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COMPLEXES OF AMIC ACIDS WITH POLAR APROTIC SOLVENTS

IX. Interpolymer complexes of a polyamic acid with polybases

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The polymer-polymer interactions of a polyamic acid (PAA) with polybases (polyvinylpyrrolidone, polyacrylonitrile and polyvinylpyridine) were studied by means of mass-spectrometric thermal analysis (MTA), TG, DTA and IR-spectroscopic methods in solution and in the solid state. The polybases were shown to substitute the solvent from its complex with PAA, forming H-bonds or salt-type polycomplexes with PAA. The MTA method proved to be very informative for the investigation of interpolymer interactions in the solid state.

Keywords: complexes, polymer-polymer interactions

Introduction

The preparation of new polymer materials corresponding to the present state of the art involves not so much the synthesis of previously unknown polymers as the modification of widely used polymers and the preparation of polymer mixtures and composite materials based on them. In this connection, it is important to search for new methods of investigation of polymer-polymer interactions, both in solution and in the solid state.

The present paper reports results of investigations of composites of poly(4,4'-oxydiphenylene)-pyromellitamic acid (PAA PM) with polyvinylpyrrolidone (PVP), polyacrylonitrile (PAN) and poly-2-vinylpyridine (PVPyr). It was established that, in addition to such methods as TG, DTA and IR spectroscopy, mass spectrometric thermal analysis (MTA) is very informative in investigations of the character of polymer–polymer interactions in the solid phase, and in particular in films of PAA PM mixtures with polybases. With the aid of MTA, such features of the sample structure as its homogeneity, the ordering of the carboxyamide groups

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and the dependence of the sample density on the composition of the polycomplexes can be determined.

Experimental

Dimethylformamide (DMF), dimethylacetamide (DMAA) and N-methylpyrrolidone (N-MP) were dried and distilled by standard methods [1]. Composite solutions were prepared by mixing a PAA PM solution synthesized by a standard method [2] with a polybase powder or its solution in an amide solvent. Industrial samples of PVP with MW 28.000, PVPyr (Ferak, Berlin) and c-PAN with MW 100.000–200.000, obtained by anionic polymerization with a degree of cyclization up to 50%, were used as polybases.

MTA was carried out on an MKh-1320 mass-spectrometer [3] at a heating rate of 2 deg/min.

TG was carried out on a MOM derivatograph (Hungary) in a platinum crucible in air at a heating rate of 5 deg/min.

IR-spectra were taken on a UR-20 instrument.

Composite films were obtained by casting and were dried in air for one day at 323 K. The film thickness was 2–3 μm for IR-spectroscopy and 20–40 μm for MTA, TG and DTA.

Results and discussion

Before considering the character of the interactions between PAA PM and polybases, it is necessary to discuss the possibility of PAA PM yielding solid complexes with amide solvents [3]. The system of hydrogen-bonds generated in the solvocomplexes of PAA PM was investigated with the aid of a model bis(N-phenyl)pyromellitic acid diamide (PMA) for which crystalline complexes with DMF and N-MP have been isolated [4]. X-ray analysis monocrystals [5, 6] has shown that in the case of DMF the crystal structure is determined by the orthoamic acid – orthoamic acid hydrogen-bonds (O carboxyl... H...O amide), and DMF is bonded to the vacant proton donor center, the amide group, forming an O carbonyl of DMF... H... amide hydrogen-bond, and does not prevent the appearance of the main system of hydrogen-bonds. The more active N-MP molecule, capable of displacing DMF from the solvocomplexes (the series of activity of the amide solvents in complexation is as follows: DMF < DMAA< N-MP< DMSO [7], reacts with PMA to form hydrogen-bonds with both the amide hydrogen and with that of the carboxylic group, and actively participates in the formation of intermolecular bonds, thereby preventing the bonding between PMA molecules and facilitating cyclodegradation. It may be assumed that more or less the same situation is observed in PAA complexes. It has been shown [8] that many carbonyl-containing compounds compete with the solvent during complexation. Since the PAA solvocomplexes contain one solvent molecule per carboxyamide group, with the aid of MTA it is possible to obtain a qualitative and quantitative picture of the competition of these compounds in the formation of a hydrogen-bond system.

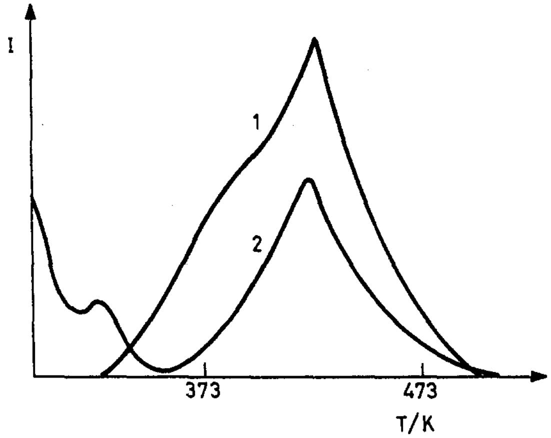


Fig. 1 MTA curves of PAA film prepared from the solution in DMFA: 1 DMFA, 2 water

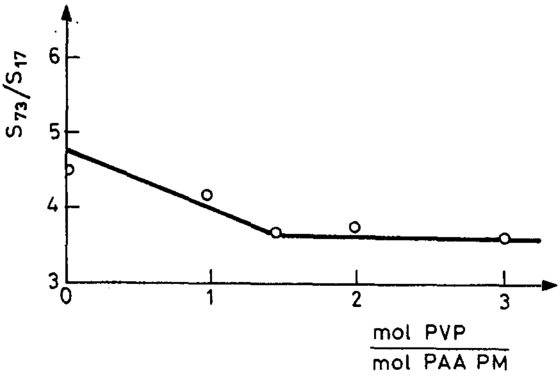


Fig. 2 Ratio of squares under the curves of evolution of solvent and water (S_{73}/S_{17}) for composition PAA-PVP films *vs*. PVP concentration in film

If a film of PAA PM and PVP is prepared from a solution of a mixture of these polymers in DMF, it is to be expected that some of the DMF molecules would be displaced from the PAA complex by the PVP units, and the corresponding DMF PAA PM hydrogen-bonds would be replaced by PVP – PAA PM bonds. Figure 1 shows a typical MTA pattern of a PAA PM film cast from a solution in DMF. As has been shown previously [3], the area under the curve of DMF yield corresponds to a content of 2 moles of the solvent per elementary PAA PM unit. Since the sensitivity of the instrument of DMF (according to the molecular ion *m/e* 73) is 4.5 times higher than that to water (according to the OH ion, *m/e* 17), the ratio of areas under the curves of DMF and water is equal to 4.5. Figure 2 shows the change in this ratio with increasing PVP content in the composite films. It is evident that, even at a concentration of 1.5 mole PVP per mole PAA PM, the ratio of these areas attains a level of 3.5 and remains constant upon further increase of the PVP concentration. In other words, in these composites the PVP molecules displace about 20% DMF complexed with PAA PM, i.e. approximately every fifth carboxyamide group loses a solvent molecule and takes part in the formation of a new system of hydrogenbonds with the participation of PVP. This naturally affects the character of PAA PM cyclodehydration and leads to a monotonous increase in the T_{max} of water elimination (Fig. 3). At a PVP concentration of 3 mole per mole PAA PM, T_{max} attains 469 K. This increase may result from both an increase in density of the composite and the increasing hindrance to cyclodehydration due to the formation of interpolymer complexes and a lower mobility of PVP units than that of the solvent molecules. The dependence of the half-width of the peak of water elimination on the PVP content, which characterizes the degree of cooperativity of PAA PM cyclodehydration and is probably due to local density distribution in the polymer composite sample, is of an extreme character. The half-width of the water peak exhibits a maximum at a PVP content of 1.5 mole per mole of the polymer and is 70 K. A further increase of the PVP content leads to a decrease in the half-width of the water peak, i.e. the structural homogeneity of the system increases.

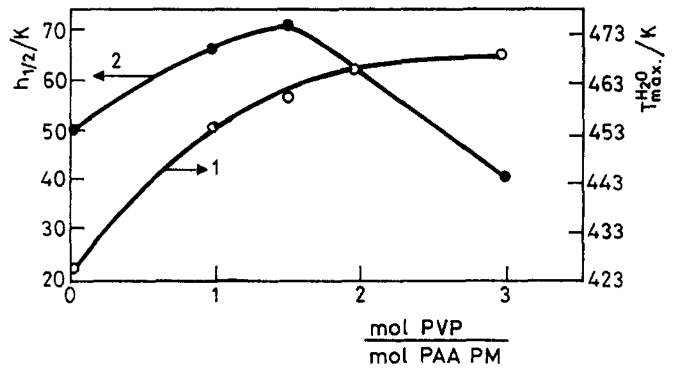


Fig. 3 Dependence of T_{max} (1) and half-width of the peak of water evolution $h_{1/2}$ (2) in composition PAA-PVP films on PVP concentration

In the case of PAA PM - PAN composites, linear PAN and PAN containing (according to IRS and elemental analysis) cyclic groups and carbonyl groups (cPAN) should be distinguished. According to the MTA data, the films of linear PAN obtained from DMF do not contain solvent, which shows that no strong donor-acceptor interaction exists between the nitrile group and the DMF molecule. It has been shown previously [9] that acetonitrile, the structure of which is close to that of acrylonitrile, is not contained in the solvocomplexes and does not displace DMF from the PAA PM film for similar reasons. A linear PAN is almost incompatible with PAA PM in solution with a high polymer concentration (from 5 to 15%) and forms cloudy films in the composites.

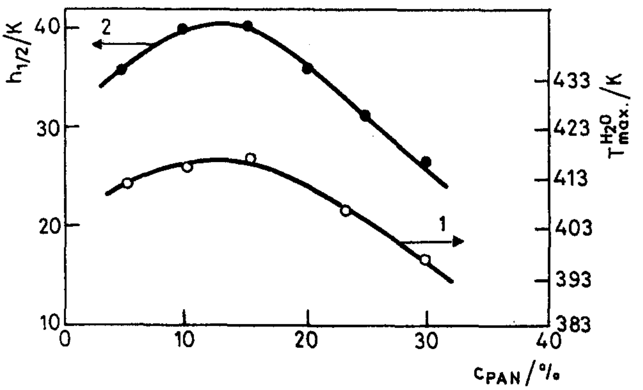


Fig. 4 Dependence of T_{max} (1) and $h_{1/2}$ (2) in composition PAA cPAN films on cPAN concentration

According to the MTA data (using a PAA PM film as an internal standard), the films obtained from a solution of cPAN in DMF contain DMF in an amount of about 0.5 mole per elementary unit, which corresponds to 1 DMF mole per cyclic structure. It might be assumed that the complexation of cPAN with DMF results from the formation of a hydrogen-bond between the imine nitrogen and the acid hydrogen of DMF. However, it has been shown that other amide solvents having no 'acid' hydrogen (DMAA and N-MP) form similar complexes with cPAN. Complexation probably proceeds as a result of the participation of unshared pairs of oxygen electrons in the carbonyl group of the solvent and the relatively electron-deficient ring of cPAN. Owing to the presence of the electron donor imine and the carbonyl groups in it, cPAN can form complexes not only with the solvent, but also with the carboxylic and amide groups of PAA PM. In contrast with the preceding pair, in which a weak polyacid is complexed to a weak polybase as a result of the formation of a system of hydrogen-bonds, the presence of imine groups means that in this case the interaction may be ionic in character, with the formation of salt-like polycomplexes. Homogeneous transparent films were obtained from a cPAN solution (with a degree of cyclization of 50%) and PAA PM solution in DMF with contents of the former of 5, 10, 15, 20, 25 and 30%. With the aid of

MTA, it was established that, with increasing concentration of cPAN, the half-width of the peak ($h_{1/2}$) of water eliminated in the cyclodehydration of PAA PM decreases. The value of $h_{1/2}$ is about 50 K for PAA PM, whereas for a mixture with a content of cPAN of 30%, it decreases to 25 K (Fig. 4). This fact shows that, as a result of the reaction with cyclic fragments of PAN, the set of energetic states of the carboxyamide groups is much narrower than in the PAA PM film. An increased c-PAN concentration leads to a decrease in the value of the maximum in the curve of elimination of cyclodehydration water (from 427 K for PAA PM to 395 K for a mixture with 30% c-PAN). These facts indicate that the density of films obtained from polymer mixtures has a tendency to level off and simultaneously to decrease as compared to PAA PM films. This was confirmed by a direct measurement of density (Fig. 5). This conclusion is supported by an investigation of the gas permeability of films. PAA PM films have a permeability coefficient P=1.2·10^{-10}, whereas films with 30% c-PAN are impermeable to gas (P=10^{-12}). In other words, in the former case the pore set is wider, and in the latter case the through-pores along which gas diffusion proceeds are virtually absent.

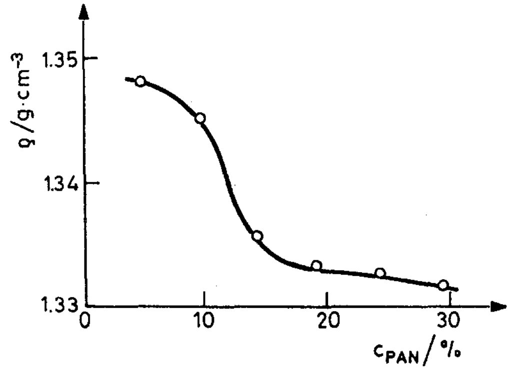


Fig. 5 Dependence of density of composition PAA-cPAN films on cPAN concentration

An MTA investigation of the kinetics and the character of the reaction of PAA PM with cPAN, depending on the conditions of preparation of the latter, is of particular interest. Figure 6 shows the MTA curves of cyclodehydration of composite PAA PM cPAN films for PAN, the times of maintenance in the reaction mixture in the presence of the cyclization catalyst being 1, 2, 3 and 4.5 h. It is clear that the three samples are characterized by a bimodal curve for elimination of the solvent and the cyclodehydration water. The first peak, with T_{max}=423 K, coincides in temperature with that for the individual PAA PM and probably characterizes that part of the PAA which is not contained in the interpolymer complex (IPC). The second peak exhibits a higher T_{max}; moreover, this T_{max} increases with the time of maintenance of cPAN in the reaction system (1–3 h), from 433 K to 458 K. Its existence may be related to the cyclodehydration of that part of the PAA PM which is contained in the IPC. The increase in T_{max} may be explained by a decrease in the mobility of carboxyamide groups because of the increasing rigidity of the IPC structure. It can be seen in Fig. 6 that the area under the second peak decreases with increasing time of cPAN maintenance, and this peak finally disappears, which indicates that the fraction of PAA PM in the IPC decreases to its complete disappearance. This conclusion is confirmed by the fact that, when cPAN is maintained in the reaction mixture for 4.5 h, it is not possible to obtain a homogeneous composite film: phase separation occurs during drying.

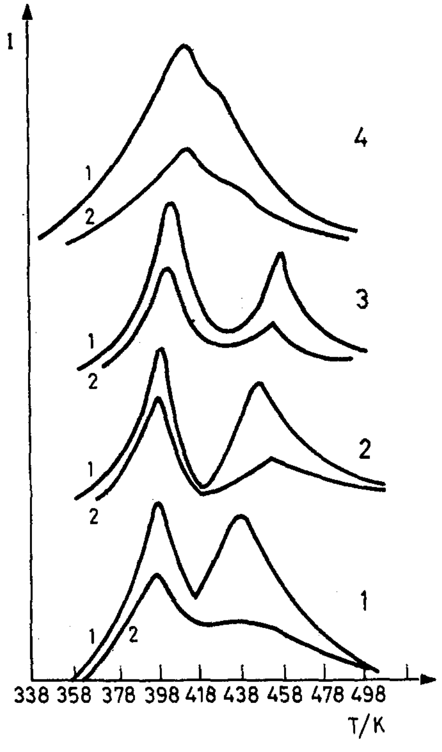


Fig. 6 Change in the character of imidization process of composition PAA cPAN films (cPAN concentration is 23 wt%) *vs.* time of maintenance of cPAN in reaction solution in the presence of catalyst. (1-1 h, 2-2 h., 3-3 h, 4-4.5 h.)

Since the chemical composition of cPAN does not vary during this experiment (the degree of cyclization is 50–51%), these results may be due to the tendency of cPAN to undergo autoassociation in solution [10], which is particularly manifested in the reaction mixture in the presence of the cyclization catalyst. The associates exhibit a dense rigid structure, and the penetration of PAA PM molecules into them is difficult.

Hence, the MTA method may be used for the qualitative characterization of cPAN autoassociation, according to its ability to take part in interpolymer interaction with PAA PM.

It should be noted that the shape of the curves obtained for PAA PM - cPAN is influenced by the time of keeping the polymer in solution before film casting. The number of contacts between the polymers increases with solution 'ripening', which is typical of polymer-polymer interactions.

As already mentioned, the complexes of weak PAA PM with a nonionogenic PVP base were described with the aid of the concepts of donor-acceptor interactions, with the formation of a hydrogen-bond system. Taking as an example a PAA PM - PVPyr interpolymer complex, a change in the interaction of the poly-

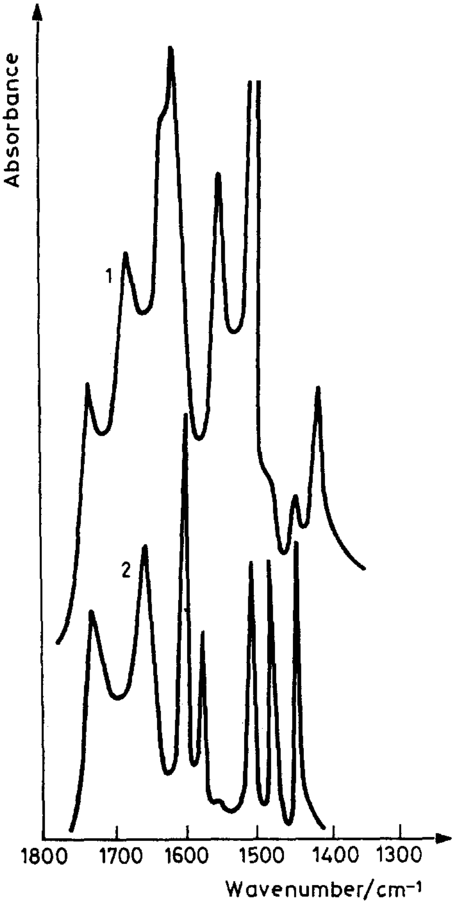
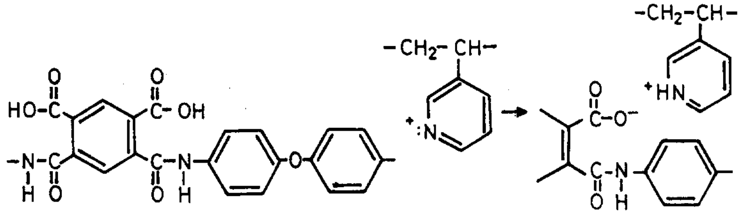


Fig. 7 IR-spectrum of composite PAA PM-PVPyr film (1) and additive spectrum of PAA PM and PVPyr films (2)

mers on passing to stronger polymer bases such as PVPyr and cPAN can be shown.

The existence of a strong interaction between PAA PM and PVPyr is detected immediately upon the dissolution of PVPyr powder in a PAA PM solution (the solvent is DMAA), as a result of a strong exo effect and the increasing viscosity of the composite solution. In contrast with PAA PM solutions, which lose viscosity relatively rapidly on storage at room temperature (T=293 K), the viscosity of the composite solution remains invariable for 10 days. This may be due to the formation of a salt-like complex, which is known to stabilize the PAA PM solution. In fact, IR-spectroscopy showed (Fig. 7) that the pyridine ring in PAA PM–PVPyr composite films is protonated. This is confirmed by the disappearance of the bands at 1420 cm^{-1} and 1470 cm^{-1} characteristic of pyridine. Simultaneously, a 1675 cm^{-1} band appears instead of the characteristic band of the carboxyl group at 1660 cm^{-1}. This band may be assigned to the carboxylate ion. Hence, a transfer of the acid proton to the nitrogen of the pyridine ring occurs in the composite film, and a salt-like complex is formed:



It is natural that, as a result of this interaction in the composite film, the amount of solvent, DMAA in this case, decreases (by about 1/7 of the usual quantity characteristic of PAA PM). This indicates that approximately every seventh carboxyamide group reacts with the pyridine ring of PVPyr. In spite of the strong interaction differing from that of the two preceding pairs, the MTA data indicate that this does not lead to an important change in the T_{max} of the evolution and in the half-width of the peak of cyclodehydration water, which shows that the rearrangement of the composite is relatively slight. In contrast, in the course of thermal treatment, chemical rearrangement occurs as a result of the reaction between the two polymers leading to a considerable change in the chemical composition of the initial mixture. It can be seen from the TG data (Fig. 8) that the curve of changes in the mass loss of the composite mixture differs greatly from that calculated for the case in which the degradation of each polymer proceeds independently of the other.

Hence, in the complexation of PAA PM with amide solvents and the competition of polymer bases with these solvents during the donor-acceptor polyacid-polybase interaction, the MTA method (in addition to TG, DTA, IR-spectroscopy, etc.) provides information on the structural changes in solid interpolymer complexes.

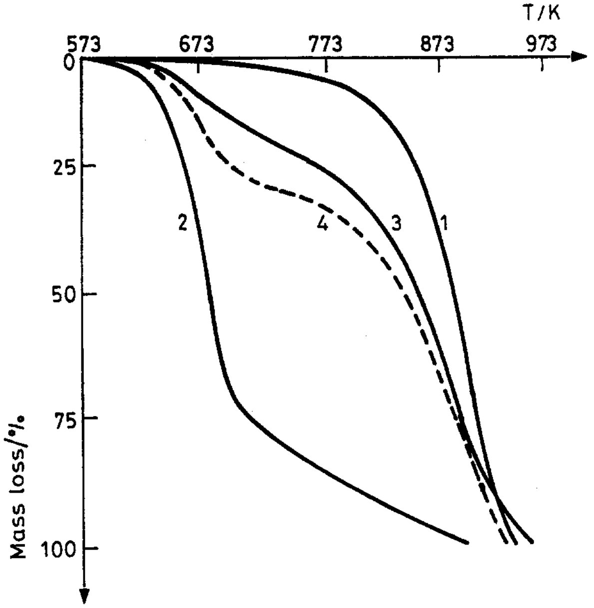


Fig. 8 Mass loss curves for films of PAA (1), PVPyr (2), PAA-PVPyr 1:2 (mol) (3) and theoretical curve of mass loss for PAA-PVPyr composition 1:2 (mol) calculated in the absence of interaction between PAA and PVPyr (4)

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Zusammenfassung — Mittels MS-Thermoanalyse (MTA), TG, DTA und IR-Spektroskopie wurden sowohl in Lösung als auch im festen Aggregatzustand die Polymer-Polymer-Wechselwirkungen zwischen Polyamicsäure (PAA) und Polybasen (Polyvinylpyrrolidon, Polyacrylnitril und Polyvinyl-pyridin) untersucht. Polybasen ersetzen das Lösungsmittel in seinem Komplex mit PAA und bilden dabei mit PAA Wasserstoffbindungen oder salzähnliche Polykomplexe. Die MTA-Methode erwies sich bei der Untersuchung von interpolymeren Wechselwirkungen im festen Aggregatzustand als sehr informativ.