij} \right\rangle = \frac{1}{3}\left(1 + 2e^{-a_v/a_H}\right).$$

The structures presented in Fig. 1 may be considered to be a model of the fluctuation domain characterizing the hypermolecular correlation order of the spatial structure of a light scattering medium. The radius of inertia of the scattering mass of a fluctuation domain can be used as its dimensional parameter:[5,6]

$$\left(\overline{R_g^2}\right)^{1/2}_{\mathrm{FD}} = a_v \cdot \sqrt{6}\,.$$

Solutions of BPE · HMDA and BPE · DADPM H-complexes in absolute and aqueous methanol with a concentration of 550 g L^{-1} with (or without) ionogenic and nonionogenic perfluorinated compounds served as the starting specimens (for experimental details, see Refs. 1, 2). The characteristics of the corresponding fluctuation domains for these solutions are presented in

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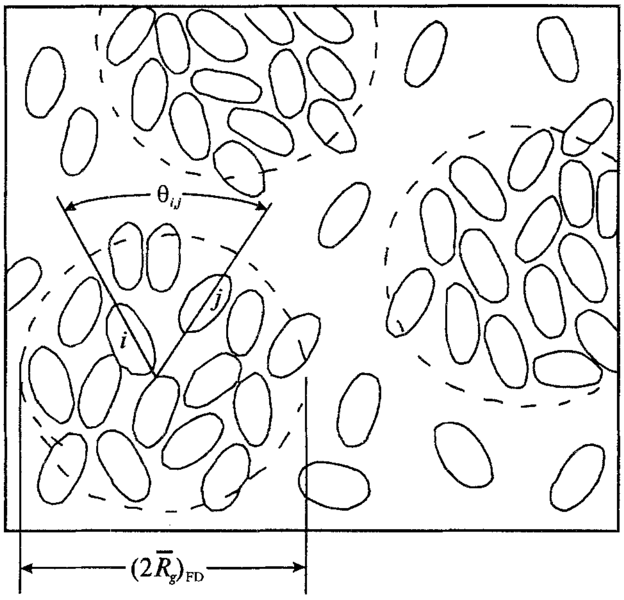


Fig. 1. The model of the fluctuation domain in solutions of H-complexes.

Table 1. Characteristics of fluctuation domains for solutions of the H-complexes (C = 550 g L^{-1})

H-complex	Medium	$(\bar{R}_g)_{FD}$ /Å	$S_D = \langle\cos^2\theta_{ij}\rangle$
BPE · HMDA	abs. MeOH	730	0.50
BPE · HMDA	MeOH—H_2O (9:1)	2000	0.42
BPE · DADPM	MeOH—H_2O (9:1)	760	0.60
BPE · DADPM	MeOH—H_2O (9:1), with an ionogenic additive	800	0.63
BPE · DADPM	MeOH—H_2O (9:1), with an nonionogenic additive	1200	0.44

Table 1. As can be seen from the data of Table 1, the addition of water to the methanolic solution of the BPE · HMDA H-complex results in an increase in the size of the fluctuation domain and a decrease in the S_D factor.

To obtain concentration plots of the structural parameters, the starting solutions were diluted with a corresponding solvent at ambient temperature. As the concentration decreased, the S_D value increased monotonically for solutions in both aqueous and absolute methanol.

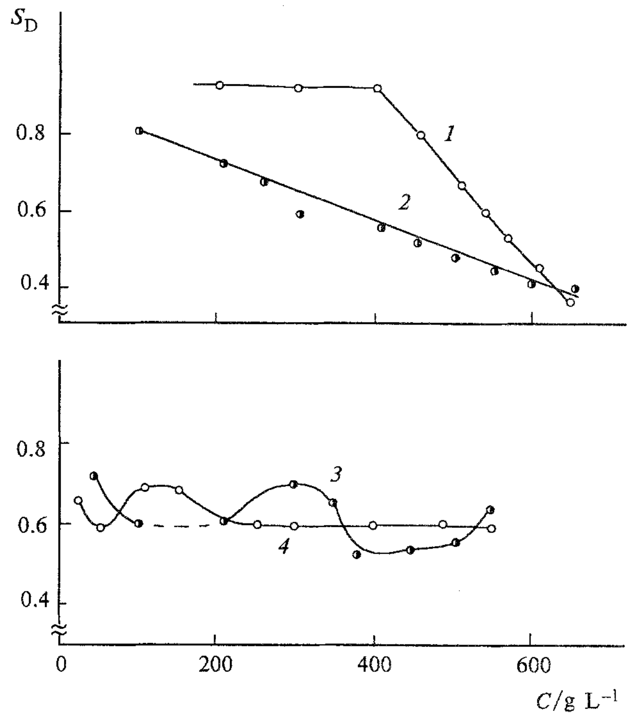
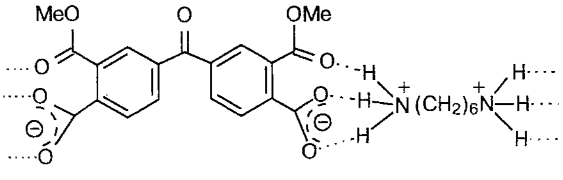


Fig. 2. The plot of the orientation factor (S_D) of fluctuation domains *vs.* the concentration of BPE · HMDA H-complexes in abs. methanol (*1*), in a MeOH—H_2O system (9:1) (*2*) and BPE · DADPM H-complexes in a MeOH—H_2O system (9:1) without additives (*3*) and with an ionogenic additive (*4*).

The results of the measurements are given in Fig. 2. The character of the dependence of the correlation radius of the polarizability fluctuations, which is proportional to $(\bar{R}_g^2)_{FD}^{1/2}$, on the concentration and the corresponding discussion of the peculiarities of its variation have been considered in previous papers.[1,2]

The very high values of S_D (0.80—0.87) for the BPE · HMDA H-complex in a wide range of concentrations, *viz.*, up to 400 g L^{-1} in absolute methanol (see Fig. 2, curve *1*) and up to 100 g L^{-1} in aqueous methanol (curve *2*) attract attention. Such S_D indicate a high ordering of the fluctuation domain, which is probably due to the dilution of the system with methanol or with a MeOH—H_2O mixture resulting in an increase in the intermolecular interactions in the H-complexes. The lower S_D values for solutions of BPE · DADPM in aqueous methanol may be due to the fact that esterification of dianhydride is accompanied by the side reaction of hydrolysis resulting in the formation of up to 10 % carboxyl groups.[7] When the diester is mixed with diamine in a MeOH—H_2O system, this introduces some disorder to the aggregation of the H-complexes (compared with the aggregation occurring after esterification in absolute methanol[1]).

The data of NMR, IR, and UV spectroscopy[8] and quantum-mechanical calculations[9] imply that in strongly polar alcoholic or water—alcoholic media, the BPE · HMDA complex possesses salt structure **1**.



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In dilute alcoholic solutions this complex apparently behaves like an undissociated electrolyte, which favors the appearance of a high orientational order of the H-complexes inside a fluctuation domain.

Increasing the concentration of the solutions (>400 g L^{-1})[1] results in an increase in the size of associates, in which the high orientation order of the H-complexes is destroyed, and hence, the S_D factor dramatically decreases. As can be seen from a comparison of curves *1* and *2* in Fig. 2, the addition of water to the alcoholic solution also results in a decrease in the order in the system.

In the solution of the BPE · DADPM H-complex with a concentration of 550 g L^{-1} the size of the fluctuation domain is smaller, while S_D is simultaneously larger. This may be due to the fact that the rigidity of the H-complex increases when an aliphatic diamine in it is replaced by an aromatic diamine.

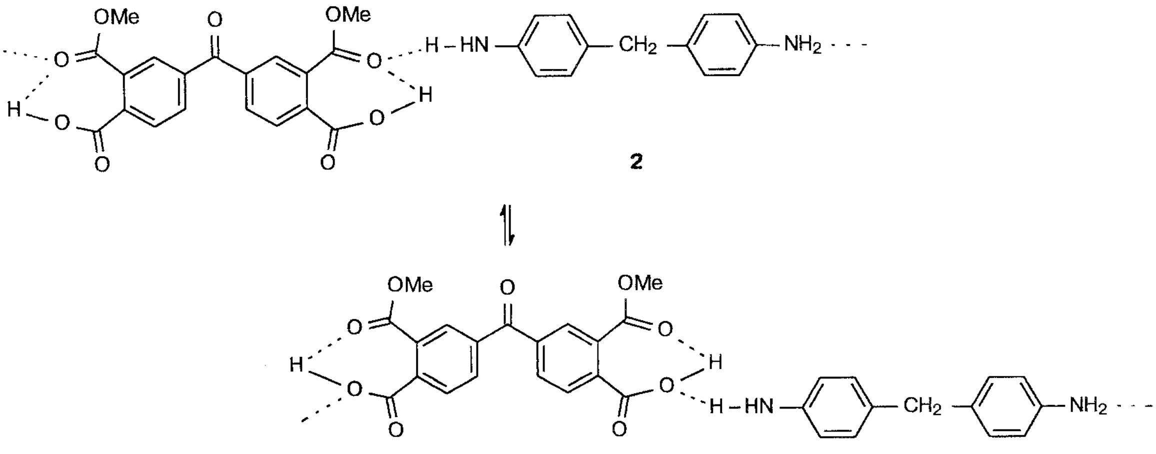
In addition, it should be noted that the structures of the BPE · HMDA and BPE · DADPM H-complexes are substantially different. The low basicity of the aromatic diamine hampers the appearance of ionic structures and favors only the formation of H-bonds, *viz.*, cyclic intramolecular and linear intermolecular bonds[8,9] (structure **2** and **3**).

It was found[2] that the absence of an integer charge on the BPE · DADPM H-complexes and their low polarization lead to instability and stratification of the solution in the 100—250 g L^{-1} concentration region. It has been suggested that an ionogenic compound, 3-(*N,N*-dimethyl-*N*-2-hydroxyethyl)aminopropylperfluoroheptan-1-amide hydrochloride, be added to stabilize the solution.[2] This compound can impart an integer charge to the associates of the BPE · DADPM H-complexes. As can be seen from Fig. 2 (curves *3* and *4*), the introduction of an ionogenic additive not only stabilizes the structure of the solution, but also helps remove the variations in the orientation factor on the curve of its concentration dependence. At the same time, curve *4* in Fig. 2 has only a small extremum, which reflects the tendency of the structure to destabilize in the region where the solution containing no ionogenic additives separates into layers.

As the data of Table 1 indicate, when the concentration of the solution is 550 g L^{-1}, the ionogenic additive has practically no effect on the size of the fluctuation domain and insignificantly changes the orientation factor.

In order to confirm the fact that it is an integer charge and not just the presence of bulky molecules of perfluoroheptanamide that favors the stabilization of the system, we added a nonionogenic substance having a structure close to that of the ionogenic additive, namely, 3-(*N,N*-dimethyl)aminopropylperfluoroheptan-1-amide, to the solution of the H-complex. At concentrations of the solution >400 g L^{-1}, the size of the fluctuation domains considerably increased (which is typical of a thermodynamically unstable system), and this was accompanied by disorientation of the H-complexes to a nearly chaotic state.

Based on the valence-optical scheme that takes into account the previously considered[10] conformational features, the differences in the polarizability ($\Delta\alpha$) for mixtures of BPE with HMDA and BPE with DADPM were calculated to be 210 $\cdot 10^{-25}$ and 240 $\cdot 10^{-25}$ cm^3, respectively. Thus, the additive magnitude of the difference in polarizability for the aromatic system was some-



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what higher than that for the system containing the aliphatic amine.

The characteristics of the optical polarizability of the BPE · HMDA and BPE · DADPM H-complexes can be, in turn, experimentally evaluated on the basis of the reduced optical anisotropy $(\overline{\delta^2/C})$. Extrapolation of the experimental values of δ^2/C to $C = 0$ made it possible to evaluate the effective optical anisotropy (γ_{eff}) from the relationship[11]

$$\gamma_{\text{eff}} = \sqrt{\frac{8\pi a^3 M}{N_A} \cdot \frac{\delta^2}{C}},$$

where M is the molecular weight of the H-complex, N_A is Avogadro's number, and a is the correlation radius of the fluctuations in orientations. The γ_{eff} values for the BPE · HMDA and BPE · DADPM complexes were found to be equal to $230 \cdot 10^{-25}$ and $190 \cdot 10^{-25}$ cm^3, respectively.

A comparison of the experimental $\Delta\alpha$ and γ_{eff} values with those calculated according to the valence-optical scheme shows that these values are close. However, an inversion of the magnitudes is observed. In conformity with the experiment, and in contrast to the calculations, the polarizability of the aromatic H-complex, BPE · DADPM, is somewhat lower than that of BPE · HMDA. To explain this fact, one should take into account the nature of the bonds that hold BPE and the amines together in both of the complexes that were considered in the additive calculation of $\Delta\alpha$.

The polarizability (P) of a molecular system placed into a polarizing field (a light field, in this case) is known[12] to incorporate the static (P_{st}) and dynamic (P_{dyn}) components of the polarization of the molecule: $P = P_{\text{dyn}} + P_{\text{st}}$. It is clear that the values of the dynamic polarization for compounds having an intramolecular H-bond (structures **2** and **3**) are somewhat reduced. It is also reasonable to assume that the static polarization of the ionic structure **1** is higher than P_{st} of structures **2** and **3**. The latter is supported by the calculation of dipole moments (μ) carried out[9] for the model system ammonia—monomethyl ester of maleic acid. It was shown that the dipole moment for the type **1** salt structure ($\mu_1 = 6.9$ D) is much higher than that for the structures with an intramolecular H-bond, similar to **2** ($\mu_2 = 4.6$ D) and especially to **3** ($\mu_3 = 3.7$ D). It is probable that superposition of the two effects, *viz.* the greater dipole moment for the BPE · HMDA salt-type complex in the static state and the smaller P_{dyn} for H-complexes with an intramolecular H-bond, BPE · DADPM, results in the greater γ_{eff} value for the system incorporating the aliphatic amine.

Thus, the inversion in the polarizability values, accounted for by taking into account the intra- and intermolecular H-bonds, once again confirms the essential role of the preliminary formation of H-complexes during the preparation of polyimides by acylation of diamines by esters of tetracarboxylic acids.

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