

THERMAL ANALYSIS OF POLYAMIC ACID-FURYL ALCOHOL COMPOSITIONS

*I. E. Simanovich, G. N. Fedorova, N. V. Mikhailova, A. S. Bobasheva,
A. V. Griбанov and Yu. N. Sazanov*

INSTITUTE OF MACROMOLECULAR COMPOUNDS OF THE ACADEMY
OF SCIENCES OF THE USSR, LENINGRAD, USSR

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Polyamic acid (PAA) feryl alcohol (FA) and their mixtures in different ratios were investigated by DTA. The effects of the solvent and the component ratio on the thermal characteristics of the final products were established. It was shown that when the PAA-FA composition is heated, PAA is the initiator of the polymerization of FA, and the interaction in the system is profoundly affected by the component ratio and the temperature.

The existence of an interaction between the components of the system was confirmed by TG, and IR and NMR spectroscopy.

The unique properties of polyimides (PI) determine the increasing interest in the interactions of these polymers with other organic compounds at high temperatures [1–3]. We have previously shown that when the PI prepolymers, polyamic acids (PAA), interact with polyvinylpyrrolidone [4], interpolymeric complexes are formed, leading to the formation of new polymeric products. The investigation of the thermal reactions of PAA-FA system is also of considerable interest. The second component was chosen because furan resins are widely used in industry [5]. Thus, it is known that the introduction of FA into the composition of carbon articles with subsequent condensation can result in an improvement of such properties as strength, gas impermeability, chemical resistance and antifriction properties [6]. The purpose of this paper is to determine the conditions and character of the reactions between the components of the PAA-FA system.

The initial components were PAA based on pyromellitic dianhydride and diaminodiphenyl ether [1] and FA ($D^{20} = 1.4851$) purified by vacuum distillation. On their basis, resins with different ratios of initial components and prepared under different conditions obtained (Table 1).

The interaction was investigated by DTA at a heating rate of 2.3 deg min^{-1} in air, in ceramic crucibles. The reaction products were investigated by IR and high-resolution NMR spectroscopy and thermal analysis.

Table 1 Characteristics of the sample

Sample no.	Composition, % and nature of sample
1	FA, liquid
2	13% PAA in DMAA
3	50% FA + 50% DMAA, mixture
4	Film prepared from a mixture of 47% PAA + 53% FA
5	PAA film
6	0.6% PAA (13% solution in DMAA) + 99.4% FA
7	9% PAA (13% solution in DMAA) + 91% FA
8	20% PAA (13% solution in DMAA) + 80% FA
9	47% PAA (13% solution in DMAA) + 53% FA
10	PI, powder heated at 400° for 3 h
11	PFA, powder obtained by heating FA at 300° for 2 h
12	25% PI powder + 75% PFA powder, N content 4.3%
13	25% PAA (13% solution in DMAA) + 75% FA, N content 4.3%, heated at 250° for 2 h

The numbers in the Table correspond to the numbers of the curves in the Figures.

In order to determine the effects of temperature on the initial components and their mixtures in different ratios by means of DTA, a PAA solution in dimethylacetamide (DMAA), a mixture of FA with DMAA, samples with different FA to PAA ratios and also PAA and PAA-FA films were analyzed (Fig. 1). It was established first that when FA is heated, it evaporates to a great extent and only a small amount polymerizes, as is indicated by two weak exothermic effects, at 300 and 450°. Secondly, the solvent of the PAA, DMAA, does not influence the structural transformations of FA (Fig. 1, curve 3). When a PAA solution in DMAA is heated (Fig. 1, curve 2), the DTA curve exhibits two effects: an endo- and an exothermic effect. The former is due to the evaporation of the solvent and to the cyclodehydration of PAA [7], while the latter, with maximum at 600°, results from the decomposition of cyclodehydration products. Third, the effects revealed by the curves of the DTA films prepared from the solutions of FA and PAA are identical. The latter effect is caused by the fact that, without heating, no interaction occurs between the initial components and FA most probably evaporates when the film is dried. Comparison of the DTA curves of the PAA film and the PAA solution (curves 5 and 2, respectively) shows that the solvent decreases the thermal activity of the end-product by approximately 50 deg. Finally, upon slow heating of a mixture of PAA and FA, even a small addition of PAA (0.6%) leads to the appearance of a complex exothermic effect. PAA evidently initiates the polymerization of FA. Moreover, with increasing quantity of PAA, both the exothermic and endothermic effects in the DTA curve change. This indicates that the initial compounds interact and new structures are formed.

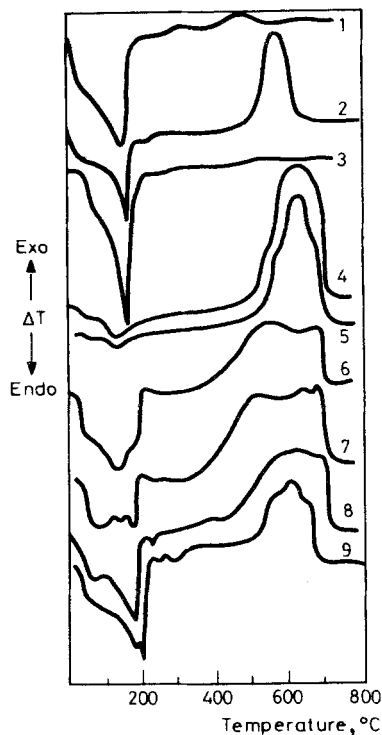


Fig. 1 DTA curves for samples 1-9

In order to confirm this assumption, the methods of TG and IR and NMR spectroscopy were used to carry out a comparative analysis of the powdered products of heating of the initial components and their mixtures, prepared both before and after heating (mechanical blend), at a PAA:FA or PI:PFA ratio of 25:75 (PFA = polyfuryl alcohol). The differences in temperature characteristics: the temperatures of the start of degradation (T_0) and of given percentage mass losses both before and after the start of the main degradation indicate that these samples differ from one another (Fig. 2). Moreover, it is clear that the product of interaction between PAA and FA in the first stage of thermooxidative degradation exhibits a greater mass loss than PI, which is more stable to high temperatures. In contrast, in the second stage, at higher temperatures its weight loss is much lower. Thus, for PI the temperature of 50% mass loss is 580°, while for the composition with FA it is 710°. With the aim of determining qualitative differences between these compounds, their IR absorption spectra were compared (Fig. 3). As a result, the non-overlapping bands at 1500 and 790 cm^{-1} due to PI and PFA, respectively, were chosen. Figure 3 shows that the absorption spectrum of a mixture of PI and

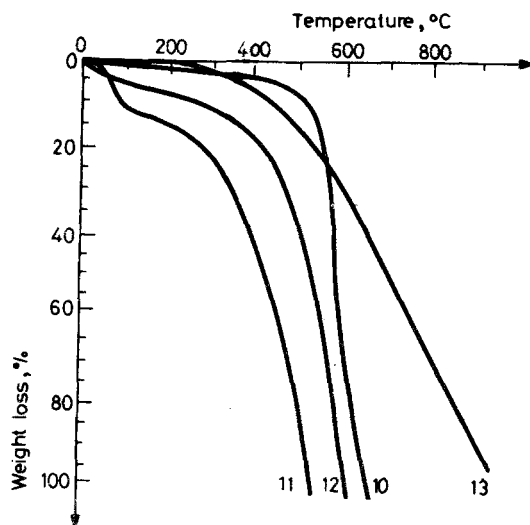


Fig. 2 TG curves for samples 10-13

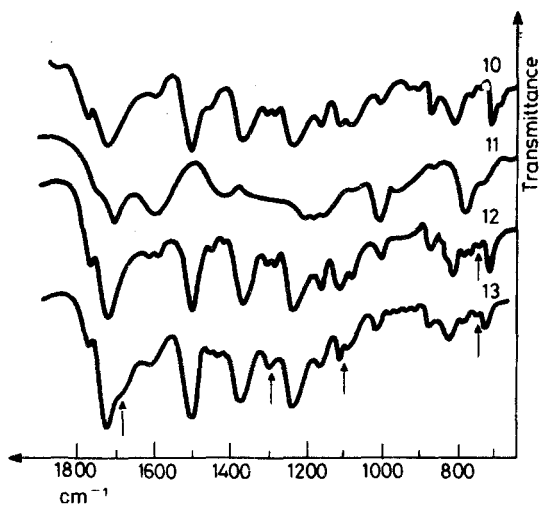


Fig. 3 IR spectra of samples 10-13

PFA powders results from overlapping of the spectra of PI and PFA. The IR spectrum of a mixture of PAA and FA heated at 250° for 2 hours exhibits some differences in the absorption bands. Thus, instead of two absorption bands at 1200 and 1300 cm^{-1} in the PI spectrum the spectrum of a heated mixture of PAA and FA exhibits one band, at 1300 cm^{-1} . The intensity of the bands at 1120 and 1090 cm^{-1}

is redistributed. The intensity of the PI band at 725 cm^{-1} decreases, and a new band appears at 745 cm^{-1} . Moreover, a band is observed at 1680 cm^{-1} , which was absent from the spectra of PI, PFA and their mixture in the form of powders. The bands in this range may be assigned to stretching vibrations of the carbonyl group of esters and amides. Hence, it might be suggested that the interaction between the components involves the formation of an ester group with the participation of amide groups.

The high-resolution ^{13}C NMR spectra of powdered samples of PFA, PI and their compositions are shown in Fig. 4. The assignment of the absorption lines in the NMR spectra to various carbon atoms of PI has been carried out in [8]. The assignment of the FA and PFA bands, and the preliminary analysis of samples 10–13, showed great changes in the spectrum of the composition as compared with those of the initial components and their mechanical blend. A decrease in mobility of the aliphatic moiety of PFA indicates that the interaction occurs without the opening of the furan rings, with the participation of side-groups. Thus, the signals in the range 10–55 ppm, evidently due to intercyyclic fragments of FA, lose their mobility almost completely, whereas those in the 100–160 ppm range, assigned by the authors to carbon atoms in the five-membered ring, do not change.

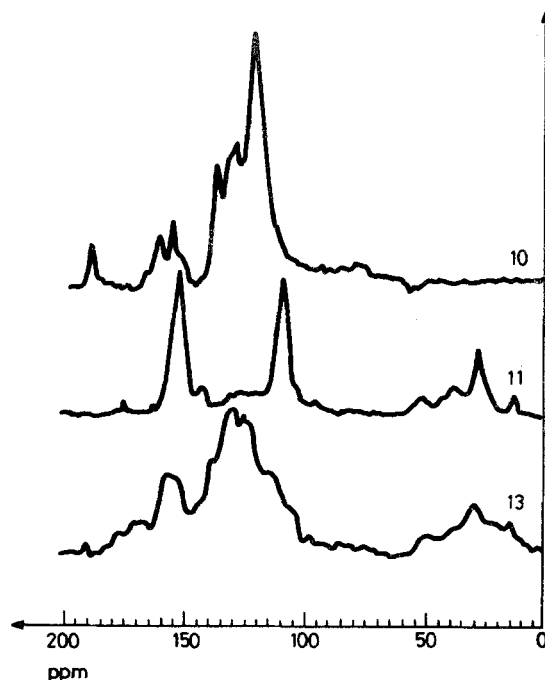


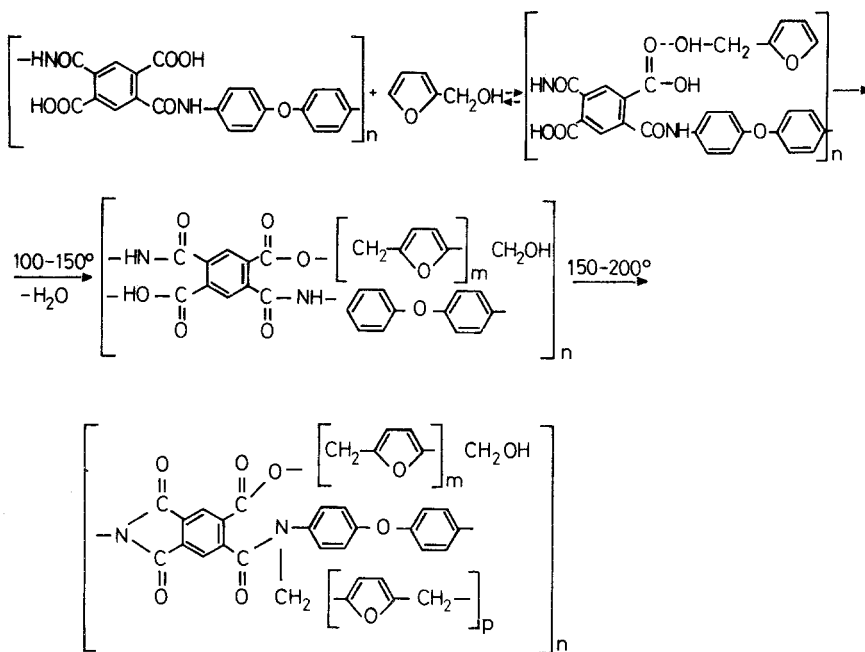
Fig. 4 High-resolution NMR spectra of samples 10–13

Hence, the above data show that, when the PAA-FA composition is heated, PAA is the initiator of the polymerization of FA, and the interaction between the components is profoundly affected by their ratio and by the temperature and duration of treatment. One of the variants of a possible interaction between the initial components at the PAA : FA ratio of 25 : 75 on heating at 250° for 2 hours can be represented by the following scheme:

a) When FA is added to PAA at room temperature or with slight heating, hydrogen-bonds are formed between the hydroxy groups of FA and the carboxyl groups of PAA.

b) Heating of the resulting mixture to 100–150° leads both to the polymerization of FA and to interaction between one of the carboxyl groups of PAA and the hydroxy end-group of FA, with formation of an ester bond.

c) Upon further heating of the mixture to 150–200°, PAA undergoes cyclodehydration, and intermolecular bonding of the amide group of PI to the hydroxy group of FA takes place:



The calculated values of the elemental composition for this final product are in approximate agreement with those determined for the product of interaction between PAA and FA. Thus, calculation of the percentage of nitrogen showed that the resulting structure contains one elementary PI unit per 2.75 FA units. If scheme

c) and this ratio are taken into account, the following percentage contents of the elements in the structure are obtained:

Calc.	C = 69.6	O = 22.6	H = 3.5	N = 4.4
Found	70.6	20.4	4.7	4.3

Bearing this scheme in mind it should be taken into account that, when the PAA-FA mixture is heated, apart from the above reactions other reactions will also occur, for example the dissociation of the PAA-solvent complex or cross-linking reactions with the formation of cross-linked structures. Higher temperatures of heating of the mixture will lead to the formation of bonds as a result of opening of the five-membered FA rings.

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Zusammenfassung — Mittels DTA wurden Polyamidsäure (PAA), Furfurylalkohol (FA) und deren Gemische verschiedenen Verhältnisses untersucht. Es wurde der Einfluß des Lösungsmittels und des Komponentenverhältnisses auf die thermischen Eigenschaften der Endprodukte festgestellt. Es konnte gezeigt werden, daß beim Erhitzen der PAA-FA-Gemische PAA die Rolle des Initiators der Polymerisation von FA übernimmt und daß die Wechselwirkungen im System von Komponentenverhältnis und Temperatur grundlegend beeinflußt werden. Die Existenz der Interaktion zwischen den Komponenten des Systems wurde durch TG-, IR- und NMR-Spektroskopie bekräftigt.

Резюме — Методом ДТА изучены полиаминовая кислота (ПАК), фурфуриловый спирт (ФС) и их смеси в различных соотношениях. Установлено влияние растворителя и соотношения компонентов на термические характеристики конечных продуктов. Показано, что при нагревании смесей ПАК-ФС, ПАК инициирует полимеризацию ФС, а взаимодействие в системе в значительной степени затрагивается соотношением компонентов и температурой. Наличие химического взаимодействия между компонентами системы подтверждено методами ТГ, ИК- и ЯМР-спектроскопии.