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, structurization 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, structurization 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 $h_m = f(t)$:

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

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 $\phi_m$ 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 (CH$_2$=CH), m/e 28 (carbon monoxide, ethylene), m/e 30 (formaldehyde), m/e 31 (CH$_2$OH), m/e 32 (oxygen, methanol), m/e 41 (CH$_2$=CH−CH$_2$), 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