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COMPLEXES OF ACID AMIDES WITH POLAR APROTIC SOLVENTS

VII. Effects of carbonyl-containing compounds and inorganic acids on complex formation and cyclodehydration of polyacid amides

L. A. Shibaev, Yu. N. Sazanov, N. G. Stepanov, S. A. Dauengauer,
T. M. Bulina and *T. I. Zhukova*

INSTITUTE OF MACRIMOLECULAR COMPOUNDS, ACADEMY OF SCIENCES
OF THE U.S.S.R., LENINGRAD, U.S.S.R.

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A study was made of the effects of organic carbonyl-containing compounds and inorganic acids on the character of complex formation of the solvent with polyacid amides, and in particular on the frequency of three-dimensional networks formed by hydrogen-bonds in solid polyacid amide films. It was found that the characteristics of the solid-phase cyclodehydration process can be varied within a wide range by means of active additives.

Pyromellitic acid dianilide (PMA), which serves as a model substance for polyacid amide (PAA) fragments, yields stable crystal solvates with amide solvents; their composition is $PMA_1 \cdot Solv_2$ [1]. It has been found that the system of hydrogen-bonds established in the crystal solvate depends on the structure of the amide solvent [2].

PAA films are typical solid solvocomplexes with an amide solvent, analogous in composition [3]. In general, they do not crystallize; one may speak only of the formation of a para-crystalline system with a rather large number of defects. In the case of the model compounds, the system of hydrogen-bonds in the crystal solvates can be studied by X-ray analysis; for the study of the hydrogen-bonds in PAA films, mass spectrometric thermal analysis (MTA) is suitable [4]. The MTA curves obtained in the cyclodehydration of PAA films yield considerable information, including information on the network formed by the hydrogen-bonds. Information of interest in studies of the acceleration or deceleration of the cyclodehydration by active additives is also obtained from the MTA curves.

In this paper we report on the effects of organic carbonyl-containing compounds and of inorganic acids on the character of the processes of cyclodehydration and on the shapes of the MTA curves.

For the study, we used poly-4,4′-oxydiphenylenepyromellitic acid amide (PPMAA) films (thickness 20–40 μm) obtained from dimethylformamide (DMF) solution.

As stated earlier [2], in the crystal solvate with pyromellitic acid amide, the DMF molecule does not hinder hydrogen-bond formation between *ortho*-acid amide and *ortho*-acid amide ($O_{carboxyl} \ldots H \ldots O_{amide}$) as a result of which crystal growth takes place, but occupies some common position by attaching itself to the vacant proton donor group, i.e. to the amide group and forming a hydrogen-bond $O_{carbonyl DMF} \ldots H \ldots N_{amide}$. It may be assumed that in PPMAA films DMF will form analogous hydrogen-bonds with the PAA. Presumably, of course, compounds of other classes containing carbonyl groups could compete with DMF and from analogous hydrogen-bonds with the amide group of the PAA, displacing DMF from the complex. However, the addition of organic acids (formic acid or acetic acid) to the PPMAA solution in amounts of 1 mol per elementary PAA unit was found to change the character of the MTA curves only slightly (Fig. 1). As concerns the products evolved in the cyclodehydration of PPMAA film, formic acid was absent and acetic acid was present only in traces, indicating that the PPMAA film retains these compounds only slightly; they practically do not displace DMF from the complex. Neither of these two acids significantly affects the maximum temperatures at which H_2O and DMF are evolved, and they only slightly reduce the reaction rate. Replacement of these weak and relatively low-boiling acids (K_{diss} $CH_3COOH = 1.82 \cdot 10^{-5}$, b.p. 118°) by the stronger and higher-boiling trichloroacetic acid ($K_{diss} = 12.1 \cdot 10^{-1}$, b.p. 197°), which is similarly not retained by the film, does not lead to the destruction of the PAA–DMF complex and displacement of the solvent; however, the evolution of water is shifted somewhat towards lower temperatures ($T^{H_2O}_{max} = 146°$). Other carbonyl-containing compounds such as acetone and acetic anhydride behave similarly to aliphatic acids.

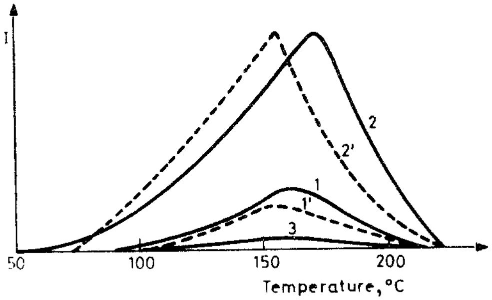

Fig. 1 MTA curves of PPMAA films with formic acid (dotted line) and acetic acid (continuous line) additives; 1, 1′ J water; 2, 2′ – DMF; 3 – acetic acid

Acetone is not retained by the film; in the case of acetic anhydride, acetic acid traces are present in the gaseous decomposition products. The PAA–DMF complex is not destroyed, but $T_{max}^{H_2O}$ is 146 and 144°, respectively.

Benzoic acid, whose dissociation constant is close to that of acetic acid (K_{diss} $C_6H_5COOH = 6.27 \cdot 10^{-5}$, b.p. 249°), is substantially retained in the PPMAA films (Fig. 2). T_{max} for its evolution in the cyclodehydration is 165°, while T_{max} for DMF evolution is shifted towards lower temperatures ($T_{max}^{DMF} = 100$–$118°$). In the case of benzoic acid one may speak of the destruction of the PAA—solvent complex and of the establishment of hydrogen-bonds between the PAA and benzoic acid. It is obviously the aromatic nature of the benzoic acid, ensuring its compatibility with the PAA, which is the decisive factor leading to these changes. The aromatic ring in the acid presumably forms a π–π complex with the aromatic fragment of the diamine or dianhydride component, while the carbonyl group is situated close to the amide bond of the PAA, forming a hydrogen-bond with the —NH-group and displacing the DMF molecule. As regards $T_{max}^{H_2O}$, its value is on the same level as in the former cases (156°). Phthalic anhydride has an even greater effect, though by a different process, on the cyclodehydration of PPMAA. If 2 mol phthalic anhydride is added per elementary unit of the polymer, the maxima in the curves corresponding to the evolution of solvent and water are shifted towards lower temperatures (T_{max}^{DMF} and $T_{max}^{H_2O} = 100°$). In MTA, large amounts of phthalic anhydride are detected, but no phthalic acid, indicating that this acid presumably remains in the film up to the dehydration temperature of the acid (150–200°) and is then evolved in the form of anhydride (Fig. 3).

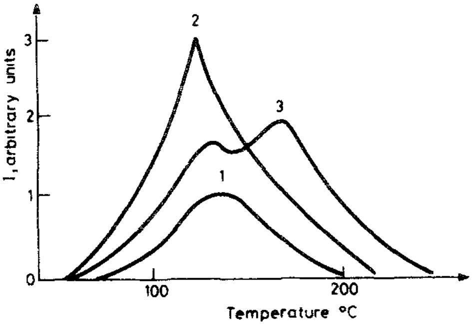

Fig. 2 MTA curves of PPMAA films with benzoic acid additive; 1 – water; 2 – DMF; 3 – benzoic acid

Aromatic compounds such as benzoyl chloride and benzoyl sulfochloride are substantially retained in the film and lower the temperature maxima. For example, on the addition of 1 mol benzoyl chloride per elementary unit of PPMAA, $T_{max}^{H_2O}$ is lowered to 83°. MTA indicates that HCl and benzoic acid, i.e. the hydrolysis

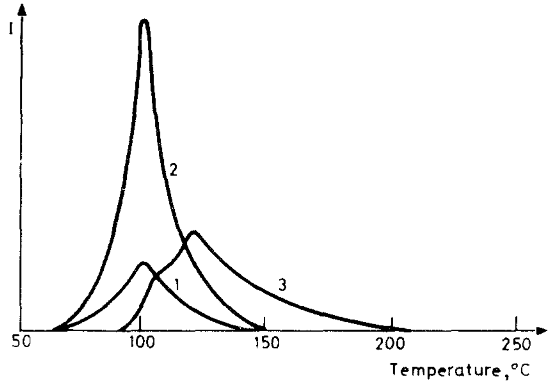

Fig. 3 MTA curves of PPMAA films with phthalic anhydride additive; 1 – water; 2 – DMF; 3 – phthalic anhydride

products of benzoyl chloride, are evolved from the film, while no benzoyl chloride itself is present in the evolved gas.

The polyimide films obtained by cyclodehydration in the presence of phthalic anhydride, benzoyl chloride and benzoyl sulfochloride are brittle; this phenomenon is due to the molecular mass decrease of the PAA resulting from transanhydridation. The appreciable decrease in the imidization temperature maximum, related both to the dehydrating action of these additives and to the lowered molecular mass of PPMAA, does not allow an unequivocal decision as to whether the solvent is displaced from its complex with PPMAA by these compounds.

A comparison of the effects of adding acetone, or acetophenone or benzophenone, also confirms the essential difference in the effects of aliphatic and aromatic compounds on the solid-phase cyclization of PAA. While acetone does not destroy the PAA—solvent complex and is not retained in the film, acetophenone competes with DMF in the complex formation and benzophenone destroys the complex formed with DMF ($T^{\mathrm{DMF}}_{\mathrm{max}} = 118°$, $T^{\mathrm{H_2O}}_{\mathrm{max}} = 152°$) and itself forms a complex with PAA ($T^{\mathrm{benzoph.}}_{\mathrm{max}} = 165°$) (Fig. 4). It should be noted that the interaction of PPMAA with benzophenone results in a brittle polyimide film, similarly as on the addition of phthalic anhydride, although the mechanisms of interaction of these additives with PAA appear to be different in nature. In order to make sure that the formation of a brittle film in the presence of benzophenone is not a result of the initially low molecular mass of the PAA, we carried out chemical imidization of the same PPMAA film containing 0.2 mol benzophenone per elementary unit, using a solution of pyridine and acetic anhydride in benzene, and obtained a satisfactorily strong polyimide film.

Thus, if the active additive contains an aromatic ring, this will increase its

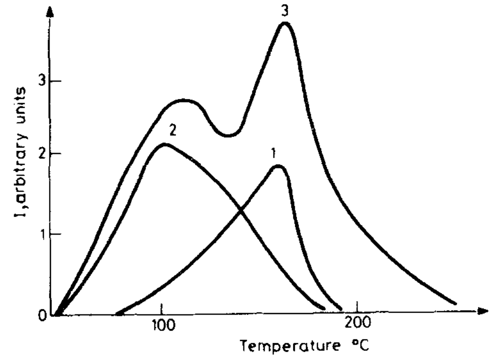

Fig. 4 MTA curves of PPMAA films with benzophenone additive; 1 – water; 2 – DMF; 3 – benzophenone

compatibility with the PAA, resulting in a rearrangement of the hydrogen-bonds between the PAA and the solvent, and in certain cases in an essential change in the cyclodehydration process and in the properties of the final polyimide. Obviously, in those cases when the compatibility of the aromatic compounds with PAA is slight, the effect of these additives will be insignificant. Thus, PAA films obtained from a mixture of amide solvent with benzene or xylene do not retain the latter, and the character of cyclodehydration does not differ much from the typical process for PAA films made with amide solvent. In contrast, if a non-aromatic compound interacts sufficiently strongly with the PAA molecule, a substantial change in the character of the MTA curves will be observed in the cyclodehydration process. Such phenomena occur, for instance, with aliphatic amines; these will be dealt with in a later communication.

Following the study of the effects of aliphatic and aromatic acids on the cyclodehydration of PAAPM, it appeared of interest to study the effects of inorganic acids that are used in the synthesis of polyimides with the aim of improving the thermal resistance and elastic properties of the polymer.

We studied the effects of acids differing in pK_A value, namely boric, phosphoric and sulfuric acids. Figure 5 presents MTA curves for films obtained by adding to a solution of PAA in DMF 0.25, 0.5 or 1 mol of boric acid per elementary unit of the polymer. Similarly as for weak aliphatic acids, a certain tendency of the temperature maximum of water evolution to shift towards higher temperatures is observed ($T_{\max}^{H_2O}$ = 166–171°). Boric acid apparently does not affect the hydrogen-bonds between DMF and the amido groups, and does not destroy the complex; however, the shift of $T_{\max}^{H_2O}$ towards higher temperatures may indicate some increase in the frequency of the three-dimensional network, presumably due to the formation of hydrogen-bonds of the type —OH...B_2O_3...H—O... The

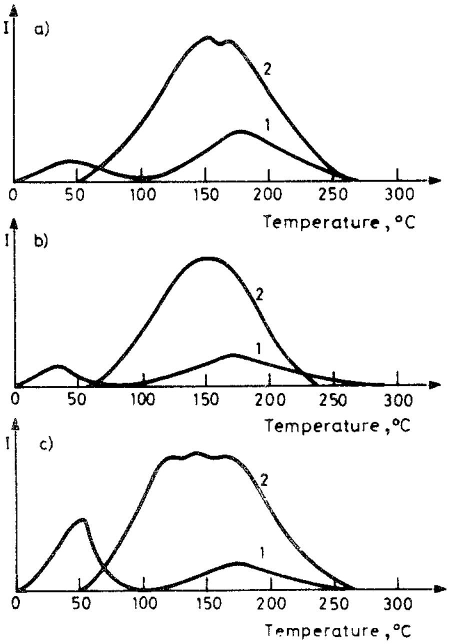

Fig. 5 MTA curves of PPMAA films with boric acid additive. H_3BO_3 concentration: (a) 0.25 mol per elementary unit of PAA; (b) 0.5 mol per elementary unit of PAA; (c) 1 mol per elementary unit of PAA. 1 – water; 2 – DMF

presence of a second peak in the water evolution curve, with $T_{\max}^{H_2O} = 52°$, may be related to the transformation of boric acid into the anhydride.

The addition of phosphoric acid to the PAA solution yields a different picture. The MTA curves for PPMAA films with 0.25, 0.33, 1 and 2 mol H_3PO_4 added per elementary unit of the polymer are shown in Fig. 6. It should be noted that 2 mol H_3PO_4 per elementary unit appears to be the upper limit that can be introduced into the 12–13% PAA solution while still allowing the production of a film (the film is brittle and cloudy). The MTA curves indicate that H_3PO_4 largely affects the solid-phase cyclodehydration of PAA. This is apparent above all from the important shift of $T_{\max}^{H_2O}$ towards the low temperature range, and from the fact that the value of $T_{\max}^{H_2O} = 91–93°$ does not change with varying concentration of H_3PO_4. Further, another peak is observed, with $T_{\max}^{H_2O} = 140–156°$, whose area increases with increasing H_3PO_4 concentration. This is presumably related to the dehydration of H_3PO_4. By reason of the strong dehydrating power of H_3PO_4, the cyclodehydration of PAA presumably proceeds intensively even in the film formation during the drying stage (50°). Part of the water evolved in this stage is retained by the phosphoric acid, and is removed later at the higher temperature corresponding to

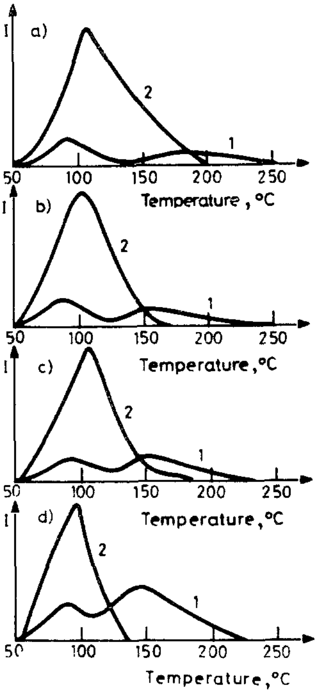

Fig. 6 MTA curves of PPMAA films with H_3PO_4 additive. H_3PO_4 concentration: a) 0.25 mol per elementary unit of PAA; b) 0.5 mol per elementary unit of PAA; c) 1 mol per elementary unit of PAA; d) 2 mol per elementary unit of PAA. 1 – water; 2 – DMF

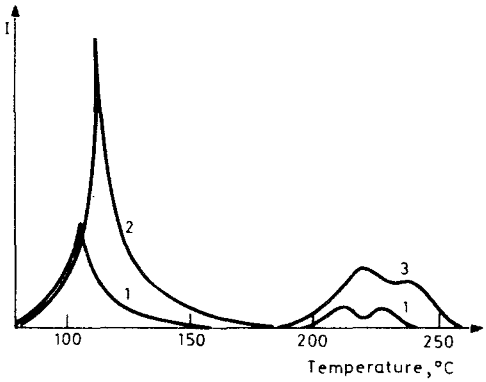

Fig. 7 MTA curves of PPMAA films with H_2SO_4 additive; 1 – water; 2 – DMF; 3 – SO_2

the second peak. In this way, an explanation could be found for the high ratio of the areas of the DMF evolution curve and the first H_2O evolution peak (from 4.5 to 12.5).

Finally, Fig. 7 present MTA results for PPMAA, to a solution.of which 0.5 mol H_2SO_4 per elementary unit of PAA was added. The amount of sulfuric acid is explained by the limited compatibility of the PAA solution with this acid. In the presence of this additive, imidization water is evolved in a sharp peak with a maximum at 108°, indicating the catalysing activity of H_2SO_4. The complex of PAA with DMF is essentially destroyed, as demonstrated by the ratio of the areas under the DMF and H_2O evolution curves equal to 2.4. The Figure also shows the evolution curves of SO_2 and H_2O (with two maxima), related to the decomposition of H_2SO_4 contained in the film.

To summarize, the experimental findings on the effects of low-molecular compounds, representing various classes of organic and inorganic compounds, on the character of the dehydration of PAA and on the MTA curves allow the development of a method for active additives by means of which information may be obtained regarding the mutual positions of solvent and PAA molecules in the solvocomplex, the frequency and type of hydrogen-bonds and the effects of these additives on the temperature intervals of the cyclodehydration of PAA.

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Zusammenfassung — Die Wirkung von organichen carbonyl-enthaltenden Verbindungen und anorganischen Säuren auf den Charakter der Komplexbildung von Lösungsmitteln mit Polysäureamiden wurde untersucht, inbesondere was die Häufigkeit von dreidimensionalen, durch Wasserstoffbindungen in den festen Polysäureamidfilmen zustande kommenden Vernetzungen betrifft. Es wurde festgestellt, daß die Kennwerte des Cyclodehydratisierungsprozesses in fester Phase innerhalb weiter Grenzen durch aktive Additive variiert werden können.

Резюме — Исследовано влияние органических карбонилсодержащих соединений и неорганических кислот на характер комплексообразования растворителя с полиамидокислотами, в частности, на частоту трехмерной сетки, образованной водородными связами в твердых полиамидокислотных пленках. Показано, что с помощью активных добавок можно изменять в широком диапазоне температурные характеристики твердофазного процесса циклодегидратации.