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COMPLEXES OF AMIC ACIDS WITH POLAR APROTIC SOLVENTS.

VI. SYSTEM OF HYDROGEN-BONDS IN COMPLEXES OF AMIC ACIDS AND POLYAMIC ACIDS WITH AMIDE SOLVENTS

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It has been established through X-ray analysis of complexes of pyromellitedianylic acid with amide solvents that the type of the system of hydrogen-bonds and the solvate structure depend on the nature of these solvents. It is shown for solvates of poly(4,4′-oxydiphenylene)pyromellite amic acid that mass spectrometric thermal analysis (MTA) may be used for the investigation of hydrogen-bonds formed in solid polyamic acid films. The MTA data may be employed to establish the mechanism of the effects of additives catalysing the solid-phase cyclodehydration of polyamic acids.

It has been shown previously by means of mass spectrometric thermal analysis (MTA) and thermogravimetric and elemental analyses that pyromellitedianylic acid (PMA), representing the main fragment of polyamic acids (PAA), forms crystalline complexes with aprotic polar solvents. These complexes, which are stable on prolonged storage, have the composition $PMA \cdot Sol_2$, where Sol is the solvent molecule [1].

The present work relates to a system of hydrogen-bonds (H-bonds) formed during the crystallization of PMA complexes with DMF and N-methyl-2-pyrrolidone (N-MP), examined by X-ray analysis. The applicability of MTA to the study of the type and significance of the H-bonds in the solid-phase cyclodehydration of poly(4,4′-oxydiphenylene)pyromellite amic acid (PAA PM) was shown for solvo-complexes of PAA PM with amide solvents.

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Experimental

The crystalline complexes of PMA with amide solvents were prepared by the method described previously [2]. The PAA PM films were obtained by the well-known method [3].

X-ray analysis was carried out with an automatic Synthex PI diffractometer (MoK radiation, a graphite monochromator). The structure of monocrystals was determined by a direct method according to the SOLV procedure of the SHELXTL program, and a more exact determination was carried out by the complete matrix—least-squares method to the anisotropic approximation for C, N and O atoms and to the isotropic approximation for H atoms up to a final *R*-factor value of 0.036 (for $PMA_1 \cdot DMF_2$) or 0.042 (for $PMA_1 \cdot N\text{-}MP_2$).

The MTA of the gaseous products evolved in the solid-phase cyclodehydration of PAA PM was carried out with an MKh–1320 mass spectrometer (USSR) [4]. The films were heated at a rate of 2 deg/min. The spectra of gaseous products taken at intervals of 1–2 min were used to plot the MTA curves as temperature functions of the intensities of the characteristic ions.

Results

The X-ray analysis of crystal solvates of PMA with amide solvents showed that their crystallization is accompanied by the formation of an ordered system of H-bonds, the type of which is determined to a considerable extent by the chemical nature of the solvent contained in the solvate: its activity [5] and the geometry of its molecule. Thus, DMF, exhibiting a low activity in complexation and small molecules, does not prevent the formation of intermolecular ortho-amic acid—

Table 1 Hydrogen bonds in $PMA_1 \cdot Sol_2$ crystallosolvates

Interacting agents	Bond type	Bond length, Å	Bonding energy*, kJ/mol
I Sol = DMF			
PMA–PMA	O—H. . .O	2.589(3)	30
PMA–Sol	N—H. . .O	2.843(3)	15
II Sol = N-MP			
PMA–PMA (absent)	—	—	—
PMA–Sol	O—H. . .O	2.603(3)	25
	N—I. . .O	2.949(3)	12

* Evaluated according to data reported in Ref. [10] taking into account the bond type and length

ortho-amic acid H-bonds forming a crystal, but occupies a certain general position, being bonded to the vacant proton donor centre: the amide group. The more bulky and active N–MP prevents the development of its own ortho-amic acid system of H-bonds, but is bonded to both proton donor centres, forming a "forked" H-bond and actively participating in the formation of the crystalline lattice. In this case the strength of the H-bonds (Table 1), the conformation of the molecule of ortho-amic acid and the parameters of the crystalline lattice (Table 2) naturally change.

It is known that in the general case PAA do not crystallize [6]. It is advisable, therefore, to assume that they form a kind of para-crystalline system with some (always considerable) degree of imperfection. However, the fact that PAA belong to the class of ortho-amic acids is expressed by their properties closely resembling those of low molecular weight ortho-amic acids. Thus, PAA films obtained from solutions in amide solvents are solid solvates containing two molecules of the solvent per PAA repeat unit. The process of intramolecular transformations of PAA (cyclodehydration and degradation) depends to a great extent on the nature of the solvent forming the solvate [7]. The PAA structure is evidently generated as a result of the formation of a well-developed system of H-bonds, a kind of network formed by H-bonds, penetrating the entire sample and similar to a crystal of low molecular weight ortho-amic acid. However, in PAA this lattice is irregular and statistically random. Although its frequency (or the density of H-bonds) and the type of the H-bonds are profoundly affected by the chemical nature of both the PAA and the solvating solvent, it is evidently difficult to detect these differences by using, for example, X-ray analysis. The existence of H-bonds in PAA has been shown by IR spectroscopy [8], but it is difficult with this method to determine relatively fine effects of change in the system of H-bonds, occurring, for example, as a result of a change in the nature of the solvating solvent. However, the major significance of intermolecular interaction in the cyclodehydration and intramolecular degradation of PAA, and hence in the properties of the final polyimide, is beyond doubt.

In many cases thermal analysis, and in particular MTA, may be of use to obtain primary information about the structures of complex systems similar to that described above. It has been shown that DTA data may be used to determine the degree of ordering of PAA complexes with amide solvents [9]. MTA may also provide information about the three-dimensional network formed by H-bonds, in particular in weakly-ordered PAA films, because such parameters as the temperatures of the maxima in the curves of the elimination of the solvent and the cyclodehydration water indicate the high density of intermolecular H-bonds, preventing the intramolecular cyclization of PAA.

MTA is a relatively new method of investigation. The MTA curves exhibit great variety and have not yet been systemized. In the case of PAA, the type of the MTA

Table 2 Structural characteristics of $PMA_1 \cdot Sol_2$ crystallo solvates

Crystallo solvate	PMA conformation (values of bihedral angles between the groups, deg.)				Parameters of the crystalline lattice							
	Ph_1–Ph_2	Ph_1–COOH	Ph_1–CONH	Ph_2–CONH	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	group	Z
$PMA_1 \cdot DMF_2$	80.3	4.3	87.1	12.1	10.32	10.47	25.73	—	—	90	Pbca	4
$PMA_1 \cdot N$-MP_2	74.2	30.3	74.2	5.2	9.70	8.83	10.40	84.7	113.3	75.0	$P\bar{1}$	1

curves is affected by the chemical structure of the polymer and the solvent, the procedure of film preparation, the purity of the additives used for the modification of the PAA with the aim of improving the physico-mechanical properties of the final polyimide, etc.

An example of the marked influence of technological factors on the temperature characteristics of the MTA curves is the dependence of the temperature maxima in the curve of water elimination ($T^{H_2O}_{max}$) during PAA cyclodehydration on the thickness of the PAA PM film obtained from solutions in DMF, DMAA and N-MP (Fig. 1). In the case of DMAA and N-MP, the curves virtually coincide, whereas in DMF the values of $T^{H_2O}_{max}$ are higher. In PAA, as in model ortho-amic acids, complexation with DMF in the solid phase evidently does not prevent the formation of the system of ortho-amic acid—ortho-amic acid H-bonds. The formation of this system leads to a stronger intermolecular interaction and, as a result, to a later (on the temperature scale) cyclodehydration than for PAA solvates with other solvents.

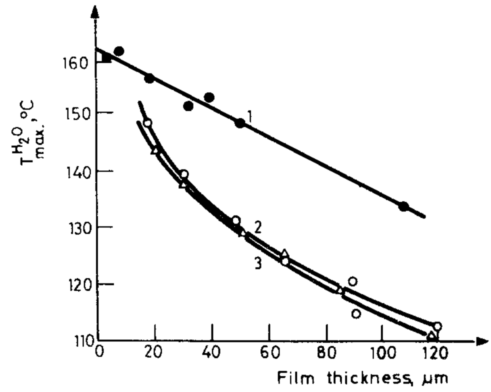

Fig. 1 Dependence of $T^{H_2O}_{max}$ on the thickness of PAA PM films obtained from the following solutions: 1) in DMF, 2) in DMAA, 3) in N-methyl-2-pyrrolidone

In subsequent investigations, films 20–40 μm thick were used. According to X-ray analysis, they exhibited no appreciable degree of ordering. For these films, $T^{H_2O}_{max}$ varies from 152° to 157° for DMF, and from 132° to 145° for DMAA and N-MP.

As already indicated [4], according to the MTA data, in contrast to crystallo solvates of low molecular weight ortho-amic acid, in the PAA film the solvent and the cyclodehydration water are eliminated simultaneously. Since the PAA in the film is less ordered, in this case the ortho-amic acid groups are evidently more mobile and cyclodehydration proceeds simultaneously with the dissociation of the initial complex with the solvent. It may be shown experimentally that the free uncomplexed solvent is removed from the film earlier than the water formed during cyclodehydration. For this purpose, an agent destroying the usual system of H-bonds should be added to the PAA solution from which the films are cast. Aromatic ketones, such as benzophenone, can be used as these agents. For the solvate of PAA PM with DMF, we may assume the approximate coincidence of the temperatures of maximum elimination of water and of DMF ($T^{H_2O}_{max}$ = 152° and T^{DMF}_{max} = 159°), whereas when bezophenone is added (Fig. 2), T^{DMF}_{max} decreases to 118° and $T^{H_2O}_{max}$ remains approximately the same. Benzophenone itself probably forms a complex with PAA (T^{benz}_{max} = 165°). It is possible to achieve a virtually complete displacement of the solvent from the film by adding to the PAA PM solution a more basic compound, e.g. imidazole (pK_a = 7.0). This compound, added in an amount of 2 moles per PAA elementary unit, displaces DMF from the film almost completely (Fig. 3) and simultaneously accelerates the cyclodehydration of the PAA ($T^{H_2O}_{max}$ = 118°).

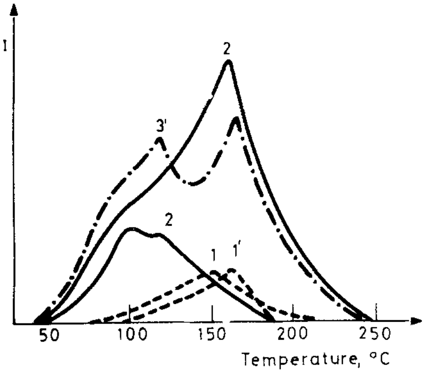

Fig. 2 MTA curves for the PAA PM film: 1) H_2O, $T^{H_2O}_{max}$ = 152°, 2) DMF, T^{DMF}_{max} = 159° and for the PAA PM film obtained in the presence of benzophenone: 1') H_2O, $T^{H_2O}_{max}$ = 158°, 2') DMF, T^{DMF}_{max} = 100°, 3') benzophenone, T^{benz}_{max} = 118 and 165°

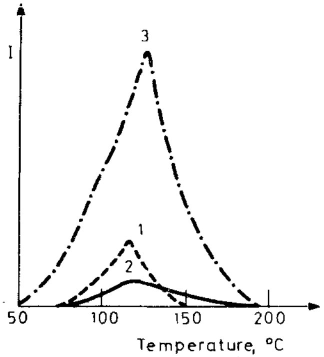

Fig. 3 MTA curve of the PAA PM film obtained in the presence of imidazole: 1) H_2O, $T^{H_2O}_{max}$ = 118°, 2) DMF, T^{DMF}_{max} = 122°, 3) imidazole, $T^{imidazole}_{max}$ = 126°

As shown above, in the complexation of DMF with ortho-amic acids, DMF is attached to the amide group, whereas the carboxy group participates in the formation of intermolecular amic acid—amic acid H-bonds. In this connection, the fact that DMF is displaced from PAA by imidazole indicates the direction of the interaction between this catalysing cyclodehydrating agent and the ortho-amic acid group. Without going into a detailed consideration of the catalysis mechanism (which is beyond the scope of the present paper), it is relatively safe to say that the amide part of the ortho-amic acid group participates in the complexation with imidazole.

The introduction into the solution for the PAA film of boric acid in an amount of one mole per PAA mole also greatly changes the system of H-bonds in the film as compared to the reference sample: the value of $T_{max}^{H_2O}$ increases to 171° and the peaks of water and DMF elimination become less sharp (Fig. 4). In this case, however, DMF is not displaced from the film and its content corresponds, as usual, to 2 moles of the solvent per PAA elementary unit. The boric anhydride formed during film heating (as indicated by the low-temperature peak of water elimination) forms a system of H-bonds as a result of interaction with the carboxy PAA groups alone, and does not form any bonds with the amide groups.

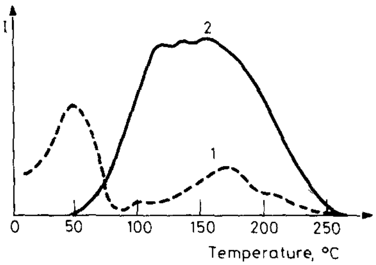

Fig. 4 MTA curves for the PAA PM film obtained in the presence of H_3BO_3: 1) H_2O, $T_{max}^{H_2O} = 171°$, 2) DMF, $T_{max}^{DMF} = 168°$

Hence, the combination of data on the X-ray analysis of crystallo solvates of PMA and those of MTA of PAA solvates makes it possible not only to follow the change in the system of H-bonds when various complexing additives are introduced, but also to determine on which active centres the interaction predominantly occurs in each case. The latter information seems very important for the establishment of the mechanism for the catalysis of the solid-phase cyclodehydration of PAA by agents of different chemical natures.

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Zusammenfassung — Durch röntgenanalyse von Komplexen von Pyromellit-dianilicsäure mit Amidlösungsmitteln wurde festgestellt, daß der Typs des Systems der Wasserstoffbindungen und die Solvatstruktur von der Natur dieser Lösungsmittel abhängt. Für Solvate der Poly-(4,4'-oxydiphenilen) pyromellit-amicsäure wird gezeigt, daß die massenspektrometrische thermische Analyse (MTA) zur Untersuchung von in festen Polyamicsäurefilmen ausgebildeten Wasserstoffbindungen herangezogen werden kann. Die MTA-Daten können zur Ermittlung des Wirkungsmechanismus von die Festphasencyclodehydratisierung von Polyamicsäuren katalisierenden Additionen herangezogen werden.

Резюме — Рентгеноструктурным анализом комплексов пиромеллитдианиловой кислоты с амидными растворителями установлено, что характер системы водородных связей и структура сольватов зависят от природы амидного растворителя. Показано, что в случае сольватов поли(4,4'-оксидифенилен)пиромеллитамидокислоты для исследования водородных связей, возникающих в твердых пленках полиамидокислоты, может быть использован масс-спектрометрический термический анализ, на основании данных которого можно установить механизм воздействия на полиамидокислоту добавок, катализирующих твердофазную циклодегидратацию полиамидокислот.