Journal of Thermal Analysis, Vol. 27 (1983) 333–340

COMPLEXES OF ACID AMIDES WITH APROTIC POLAR SOLVENTS IV. COMPLEXES OF POLY(ACID AMIDES) WITH APROTIC SOLVENTS

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(Received January 1, 1983)

The process of solid-phase cyclodehydration of films cast from solutions of poly(acid amides) (PAA) in dimethylformamide, dimethylacetamide and N-methyl-2-pyrrolidone has been investigated by mass-spectrometric thermal analysis (MTA). It is shown that MTA is a structure-sensitive method making it possible to follow the appearance and changes in the character of ordered structures formed in PAA films. The authors relate these structures to the process of crystallization of complexes of PAA with aprotic polar solvents.

It has been shown previously [1] that with aprotic polar solvents (dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (N-MP)) pyromellitedianil acid (PMA), representing fragments of poly(acid amides) (PAA), forms crystalline complexes stable on prolonged storage. It has been established by mass-spectrometric thermal analysis (MTA), elemental analysis and thermogravimetric analysis (TG) [2] that these compounds have the composition PMA Sol_2, where Sol is the solvent molecule.

As shown by the MTA and TG data, when these compounds are heated under dynamic conditions the complex dissociates with evolution of the solvent (Fig. 1, the first peak in the MTA curve and the first step of mass loss in the TG curve) and the acid amide then undergoes cyclodehydration accompanied by partial decomposition to aniline and pyromellitic dianhydride. During the process of complex decomposition the solvent evolution is recorded in the MTA curves as narrow peak with a maximum at about 140°.

It was of interest to investigate similar MTA curves obtained as a result of PAA cyclodehydration, in order to establish the factors affecting both the complexation of PAA with the solvent and the main features of PAA cyclodehydration. This investigation should contribute to the establishment of the main features of the formation of a polyimide structure exhibiting certain physico-mechanical and thermal characteristic.

A comparison of Fig. 1 with Figs 2–4 shows that the MTA curves obtained for PAA differ greatly from the analogous curves for model complexes. The temperature

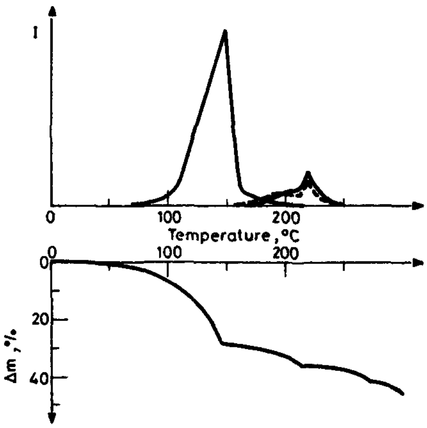

Fig. 1 Thermal analysis of the crystalline PMA • DMA_2 complex. a) Mass-spectrometric thermal analysis. Evolution curves: 1) DMA (mass. eq. = 87), 2) H_2O (mass. eq. = 17) and 3) aniline (mass. eq. = 93) b) TG

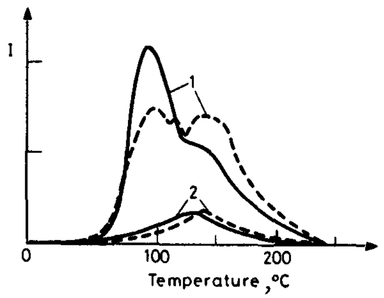

Fig. 2 Characteristic MTA curves for PAA PM films obtained from DMA. Evolution curves: 1) DMA (mass. eq. = 87) and 2) H_2O (mass. eq. = 17)

range in which the solvent is evolved from PAA is much wider, and the curve of the elimination of water in the cyclodehydration of PAA is located below that of the solvent. The curve of solvent evolution for PAA usually exhibits two maxima, although both limiting cases are possible, in which only a low- or only a high-temperature peak is present (Fig. 2).

The presence of solvent weakly retained by PAA and recorded by MTA as a low-temperature peak is the reason for the fact that the amount of solvent remaining in the PAA film varies in various experiments, depending on the intensity of film drying. However, at the moment of transition of a concentrated PAA solution into the solid state (at this moment the film begins to be easily separated from the glass support) this amount corresponds to the existence of a solid complex with the following

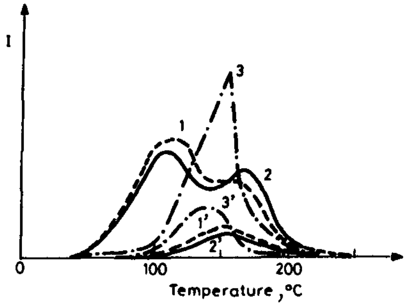

Fig. 3 MTA curves for PAA PM–pPh films obtained by slow drying from solutions: 1) DMA (mass. eq. = 87), 2) N-MP (mass. eq. = 99) and 3) DMF (mass. eq. = 73); 1', 2' and 3' are evolution curves of H_2O (mass. eq. = 17)

composition: repeat unit • Sol_2. This relationship was confirmed for (PAA) based on dianhydrides of pyromellitic acid, diphenyloxytetracarboxylic acid and benzophenonetetracarboxylic acid and two diamines: 4,4'-diaminodiphenyl oxide and para-phenylenediamine.

In order to elucidate the reasons for the existence of a low- and a high-temperature peak representing the solvent in the MTA curves, the dependence of their relative areas on such factors as the chemical structure of the PAA and the solvent, the time of film aging, the method of its preparation, etc. should be considered.

Figure 3 shows the MTA curves for freshly-prepared PAA films obtained under identical conditions on the basis of pyromellitic dianhydride and para-phenylenediamine (PAA PM–pPh) in amide solvents. Whereas the evolution curves of DMA and N-MP exhibit two broad peaks, a single, relatively sharp high-temperature peak is observed for DMF. This peak is similar in shape and temperature range to the solvent peaks recorded by MTA for crystalline complexes of PMA and solvents. It might be assumed that for PAA PM–pPh and DMF the complexes of polymer chains with the solvent form an ordered structure fairly rapidly. This is actually confirmed by X-ray investigations. However, this case should be considered rather as an exception because, owing to kinetic factors, crystallization processes in polymers are appreciably hindered as compared to those in low molecular weight compounds. It might be assumed that a part of the polymer chains of a PAA complex with the solvent usually exists in the disordered regions of the polymer film and another part is located in more or less ordered regions. Furthermore, it is natural to assume that, when the polymer complex is heated, the evolution of the solvent from amorphous regions proceeds much more readily than from the quasi-crystalline regions. If this assumption is valid, then this leads directly to the explanation of the existence of two solvent peaks in the MTA of PAA complexes. Broad high-temperature peaks in the MTA curves evidently indicate that slightly ordered structures (of the type of mesomorphic structures) are formed in the PAA film. Judging from the type of solvent elimination in the case of PAA–pPh and DMF a more ordered structure is formed. This may be due to the bulk and geometrical configuration of the PAA PM–pPh repeat unit and the DMF molecule. For PAA PM–pPh and DMF films the evolution curve of DMF undergoes little change with time, whereas the PAA film based on pyromellitic dianhydride and 4,4′-diaminodiphenyl oxide is characterized by a gradual change in the shape of the curves and the ratio of the areas under the low- and high-temperature peaks of the solvent, as is clearly seen in Fig. 4. For a fresh PAA PM film the evolution curve of DMF is a single broad, low-temperature peak. As aging continues, a high-temperature peak appears and in time becomes larger than the low-temperature peak. Evidently, in this case it might be assumed that a slow process of formation of a quasi-crystalline structure

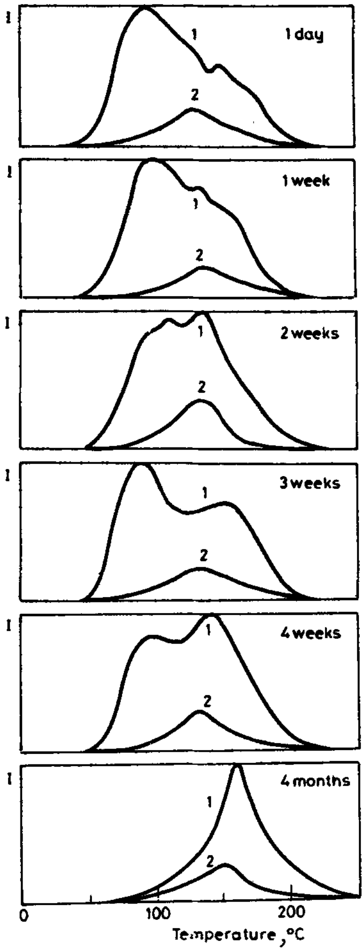

Fig. 4 Change in the type of MTA curves for PAA PM films cast from DMF *vs.* time of film aging: 1) DMF (mass. eq. = 73) and 2) H_2O (mass. eq. = 17)

of the complex of PAA PM with DMF occurs as the film undergoes aging. Since DMF exists for a long time in amorphous film regions where it is relatively weakly retained, it is characteristic of the PAA PM–DMF system that the solvent content in the film gradually decreases with its aging.

The PAA PM–DMA and PAA PM–N–MP systems are characterized by a much smaller change in the ratio of the areas of the low- and high-temperature peaks with film aging. This probably indicates that the crystallization rate of PAA complexes with DMA and N–MP is lower (similarly as in the case of PAA PM–pPh with the same solvent, Fig. 3). The considerable stability of these systems in time makes it possible to investigate the effect of another factor on the type of solvent evolution from the film. If samples for analysis are cut out, starting from the film edge, moving to the middle and then to the opposite side, it is possible to obtain the dependence of the type of solvent evolution from the film on the location of the sample taken for analysis (Fig. 5) with respect to the film edge. It is clear that the MTA curves for samples located directly at the film edge exhibit both the low- and the high-temperature peak of the solvent, whereas only the low-temperature peak is present for samples taken from the central part of the film. In this case the orienting effect of the support probably becomes evident. It is more pronounced at the film edge than in the middle, and hence the conditions for the crystallization of the PAA complex with the solvent are more favourable at the film edge than in the middle.

Naturally, the conditions for film preparation, and in particular for drying, should appreciably affect the formation of a supermolecular structure in the film. Figure 6 shows the MTA curves for the same PAA PM–pPh obtained from DMF as in Fig. 3, but under the conditions of fast drying unfavourable for the crystallization of the PAA–DMF complex. It is clear that a proportion of the solvent is evolved to yield a broad low-temperature peak, while another part gives a sharp high-temperature peak. Hence, the films contain amorphous and quasi-crystallin structures, and therefore the method of preparation is important for the formation of a certain structure of the PAA film. By evaluating the relative amounts of solvent represented by the low- and high-temperature peaks, it is possible to establish the ratio of amorphous and crystalline regions in the PAA film.

It has been shown [3] that the formation of crystalline complexes of PAA with amide solvents may be accelerated if precipitants of the type of benzene, acetone, etc. are added to the PAA solution. It was of interest to elucidate the effects of these additives on the formation of an ordered structure in PAA. For this purpose PAA PM was synthesized in DMF with the addition of 30% of o-xylene. Figure 7 shows the MTA curves for the film of this polymer. It is clear that, in contrast to the MTA curves obtained for the freshly-prepared PAA PM in pure DMF, the solvent, or more precisely DMF (because o-xylene is completely volatilized on film drying although its boiling point is the same as that of DMF), forms a high-temperature peak. This fact, together with the foregoing considerations, may indicate the formation of an ordered quasi-crystalline structure in the PAA PM film.

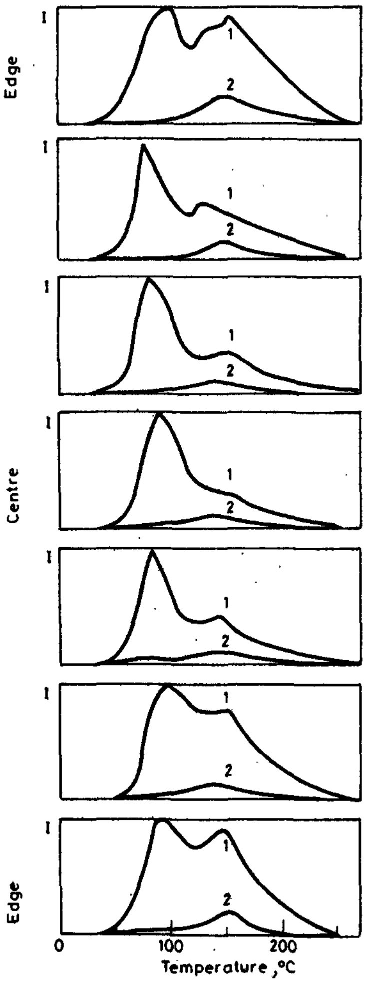

Fig. 5 Change in the type of MTA curves for PAA PM films cast from N-MP *vs.* location of the sample: 1) N-MP (mass. eq. = 99) and 2) H_2O (mass. eq. = 17)

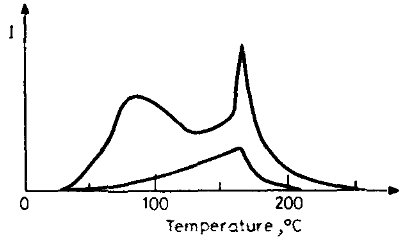

Fig. 6 MTA curves of the PAA PM–pPh film obtained by fast drying from a DMF solution. Evolution curves: 1) DMF (mass. eq. = 73) and 2) H_2O (mass. eq. = 17)

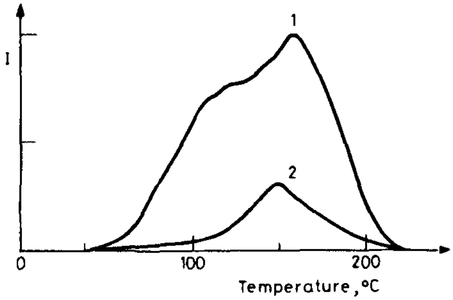

Fig. 7 MTA curves for the PAA PM film obtained from a DMF solution containing 30% of o-xylene. Evolution curves: 1) DMF (mass. eq. = 73) and 2) H_2O (mass. eq. = 17)

Hence, these results show that MTA may be used as a structure-sensitive method, making it possible to follow the appearance and changes in the type of ordered structures formed in PAA films. We suggest that these structures are related to the crystallization of polyamic acid complexes with aprotic polar solvents.

Experimental

The synthesis of PAA and the preparation of films from solutions in polar aprotic solvents were carried out by published methods [4]. Films were dried in a thermostat at 50° for 24 hr (slow drying) or in a container at 50° with a continuous helium flow (fast drying).

The preparation of model PMA complexes with solvents was described in ref. [3].

Mass-spectrometric thermal analysis of PAA complexes and pyromellitdianil acid was carried out with heating at a rate of 2 deg/min. The sample (2–3 mg) was placed in a glass ampoule connected by a flange with the direct inlet system of an MX-1320 mass-spectrometer (USSR). Volatile products evolved during sample heating were continuously fed into the ion source of the mass-spectrometer. The mass-spectra were recorded every 1–3 min. The data obtained were used to plot the MTA curves showing the dependence of the intensity of ions characterizing the products on sample temperature.

The thermogravimetric analysis of complexes was carried out with a MOM derivatograph (Hungary). Samples with a mass of 50 mg were heated at a rate of 2.5 deg/min in an open ceramic crucible in an atmosphere of air.

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Zusammenfassung — Der Vorgang der Festphasen-Zyklodehydratation der Filme, die von Lösungen der Ply(Aminosäuren) (PAA) in Dimethylformamid, Dimethylazetamid und N-Methyl-2-Pyrrolidon ausgeschlagen wurden, wurde mit massspektrometrischer Thermoanalyse (MTA) untersucht. Es wurde erwiesen, dass die MTA eine struktursensitive Methode ist, die es ermöglicht, die Erscheinung und die Charakteränderungen der in den PAA-Filmen geformten, geordneten Strukturen nachzufolgen. Die Verfasser bringen diese Strukturen mit dem Kristallisationsprozess der Komplexe, bestehend aus PAA mit aprotischen, polaren Lösungsmitteln, in Zusammenhang.

Резюме — Методом масс-спектрометрического анализа (МТА) исследован процесс твердофазной циклодегидратации пленок, отлитых из растворов полиамидокислот в диметилформамиде, диметилацетамиде и N-метил-2-пирролидоне. Показано, что МТА является структурно-чувствительным методом, позволяющим следить за возникновением и изменением характера упорядоченных структур, возникающих в пленках полиамидокислот, которые авторы связывают с процессом кристаллизации комплексов полиамидокислот с апротонными полярными растворителями.