Journal of Thermal Analysis, Vol. 35 (1989) 947–954

MASS-SPECTROMETRIC ANALYSIS OF POLYMERS BASED ON FURYL ALCOHOL-POLYAMIC ACID COMPOSITIONS

L. A. Shibaev, Yu. N. Sazanov, N. G. Stepanov and *A. A. Boiko*

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

(Received February 12, 1988)

Polymer compositions based on furyl alcohol and polyamic acid were investigated by using mass-spectrometric thermal analysis. It was established that polyamic acid catalyses both the polycondensation of furyl alcohol and the formation of a three-dimensional network of furan polymer.

Polymers based on furyl alcohol (PFA) are widely used as adhesives for polymer composition materials. It has been shown that the characteristics of these polymers can be improved considerably by the introduction of a small amount (10% by weight) of polyamic acid (PAA PM) [1]. Study of the structural features of such polymer–polymer compositions is of interest. Mass-spectrometric thermal analysis (MTA) can provide important information about the polymer structure.

In the present work, MTA was used for analysis of the gas products evolved upon the heating of the composition in the temperature range 20–1200°. It was established that PAA PM catalyses both the polycondensation of furyl alcohol and the formation of a three-dimentional network as a result of the opening of double bonds in the furan ring. On the other hand, the furan polymer slightly decreases the thermal characteristics of the polyamide component of the end-product as compared to pure polyimide.

Experimental

Sample preparation. The samples were based on the following compositions: (1) furyl alcohol + 0.5% H_3PO_4, (2) furyl alcohol + a 12.5% solution of PAA PM in N-methyl-2-pyrrolidone, the furyl alcohol content of the solution being 5, 10, 25

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

or 75%, (3) a solution of PAA PM with the same furyl alcohol content as in (2) + 0.5% H_3PO_4. Sample curing was carried out at 100, 250 and 300 for 2 h.

Mass-spectrometric thermal analysis was carried out with an MKh–1320 mass spectrometer (USSR) by a published method [2]. The polymers were heated under non-isothermal conditions at a rate of 6.5 deg/min, with simultaneous recording of the gas products with the mass spectrometer. The relative quantities of unsaturated compounds and fragments were determined from the areas under the evolution curves of the corresponding products with m/e = 27, 81, 96, 161 and 178, using methane evolved during degradation (m/e 16) as the internal standard. The quantity of methane was taken to be approximately constant, regardless of the conditions of sample preparation. The degree of unsaturation was determined as the ratio of the quantity of units containing unsaturated bonds to the total quantity of furyl alcohol molecules undergoing polycondensation.

Discussion

Samples of furan polymers obtained via the curing of furyl alcohol without a catalyst were previously investigated with the aid of MTA [1]. However, the polycondensation of furyl alcohol is usually carried out in the presence of catalysts such as inorganic acids, organic acids and anhydrides, amines, amides, etc. [3]. The results obtained for pure furyl alcohol (in particular the amount of unsaturated compounds in the gas products and the degree of unsaturation determined by sample heating) are reference values in the investigation of the curing of compositions in the presence of catalytic agents.

The use of phosphoric acid in the polycondensations in an amount of 0.5% of the weight of furyl alcohol, greatly changes the quantitative composition of the gas products evolved during the MTA of furan polymer samples, whereas the qualitative composition of the volatile products remains approximately the same (Fig. 1) as in curing without a catalyst. Thus, when polycondensation was carried out at 150° in the presence of H_3PO_4, only a small amount of the furyl alcohol dimer (m/e 178) was formed; at a polycondensation temperature of 250°, the gas products formed during MTA contained no substances with m/e 161 or 178, and the samples obtained at 300° contained no volatile substances with m/e 96, 161 or 178. Table 1 gives the relative amounts of the unsaturated substances and fragments formed in the MTA of samples of furan polymers cured in the presence of 0.5% H_3PO_4. The degree of unsaturation of samples cured at 150, 250 and 300° was 40, 12 and 3%, respectively.

Phosphoric acid is usually considered to be a catalyst of polycondensation. However, a comparison of the above values with the results of the investigation of

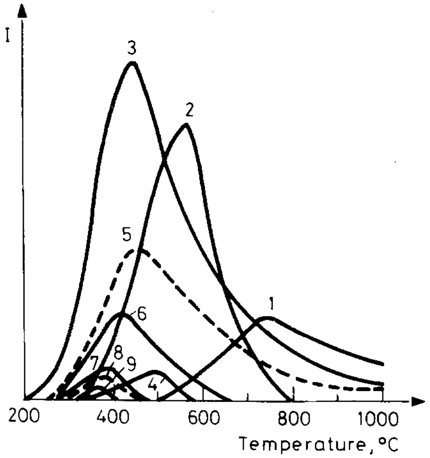
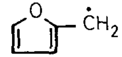
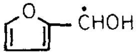
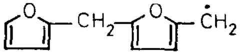
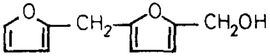


Fig. 1 MTA curves for a furan polymer obtained in the presence of 0.5% of H_3PO_4 and cured at 250°. (1) *m/e* 2 (hydrogen, (2) *m/e* 16 (methane), (3) *m/e* 18 (H_2O), (4) *m/e* 27 ($CH_2=\dot{C}H$), (5) *m/e* 28 (CO, ethylene), (6) *m/e* 44 (CO_2), (7) *m/e* 81, (8) *m/e* 96, (9) *m/e* 161

substances obtained by the curing of furyl alcohol without the catalyst shows that the acceleration of polycondensation is accompanied by a decrease in sample unsaturation. This may be due to the acceleration of crosslinking. It cannot be ruled out, however, that the acceleration of the opening of the furan ring in the presence of H_3PO_4 is also possible, although the general picture of MTA and the temperatures of peak maxima for the individual substances remain the same as for thermal polycondensation (Table 2).

Since the PAA PM molecule contains both amide and acid groups, it might be expected that the polyamic acid will accelerate the polycondensation of furyl alcohol. In fact, the introduction of a 12.5% solution of PAA PM in N-methyl-2-pyrrolidone into furyl alcohol (the furyl alcohol: PAA PM solution ratio is 75:25) catalyses polycondensation. Thus, at 150° pure furyl alcohol in an open volume is volatilized before the formation of the furan polymer, whereas at the same temperature the above composition is transformed into a solid polymer after 2 h. The qualitative composition of the gas products (Fig. 2) and the temperatures of the maxima in the evolution curves of the gas products remain approximately the same as in the case of pure furyl alcohol (Table 2). The relative amounts of unsaturated fragments evolved during MTA are intermediate between those for polymers of furyl alcohol and polymers obtained from furyl alcohol with the addition of H_3PO_4 (Table 1). Calculation of the extents of unsaturation for the samples based on a composition consisting of 75% of furyl alcohol and 25% of PAA PM solution cured at 150, 250 and 300° gave values of 73, 17 and 17%, respectively. The equal unsaturation values in the two latter cases may be due to defects in the technological treatment of the samples.

Table 1 Quantity of unsaturated compounds in degradation products of furan polymers

Fragment mass	Chemical structure of fragment	Relative quantity of fragments in gas products of degradation											
		polymer of furyl alcohol			polymer based on the composition furyl alcohol+ +0.5% H_3PO_4			polymer based on the composition furyl alcohol+ +PAA PM			polymer based on the composition furyl alcohol+ +PAA PM+0.5% H_3PO_3		
		*200	250	300	150	250	300	150	250	300	150	250	300
27	$CH_2=\dot{C}H$, HCN	0.29	0.19	0.12	0.07	0.06	0.04	0.052	0.12	0.08	0.42	0.05	0
81		1.77	0.17	0.11	0.25	0.06	0.02	0.51	0.08	0.07	0.46	0.06	0
96		0.24	0.08	0.11	0.11	0.03	0	0.35	0.04	0.07	0.15	0.002	0
161		0.46	0.07	0.01	0.10	0.06	0	0.32	0	0	—	0	0
178		0.16	0.07	0	0.02	0	0	0.06	0	0	—	0	0

* Temperature of sample curing, °C

Table 2 Temperatures of maxima in curves of gas product evolution in degradation of furan polymers

	Curing temperature: 160°					250°					300°				
Fragment mass	Furyl alcohol*	Furyl alcohol +0.5% H_3PO_4	Furyl alcohol + PAA PM solution (75% : 25%)	Furyl alcohol + PAA PM solution (75% : 25%) + 0.5% H_3PO_4	Furyl alcohol + PAA PM solution (25% : 75%)	Furyl alcohol	Furyl alcohol +0.5% H_3PO_4	Furyl alcohol + PAA PM solution (75% : 25%)	Furyl alcohol + PAA PM solution (75% : 25%) +0.5% H_3PO_4	Furyl alcohol + PAA PM solution (25% : 75%)	Furyl alcohol	Furyl alcohol +0.5% H_3PO_4	Furyl alcohol + PAA PM Solution (75% : 25%)	Furyl alcohol + PAA PM solution (75% : 25%) +0.5% H_3PO_4	Furyl alcohol + PAA PM solution (25% : 75%)
16	540	540	520	530	530	560	540	570	550	545	550	530	515	550	530
18	330/480	425	465	475	490/570	470	430	490	425/500	545	460	425	470	470	530
27	340/490	500	380/470	360/470	380/675	470	490	405/485	500	365	480	495	470	—	475
28	450	450	465	455	470/600	450	440	465	450	465/585	450	450	450	465	455
44	420	445	440	450	410/570	450	410	400	405	505	420	440	435	450/550	475
81	190/370	345	390	390	195/400	380	380	400	390	385	415	420	390	—	410
96	370	390	400	410	410	390	390	—	390	405	410	—	400	—	415
161	330	345	370	—	340	370	390	—	—	—	400	—	—	—	—
178	360	385	—	—	—	370	—	—	—	—	—	—	—	—	—

* Furyl alcohol without additives is cured at 200°

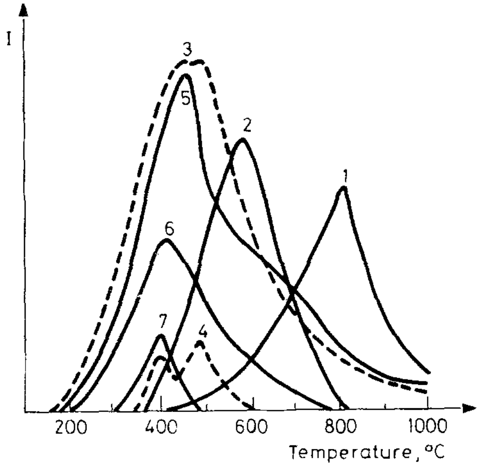


Fig. 2 MTA curves for a polymer based on a composition consisting of 75% of furyl alcohol and 25% of PAA PM and cured at 250°. Curve 4: *m/e* 27 ($CH_2=\dot{C}H$, HCN). Other symbols see Fig. 1

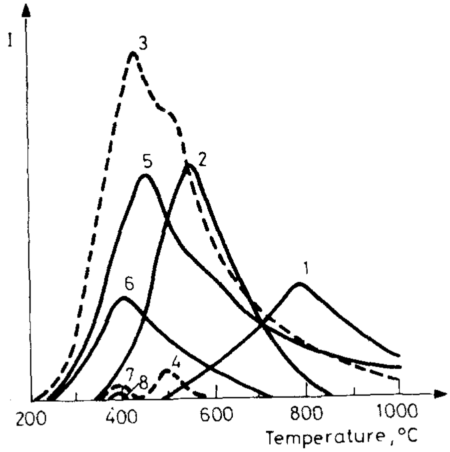


Fig. 3 MTA curves for a polymer based on a composition consisting of 75% of furyl alcohol + 25% of PAA PM in the presence of 0.5% of H_3PO_4 (with respect to the mass of furyl alcohol) and cured at 250°. Symbols as in Fig. 2

Investigation of the composition furyl alcohol + 25% PAA PM solution + 0.5% H_3PO_4 revealed overall the maximum rate of the processes of polycondensation and crosslinking of the furan component. As a result of heating at 150°, the amount of unsaturated gas products on MTA is slightly higher than for the furyl alcohol + H_3PO_4 composition. For samples cured at 250°, the amount of these products is considerably lower, and for samples obtained at 300°, the ions corresponding to unsaturated compounds are absent from the mass spectra. The extent of unsaturation calculated for these compounds was 51%, 5% and 0%, respectively. These data show that in this case the maximum temperature required for the preparation of a completely crosslinked polymer based on furyl alcohol can be decreased to approximately 250°, because the extent of unsaturation of the sample obtained by using only phosphoric acid as the catalyst at the curing temperature of 300° was 3%.

Table 2 gives the temperatures of the peak maxima in the curves of evolution of gas products for the compositions considered above and for those containing furyl alcohol and 5, 10 and 75% of the PAA PM solution. The conclusion which can be drawn from these results reduces to the fact that the values of the temperature maxima remain reasonably constant for the samples based on pure furyl alcohol and the compositions containing 5, 10 and 25% of PAA PM solution. Apart from the gas products characteristic of the MTA of furan polymers, peaks with *m/e* 93 (phenol) and *m/e* 103 (benzonitrile) and the second maxima with *m/e* 28 (CO) and *m/e* 44 (CO_2) also appear. All these peaks result from the degradation of the imide structure, and their temperature maxima are slightly lower than those for common polyimides. This is natural if it is taken into account that the degradation products of the furan polymer contain hydrogen, water and other reactive agents accelerating the thermal degradation of polyimides. Figure 4 shows a typical picture of the MTA of a composition containing a large (about 50% with respect to the final product) amount of polyimide. Unfortunately, the MTA data cannot give an unequivocal answer to the problem of whether two independent structures, the

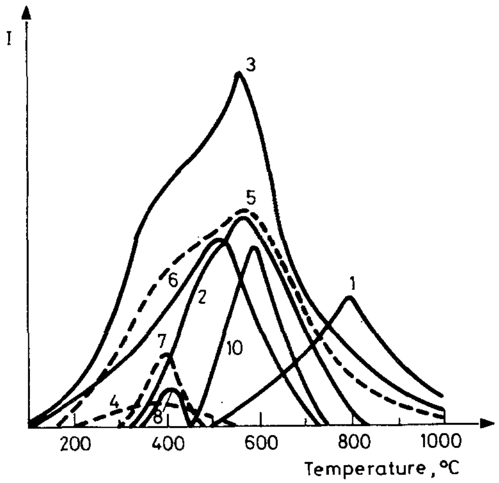


Fig. 4 MTA curves for a polymer based on a composition consisting of 25% of furyl alcohol + 75% of PAA PM and cured at 250°. Curve 10: *m/e* 94 (phenol). Other symbols as in Fig. 2

furan polymer and polyimide, exist, or whether a new unique structure containing the elements of both types is formed upon thermal treatment as a result of the polymer–polymer interaction. In order to establish the structure of the final polymer, additional investigations are necessary with the application of other methods of study of polymer systems in the solid state.

Hence, MTA was used for study of the qualitative composition of the gas products evolved upon the heating of polymers based on the furyl alcohol + PAA PM compositions in the temperature range 20–1200°. The kinetics of formation of a three-dimensional structure of furan polymers was followed as a function of the initial composition. It was established that polyamic acid accelerates both the polycondensation of furyl alcohol and the formation of a three-dimensional polymer structure. It has been shown, in particular, that for the composition containing furyl alcohol, 25% of PAA PM solution and 0.5% H_3PO_4, the maximum crosslinking density is attained at a temperature 50 deg lower than that for the furyl alcohol + 0.5% H_3PO_4 composition. The temperatures of the maxima in the curves of evolution of gas products remain constant for the following systems: furyl alcohol, furyl alcohol + 0.5% H_3PO_4, furyl alcohol + 5, 10 and 25% of PAA PM solution, and furyl alcohol + 25% of PAA PM solution + 0.5% H_3PO_4. In the case of high PAA PM concentrations (50% polyimide in the cured product) in the initial compositions, the MTA curves exhibit peaks characteristic of the thermal degradation of polyimides, but displaced towards a lower temperature range.

References

S. A. Dauengauer, T. N. Spirina, L. A. Shibaev, T. E. Pogodina, N. G. Stepanov and Yu. N. Sazanov, Abstracts of papers at the first USSR Conference "Polymer Mixtures", Ivanovo, 1986, p. 122.

2 L. A. Shibaev, S. A. Dauengauer, V. M. Denisov, A. I. Koltsov, Yu. N. Sazanov and T. I. Zhukova, Acta Polymerica, 35 (1984) 291.

3 Yu. M. Mamatov, "Furanovye smoly. Proisvodstvo i primenenie", Moscow 1974.

Zusammenfassung — Mittels massenspektroskopischer Thermoanalyse wurden auf Furylalkohol und Polyamidsäure basierende Polymergemische untersucht. Es wurde festgestellt, daß Polyamidsäure sowohl die Polykondensation von Furylalkohol als auch die Bildung eines dreidimensionalen Furanraumnetzes katalysiert.

Резюме — Методом масс-спектрометрического термического анализа исследованы полимерные композиции на основе фурилового спирта и полиамидокислоты. Показано, Что полиамидокислота катализирует как поликонденсацию фурилового спирта, так и образование трехмерной структуры фуранового полимера.