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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Molecular Structure of H Complexes of Dialkyl Dihydrogen Benzophenonetetracarboxylates with Aromatic Diamines on the Viscosity of Their Melts

V. N. Artem'eva, Yu. G. Baklagina, N. V. Kukarkina, T. A. Kostereva, V. P. Samarin, V. K. Lavrent'ev, Yu. N. Panov, and V. V. Kudryavtsev

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

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Abstract—The possibility of preparing from dialkyl dihydrogen 3,3',4,4'-benzophenonetetracarboxylates and 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenyl ether H complexes of both amorphous and crystalline structures was elucidated. Methods were proposed for disordering the supramolecular structure of the H complexes, which is technologically essential for reducing the melt viscosity when preparing polyimide carbonfilled plastics and foamed composites.

When aromatic diamines are dissolved in solution of dialkyl dihydrogen tetracarboxylates in alcohol (methanol or ethanol) or in a water-alcohol mixture, complexes with hydrogen bond (H complexes) are formed spontaneously between the amino group of diamine and the ester and carboxy groups of dialkyl dihydrogen carboxylate [1, 2]. Despite high polarity of the solvents used, hydrogen bonds are formed even in solutions with a low concentration of the initial components (0.01% solutions) [1]. In 7-8% solutions, H complexes occur as di- and trimers (n = 2, 3) [3]:



At higher solution concentrations, the *n*-size of the H complexes increases (n > 5, 6), and the solution gets anisotropic owing to formation of fluctuation domains [3], i.e., an ordered supramolecular packing of such supramolecular structures as H complexes. Even insignificant changes in the concentrations of such solutions cause fluctuations of the orientation ordering factor characterizing the ordering of the H complexes inside the fluctuation domains [4].

Under virtually identical conditions, it is possible to obtain H complexes with different supramolecular structures because of fluctuations of ambient temperature and humidity, solvent purity, etc.

The above-mentioned supramolecular structures can yield polyimide materials such as EPPI foamed polyimides [5], carbon-filled plastics [6], and foamed composites [7] promising for modern aviation and space technology, as well as for ship-building applications. Since all the above-listed materials can be prepared from molten H complexes with low viscosity only, of special importance are data on how the melt viscosity is influenced by the structure of the initial H complexes.

In this work, we proved experimentally that H complexes with amorphous and crystalline supramolecular structures can be obtained by slightly modifying the conditions of their preparation. Also, we studied how the melt viscosity is influenced by the crystallization of H complexes and suggested a method for directed modification of the supramolecular structure of H complexes.

EXPERIMENTAL

Dialkyl dihydrogen 3,3',4,4'-benzophenonetetracarboxylates (BZPMe and BZPEt, respectively) were prepared by refluxing 0.03 mol of 3,3',4,4'-benzophenonetetracarboxylic dianhydride [TU (Technical Specifications) TSR 2159-69; purified by refluxing in acetone; mp 225°C] in 50 ml of the appropriate alcohol or alcohol with addition of 6 vol % water. The H complexes were prepared by dissolving at room temperature equimolar (with respect to BZPMe or BZPEt) amounts of 4,4'-diaminodiphenylmethane (DADPM) or 4,4'-diaminodiphenyl ether (DADPE) (purified by distillation at 1-3 mm Hg; mp 90-92

and 190°C, respectively) in solutions of BZPMe or BZPEt in the appropriate alcohol. Solid H complexes were recovered by alcohol evaporation at 1-3 mm Hg and 20-30°C.

X-ray studies of the samples of H complexes were carried out on a DRON-2 diffractometer (nickel-filtered copper radiation). The viscosity of molten H complexes was measured on a PIRSP rheometer (cone-plane working unit; angle at the cone vertex 1° , cone diameter 40 mm) at 95 and 105°C at a shear rate of 0.02 s⁻¹ [8].

In most cases, mixing dialkyl dihydrogen benzenetetracarboxylates with aromatic diamines yields H complexes with amorphous structure. Preparation of crystalline H complexes, though practically unpredictable, is rather common. Essential for preparing ordered structures are, typically, seasonal fluctuations of ambient temperature and humidity, uncontrollable changes in the solvent quality, or minor fluctuations of the stoichiometry or concentration of the initial components. Virtually any H complex of any chemical composition can be prepared with amorphous or differently ordered structures.

Figure 1 presents as an example the X-ray diffraction patterns of selected H complexes of various chemical compositions formed in alcohols or aqueous alcohols. It is seen that H complexes with identical compositions BZPEt–DADPE prepared in ethanolic solution (Fig. 1, curves 1, 1') can have both amorphous (curve 1) and low-crystalline structures (curve 1'). In the case of BZPMe–DADPE H complexes prepared in aqueous methanol, it is possible to obtain supramolecular structures with various degrees of crystallinity (curves 2, 2'). With DADPM as amino component, the degree of ordering of the H complexes is also diverse (curves 3, 3').

In this connection, it was of interest to elucidate how the crystalline structure of the H complexes affects their viscosity, which governs the preparation of polyimide materials.

Figure 2 shows how the viscosity of molten H complexes with different structures varies with time. Curves 1 and 1' characterize the variation with time of the viscosity of molten BZPEt–DADPE H complexes, isolated from ethanolic solution, with amorphous (Fig. 1, curve 1) and low-crystalline (Fig. 1, curve 1') structures. It is seen that the viscosity of the more highly ordered H complex in the melt is two orders of magnitude higher than that of the amorphous H complex. Curve 2 refers to the BZPMe–DADPE H complex with low-crystalline structure (Fig. 1, curve 2)



Fig. 1. X-ray diffraction patterns of H complexes (1, 1') BZPEt–DADPE prepared in ethanol, (2, 2') BZPMe–DADPE prepared in aqueous methanol, (3, 3') BZPMe–DADPM prepared in methanol, and (4, 4') BZPEt–DADPM prepared in aqueous ethanol with and without benzimidazole addition, respectively. (2θ) Bragg's angle; the same for Figs. 3 and 4.



Fig. 2. Variation of the viscosity η with time τ of molten H complexes (1, 1') BZPEt–DADPE prepared in ethanol, (2) BZPMe–DADPE prepared in aqueous methanol, (3, 3') BZPEt–DADPM prepared in aqueous ethanol with and without benzimidazole addition, respectively, and (4, 4', 4'') BZPMe–DADPE prepared in methanol. Temperature, °C: (1, 1', 2, 3, 3', 4'') 105 and (4, 4') 95.

isolated from aqueous methanol. The BZPMe– DADPE H complex with a high degree of crystallinity (Fig. 1, curve 2') does not melt at all at 105°C. Thus, the more highly ordered the supramolecular structure of the initial H complex, the higher the melting point

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Fig. 3. X-ray diffraction patterns of BZPMe–DADPE H complexes prepared in methanol. Sample nos.: (1) 1, (2) 2, and (3) 3.



Fig. 4. X-ray diffraction patterns of the BZPEt–DADPM H complex prepared in aqueous ethanol: (1) initial and (2) after melting at 105°C.

of the H complex and the higher the viscosity of its melt.

As known, in preparing foamed polyamides EPPIs, samples of H complexes are foamed at temperatures above 180° C [5]. Therefore, high viscosities of molten crystalline H complexes at $100\pm5^{\circ}$ C are of no importance for foam formation. However, prepregs for carbon-filled plastics and foamed composites are obtained at temperatures close to 100° C [6, 7]. This makes undesirable the use of crystalline H complexes for these purposes.

In this connection, we suggest a method for disordering the supramolecular structure of H complexes. It was found that adding minor amounts of benzimidazole (3 wt % with respect to dialkyl dihydrogen carboxylate) to the initial reaction mixture yields H complexes with less highly ordered structure, all other conditions being the same. For example, the degree of ordering of the crystalline BZPEt–DADPM H complex prepared from aqueous ethanol (Fig. 1, curve 4') significantly decreases on adding benzimidazole (Fig. 1, curve 4). The viscosity of the molten complex decreases, as expected, by two orders of magnitude relative to the crystalline sample (Fig. 2, curves 3, 3').

In the case of BZPMe–DADPE H complex isolated from methanolic solution, we succeeded in preparing samples with significantly differing viscosities of melts. Curves 4 and 4' (Fig. 2) show how the viscosities of melts of these H complexes, as measured at 95°C (sample nos. 1 and 2), vary with time. Curve 4" refers to sample no. 3 of this H complex at 105°C. At 95°C sample no. 3 does not melt.

The X-ray diffraction patterns of these samples (Fig. 3) show that none of them has highly ordered crystalline structure. Unlike amorphous sample no. 1, however, the X-ray diffraction pattern of sample no. 2 in the region of $2\theta = 10^{\circ}-20^{\circ}$ exhibits clear reflections which evidence formation a more ordered structure in it. Sample no. 3 exhibits in the $2\theta \sim 18^{\circ}-27^{\circ}$ region low-intensity reflections against the background of an amorphous halo. This suggests formation of ordered domains, similar to crystalline domains in the BZPMe–DADPE sample prepared from aqueous methanol (Fig. 1, curve 2').

The diffraction patterns (Fig. 3, curves 2 and 3) suggest that the samples can contain various ordered domains responsible for formation at a later time of both low-crystalline (Fig. 1, curve I') and highly ordered crystalline (Fig. 1, curves 2'-4') structures.

Figure 4 presents the X-ray diffraction patterns of the BZPEt–DADPM H complex isolated from aqueous ethanolic solution (curve 1) and of the sample obtained on melting this H complex at 105°C (curve 2). It is seen that the initial sample has a crystalline structure. On melting and subsequent cooling, the sample gets amorphous. Similar structural changes were also observed for crystalline H complexes of other compositions.

CONCLUSIONS

(1) The H complexes prepared from dialkyl dihydrogen 3,3',4,4'-benzophenonetetracarboxylates and 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenyl ether can have both amorphous and crystalline structures. With growing degree of ordering of the H complex, the initial viscosity of its melt tends to increase. The viscosity of molten crystalline H complex exceeds by two orders of magnitude that of amorphous or low-crystalline H complexes with identical chemical compositions. (2) To obtain low-viscosity melts required for successfully preparing prepregs, it is recommended that minor amounts of benzimidazole, which exerts a disordering effect on the supramolecular structure of the forming H complex, be added to the initial reactant mixture.

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