

КРАТКИЕ СООБЩЕНИЯ

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Obtainment of cold-curing resin based on acetone and formaldehyde

The reaction of aldol condensation of acetone and formaldehyde depending on the synthesis conditions allows obtaining different products possessing a controllable set of useful consumer properties, which is very convenient for creation of materials with desired properties based on the same reagents. At the same time, such universality can create technological problems in the absence of identification of the process regularities and without studying the kinetics of this reaction in different conditions.

Preliminary experiments showed that the reaction kinetics of the aldol condensation of acetone with formaldehyde is mostly influenced by temperature and catalyst concentration, and the properties of the final products (oligomers) – by the ratio of reagents. In this paper, the kinetics of condensation reactions of acetone with formaldehyde and without it, as well as formation of intermediate reaction products – oligomers in the alkaline medium, was researched. The influence of the temperature on the kinetics of this process was studied with the fixed concentrations of components of the base mixture in the isothermal mode.

The experiments were conducted using a calorimetric plant «ATLAS» (Syrris) in the mode of the heat compensation method with automatic control of pH, temperature of the reaction mixture and reaction enthalpy. The reaction temperature varied in the range of 25 ÷ 55 °C with a constant initial concentration of acetone and formaldehyde in the presence of carbonates of alkali metals used as a catalyst. Formaldehyde was used in the form of the 37 % liquid solution, stabilised by methanol. Acetone of reagent grade and sodium and potassium carbonates were used without additional purification.

The reaction mass was analysed by the methods of gas chromatography (GCA-MS), high-performance liquid chromatography (HLCA-MS) with a mass-spectrometer. Identification of intermediate products and oligomers was also carried out on the time-of-flight mass spectrometer during electrospraying ionization (Time of Flight - ToF). Resins obtained after concentration of the oligomers' solution and products of their polymerization were additionally analysed by the method of synchronous TG-DTA/DSC analysis.

The results of the kinetic analysis show that formaldehyde reacts with acetone in the mole ratio of $\sim 3/1$, which is preserved independently of the reaction temperature in the interval of 25 – 50 °C. In the structure of intermediate products – oligomers – it was found that this ratio was also retained for repeating units of oligomers. The detailed analysis of mass-spectra ToF (fig. 1) of the reacting mass allows concluding that the structure of the main oligomers includes a base fragment of diacetone alcohol (DAA), which is evidence of the process of self-condensation of acetone at the initial stage of oligomers' formation (route A). Later, an interaction of formaldehyde molecules with DAA, accompanied by formation of corresponding methylol derivatives, takes place. The results of the chromatographic analysis indicate to equilibrium formation of DAA. In conditions of the process, products of immediate condensation of acetone with formaldehyde were found (Route B).

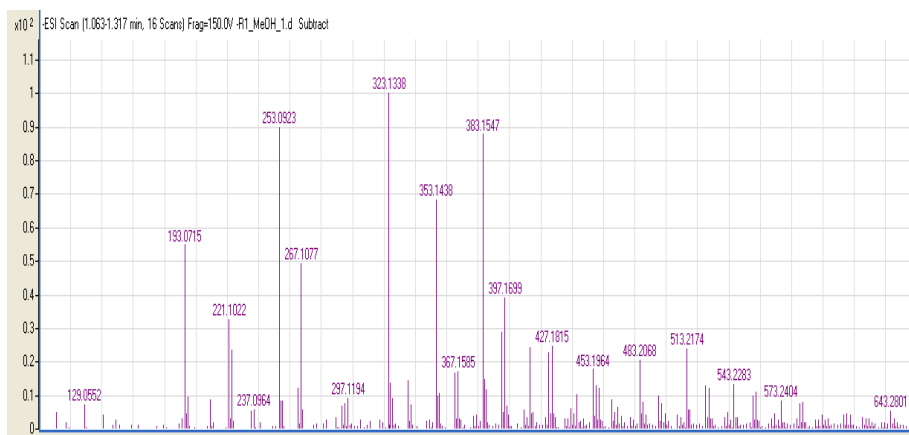
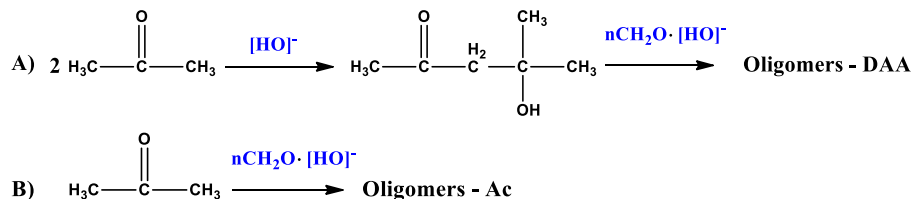
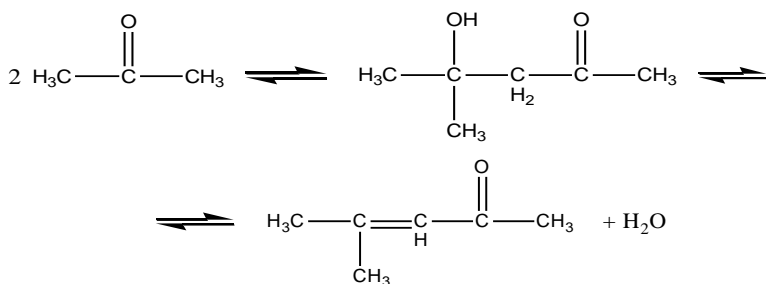


Fig. 1. Mass spectrum of reacting mixture (ToF)

Based on the analysis of the data received, a reaction scheme was proposed; intermediate and stable products of the process were identified; rate constants of main reactions were determined:



To assess the share of the mentioned routes, the reaction of acetone self-condensation in conditions of the process without addition of formaldehyde was studied separately. The results show that in the presence of sodium and calcium carbonates, the reaction of aldol condensation proceeds with a fast identification of equilibrium concentration of diacetone alcohol, which later transforms mainly to mesitylene oxide according to the scheme:



Each of these products can originate oligomerization with formaldehyde forming products of different masses and substitution degrees. Owing to high activity of formaldehyde in the alkaline medium, successive attachment of formaldehyde takes place, which is evidenced by the weight gain of components of the reaction mixture by 30 units. Analysis of the massive of the molecular mass of components shows that in conditions of the process, detachment of the water molecule occurs accompanied by formation of unsaturated groups C=C in the oligomers' structure. Owing to these bonds as well, depending on the alkali concentration, further growth of molecular mass takes place accompanied by formation of both solid and ductile polymer materials. Varying the initial ratio of acetone/formaldehyde, it is possible to obtain resins of cold curing with formation of a number of final products with desired properties.

The paper presents the test results and properties of the obtained products and composite materials.