

MASS-SPECTROMETRIC THERMAL ANALYSIS OF POLYMERS BASED ON FURYL ALCOHOL

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Mass-spectrometric thermal analysis of samples of furan polymers obtained by heating furyl alcohol in a closed volume at 200 °C, 250 °C and 300 °C permitted determination of the qualitative composition of the gas products evolved from the polymers upon non-isothermal temperature increase from 20 to 1200 °C. The degree of unsaturation of the samples was evaluated quantitatively. The main features of the formation, degradation, structuration and carbonization of furan polymers were considered.

Furyl alcohol is widely used for the preparation of adhesives in the manufacture of chemically resistant plasto-concrete, anticorrosive coatings and pressed materials, and for the impregnation of carbon materials in the manufacture of electroconducting contacts [1]. However, the polycondensation of furyl alcohol has not been studied in detail because of the difficulties involved in the formation of a three-dimensional network and transition of the reaction product into the insoluble state [2]. The processes of carbonization of furan polymers have been studied even less.

In the present paper, some features of the formation, degradation, structuration and carbonization of furan polymers were studied via mass-spectrometric thermal analysis (MTA) of the gas products evolved upon the heating of polymers based on furyl alcohol. The extent of crosslinking of the samples investigated was evaluated quantitatively.

Experimental

Sample preparation

The polymers based on furyl alcohol were obtained in a closed volume by heating the monomer without the catalyst at 200, 250 or 300° for 2 h.

Mass-spectrometric thermal analysis (MTA)

Polymer samples were investigated with an MKh-1320 mass spectrometer by a method described in [3]. The polymers were heated at a rate of 6.5 deg/min, with simultaneous recording of gas products with the mass spectrometer.

The evolution curves of gas products express the time (t) and temperature (T)—dependences of peak heights (h) for the corresponding values of m/e . The quantitative analysis of these products was carried out with the aid of graphical integration of the curves $h_m = f(t)$:

$$Q_m = \varphi_m \int_{t_1}^{t_2} h_m(t) dt$$

where Q_m is the content of the gas product m in the temperature range corresponding to the time interval $t_2 - t_1$, and φ_m is the coefficient of sensitivity to the substance m .

The relative quantities of unsaturated fragments were determined from the areas under the curves for the products with $m/e = 27, 81, 96, 161$ and 178 , by using the methane ($m/e 16$) evolved during degradation as the internal standard. The quantity of methane was considered to be approximately constant, regardless of the curing temperature of the sample. Degree of unsaturation was determined as the ratio of the number of fragments containing unsaturated bonds to the total number of furyl alcohol molecules participating in the polycondensation process.

Results and discussion

The results of MTA (Fig. 1) on a sample obtained by heating furyl alcohol without the curing catalyst at 200° make it possible to establish the main characteristic ions of the mass spectrum and the corresponding qualitative composition of the products evolved during the heating of the furyl polymer: $m/e 2$ (hydrogen), $m/e 16$ (methane, oxygen), $m/e 17, 18$ (water), $m/e 27$ ($\text{CH}_2 = \dot{\text{C}}\text{H}$), $m/e 28$ (carbon monoxide, ethylene), $m/e 30$ (formaldehyde), $m/e 31$ ($\dot{\text{C}}\text{H}_2\text{OH}$), $m/e 32$ (oxygen, methanol), $m/e 41$ ($\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$), $m/e 42$ (propylene), $m/e 44$ (carbon dioxide, propane) and unsaturated compounds with furan rings. The composition of the gas products formed upon heating of the furyl polymer under non-isothermal conditions in the temperature range 20 – 1200° is a result of the superposition of four processes occurring in different temperature ranges, but having a common interval in which all four processes take place simultaneously.

First, the processes of completion of polycondensation probably occur from low temperatures up to 300° . Further, in the range 150 – 450° , the three-dimensional

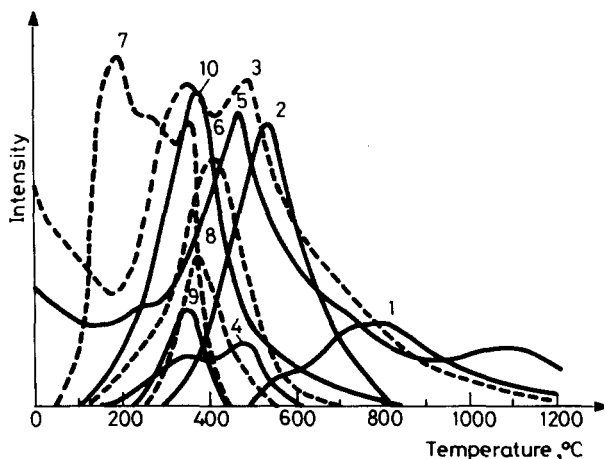


Fig. 1 MTA curves for a furan polymer cured at 200 °C: (1) m/e 2 (hydrogen); (2) m/e 16 (methane); (3) m/e 18 (water); (4) m/e 27 ($\text{CH}_2=\dot{\text{C}}\text{H}$); (5) m/e 28 (CO, ethylene); (6) m/e 44 (CO_2); (7) m/e 81; (8) m/e 96; (9) m/e 161; (10) m/e 178

structure is formed as a result of opening of the double bonds of the furan rings. Finally, in the range 200–1200°, the molecules of the furan polymer undergo degradation and structurization, with the carbonized residue as the final product. The entire temperature range is characterized by the elimination of water molecules produced in the above processes (with the exception of the formation of the three-dimensional network as a result of the opening of double bonds). The range 250–600°, in which the majority of volatile products is evolved, is characterized by the most intensive degradation process, and the evolution exhibits a maximum at 350–500°. In this range, not only the constant gases (H_2 , CO, CO_2), but also the fragments with unsaturated furan rings (m/e 81, 96, 161, 178, etc.) and water are evolved. The peak at m/e 16 in the temperature range 350–750° deserves attention. Since the peak at m/e 32 is absent in this range, it may be concluded that the peak at m/e 16 is due to methane and not to oxygen. In the range 450–1200°, hydrogen is evolved with a maximum at 780°. The last peak, at m/e 28, exhibits a maximum at 1080° and refers to carbon monoxide. Among the degradation products, relatively large amounts of polymer chain fragments containing furan rings (including a product with m/e 178, corresponding to the furyl alcohol dimer) are observed. According to the MTA data, the amounts of these products decrease for samples prepared at 250° and 300° (Figs 2 and 3). Moreover, the locations of the peaks of the corresponding products remain constant on the temperature scale. This permits conclusions about the general processes occurring in various samples of furan polymers. This refers to both unsaturated products and methane. Figure 1 shows that the products with m/e 81 and 27 display two peaks and begin to be evolved at

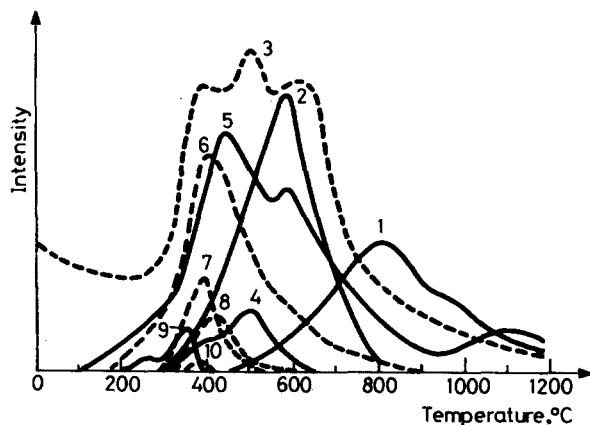


Fig. 2 MTA curves for a furan polymer cured at 250 °C. Symbols as in Fig. 1

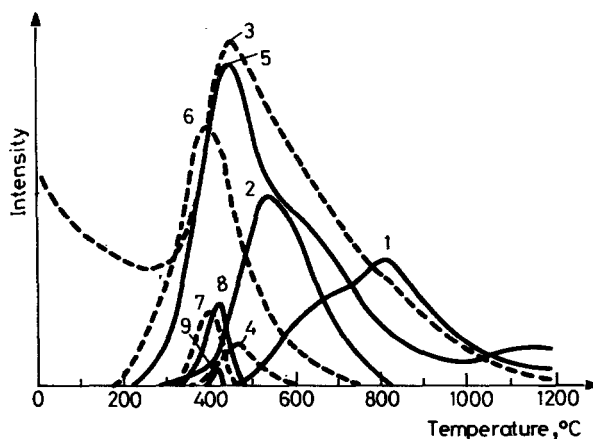


Fig. 3 MTA curves for a furan polymer cured at 300 °C. Symbols as in Fig. 1

about 100°. Hence, it may be concluded that low molecular weight volatile products containing furan rings are present in the condensate. This fact and the existence of two maxima in the curve of water elimination indicate that the polycondensation process is to a large extent incomplete. The MTA of a sample obtained at 250° (Fig. 2) shows that the low-temperature peak with m/e 81 is absent on the corresponding curves, but a low-temperature water peak appears, which overall leads to the conclusion that polycondensation proceeds to a larger extent. The peaks in the curves obtained for a sample cured at 300° (Fig. 3) have only one maximum, and it may be supposed that in this case the polycondensation process is essentially complete.

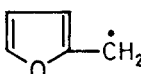
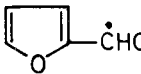
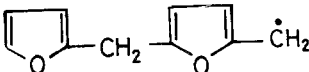
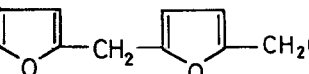
The presence of a large amount of unsaturated compounds in a sample cured at 200° (Table 1) shows that in this case the three-dimensional structure formed when the double bonds of the furan ring are opened is weakly expressed. At the curing temperatures of 250° and 300°, the amounts of unsaturated products evolved from the corresponding samples are lower. However, the MTA data show that even the sample cured at 300° contains fragments with unsaturated bonds.

When the sample undergoing MTA is heated to 350°, methane (*m/e* 16) appears in the gas products. In our opinion, its formation is mainly due to the abstraction of methylene groups located between the cross-linked fragments formed as a result of opening of the double bonds of the furan ring.

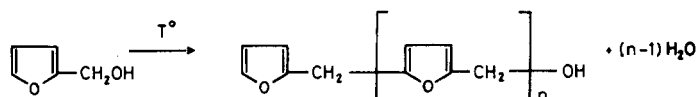
Molecular hydrogen is recorded beginning from 450–500°, and its evolution does not stop even at 1200°. Oxygen is isolated from the furan polymer in the form of H₂O (*T*_{max} 470°), CO (*T*_{max} 450°) and CO₂ (*T*_{max} 425°). The evolution of CO, CO₂ and H₂O proceeds over a wide temperature range (200–700° for CO₂ and up to 1000° for CO and H₂O), which indicates that the processes of opening of the furan ring (at low temperatures) and the degradation of five-membered rings occur after the formation of the crosslinked structure. It should be noted that the evolution of CO (*m/e* 28) continues up to 1200°, and at 1080° the second maximum appears.

Hence, as a result of the MTA of the samples of furan polymers, several structures may be singled out, which appear with increasing temperature.

Table 1 Contents of unsaturated compounds in degradation products of furan polymer samples

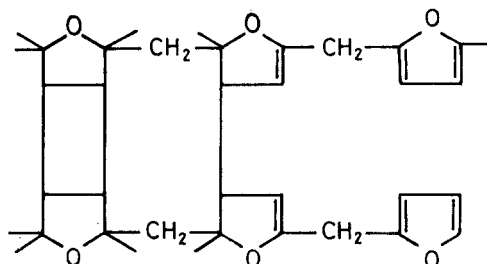
Mass of compound (fragment)	Chemical structure of compound (fragment)	Relative quantity of compound (fragment) upon thermal treatment		
		200 °C	250 °C	300 °C
<i>m/e</i> 27	$\text{H}_2\text{C} = \dot{\text{C}}\text{H}$	0.29	0.19	0.12
<i>m/e</i> 81		1.77	0.17	0.11
<i>m/e</i> 96		0.24	0.08	0.11
<i>m/e</i> 161		0.46	0.07	0.01
<i>m/e</i> 178		0.16	0.07	0

First, linear molecules are formed when furyl alcohol is heated to 200–250° :



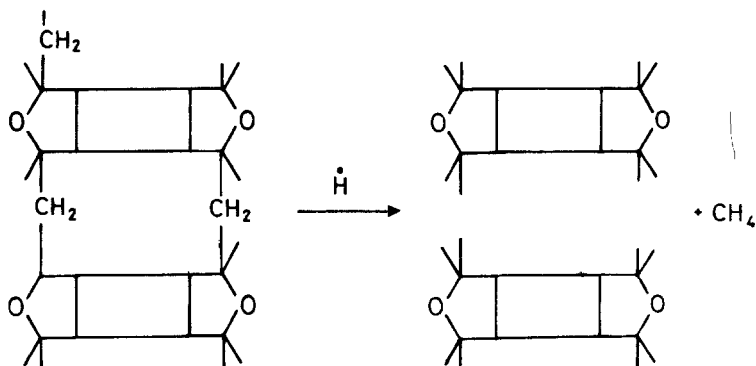
When furyl alcohol is cured at 200°, apart from the polymer large amounts of the dimer and oligomers are formed. The degree of unsaturation of this sample is 80%. During MTA, degradation of the linear molecule can be observed, beginning from 200°.

Secondly, the three-dimensional network appears as a result of double bond opening:



Polymer samples cured at 250° and 300° contain considerably fewer unsaturated structures as a result of both the partial degradation and the opening of double bonds in the furan ring. The degrees of unsaturation of these samples are 36 and 24%, respectively.

Thirdly, beginning from 350°, linear parts of the structures undergo degradation with the evolution of methane during the MTA process. As a result, the layer structure of the crosslinked polymer is formed:



The maximum rate of formation of the layer structure is probably in the temperature range 550–600°.

Finally, as a result of the evolution of molecular hydrogen, water and CO, the final structure of the polymer residue is formed. It is a three-dimensional network in which the rings with 5 and 6 carbon atoms can presumably be distinguished.

References

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Zusammenfassung — Durch massenspektrometrische Thermoanalyse von Furanpolymerproben, hergestellt durch Erhitzen von Furylalkohol in einem abgeschlossenen Volumen bei 200 °C, 250 °C und 300 °C, wurde es möglich, die qualitative Zusammensetzung der beim nichtisothermen Erhitzen von 20 auf 1200 °C, aus den Polymeren entstehenden Gasprodukte zu ermitteln. Der Grad an Ungesättigtheit der Proben wurde quantitativ bestimmt. Die Hauptmerkmale von Bildung, Degradierung, Strukturisierung und Karbonisieren wurden gegeben.

Резюме — Масс-спектрометрический термический анализ образцов фурановых полимеров, полученных в результате нагрева фурилового спирта в замкнутом объеме при 200 °C, 250 °C, 300 °C позволил установить качественный состав газообразных продуктов, выделяющихся из полимеров при динамическом подъеме температуры от 20 до 1200 °C. Произведена количественная оценка степени неурядности образцов. Рассмотрены особенности образования, деструкции, структурирования и карбонизации фурановых полимеров.