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SYNTHESIS OF NOVOLAC TYPE PHENOL FORMALDEHYDE OLIGOMERS

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ABSTRACT

Mixed novolac-type oligomers are synthesized in the melt on the base of oxibenzene and its alkilsubstituted. The content of dioxibenzene changes in the range of 0,1 – 0,5 mol. The influence of temperature and duration of the reaction of initial components, transformation has been studied.

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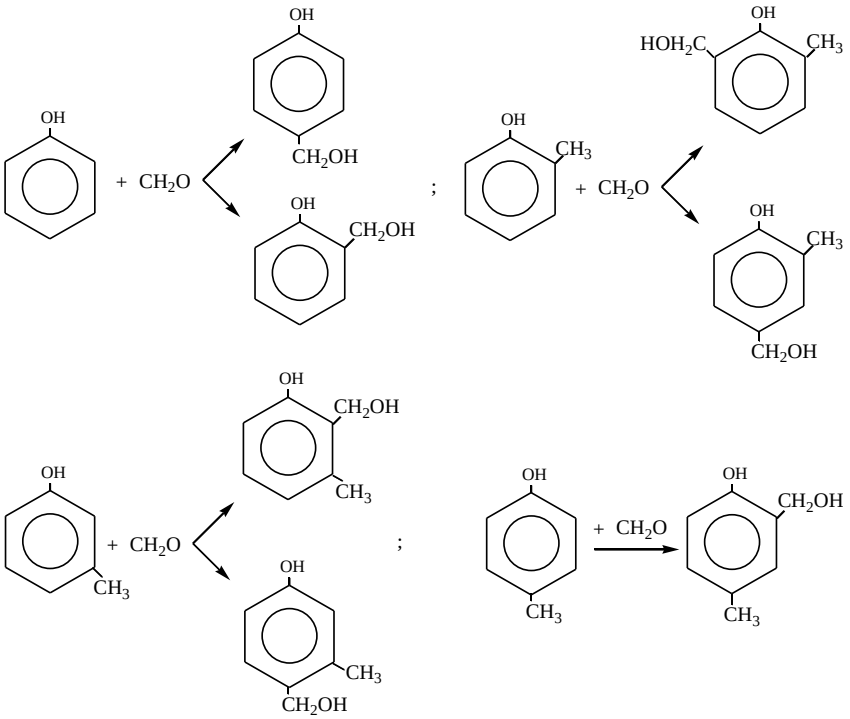
For the synthesis of oligomers of the novolac type, oxybenzene and its alkyl derivatives are used as starting components. Formaldehyde is used as the second component. A technology has been developed for obtaining oligomers in a melt, in which there is no wash water. The resulting oligomer contains a minimum amount of unreacted oxybenzene.

To obtain mixed oligomers, along with oxybenzene, its alkyl-substituted derivatives were used. The presence of alkyl groups in the oligomer has a plasticizing effect, which is important during the processing of plastics.

When carrying out the synthesis reaction of the oligomer in the melt, paraform is used as the second component, which depolymerizes when heated and releases formaldehyde. Formaldehyde, when formed, immediately reacts with oxybenzene and its alkyl-substituted derivatives and forms methylol derivatives:



In the production of novolac, the reaction is carried out in the presence of an excess of hydroxy derivatives of benzene. The reaction temperature and catalyst concentration affect the reaction rate, while the duration affects the average molecular weight of the oligomer.

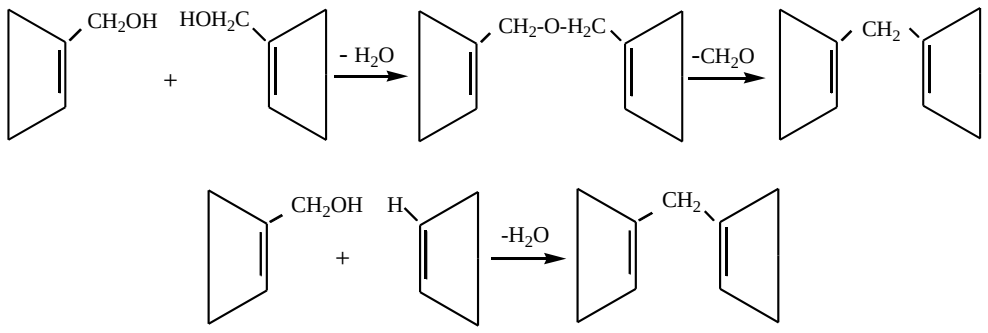
In the synthesis of mixed oligomers, as the second component, together with oxybenzene, we used 1-hydroxy-2-methyl-, 1-hydroxy-3-methyl- and 1-hydroxy-4-methylbenzene.

Since the oxybenzene derivative is used in excess, and, besides, the rate of the condensation reaction is higher than the rate of the addition reaction, the oligomers practically do not contain methylol groups, which is confirmed by a spectroscopic study.

The intensity of the absorption bands characteristic of methylol groups in the region of 1030 cm-1 first appears, and then gradually decreases and by the end completely disappears.

The process of interaction of oxybenzene and its methyl-substituted derivatives with formaldehyde was studied. The results are shown in Figure 1. The molar ratio of oxybenzene and its methyl derivative in the mixture was 0.5: 0.5, the reaction temperature was 40-100 °C. The molar ratio of the mixture of oxybenzene and its methyl derivative to formaldehyde was 1.15: 1, respectively.

As can be seen from the data in the figure, the course of the reaction is influenced by both the temperature and the duration of the reaction. With increasing reaction time and temperature, the conversion increases. For example, in the interaction of oxybenzene and 1-hydroxy-2-methylbenzene with formaldehyde at 40 ° C, after 20 minutes the degree of conversion is 58.8%, at 60 °C - 67.3, at 80 °C it increases to 82, and at 100 °C it reaches 87%.



In the course of the reaction, formaldehyde can interact with the already formed methylol derivative, or with the oligomer. In parallel, methylol derivatives interact with each other, or with hydroxy derivatives of benzene, or with oligomers. During this interaction, along with the addition reactions,

polycondensation reactions proceed in parallel. The addition in the molecule of the oxy derivative occurs with the participation of active hydrogen atoms in the ortho and para positions to the hydroxyl.

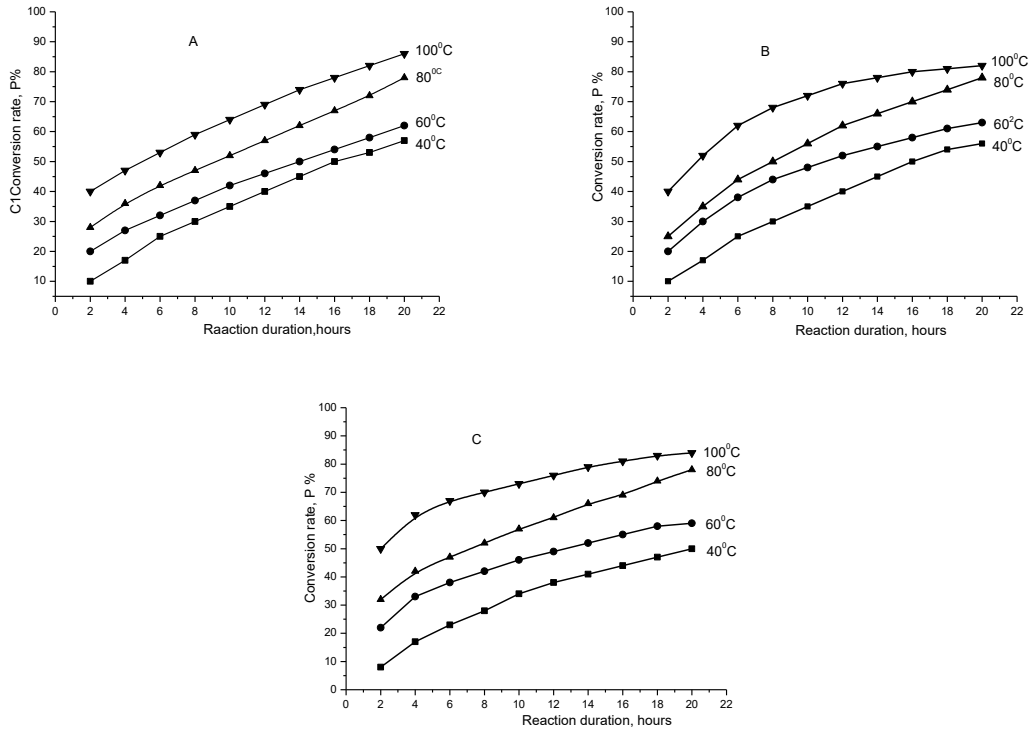


Fig.1. Change in the degree of conversion of oxy- and 1-hydroxy-2-methylbenzene (a), oxy- and 1-hydroxy-3-methylbenzene (b) and oxy- and 1-hydroxy-4-methylbenzene (d) with formaldehyde in the melt.

In the case of oxybenzene and 1-hydroxy-3-methylbenzene, the conversion degree increases in the following sequence: 55.1> 64.3> 79.3> 83.6%; in the case of oxybenzene and 1-hydroxy-4-methylbenzene - 59.8> 69.4> 84.0> 88.8%.

Schematically, the condensation process in an acidic medium can generally be expressed as follows:

$$(x + 1) [\ C_6H_5OH + \ C_6H_4CH_3OH \ ] \ + \ xCH_2O \ \rightarrow \ x \ H_2O \ +$$
$$H [- (C_6H_3OH) – CH_2 – (C_6H_2(CH_3)OH) –CH_2 -]- C_6H_3(CH_3)OH ,$$

where x = 10 – 14

The degree of polymerization of the novolac oligomers obtained in the melt is 10-14. As can be seen, at the increase of the process duration, the amount of formaldehyde that doesn't enter the reaction decreases. The intensity of the decrease is higher in the initial stage. For example, if during the course of the reaction at 40 °C in the case of oxybenzene and 1-hydroxy-2-methylbenzene, after 2 minutes the amount of formaldehyde not reacted is 91.1%, after 5 minutes it decreases to 74.7, after 10 minutes - 59.5, after 15 minutes -48.9, and after 20 minutes to 41.1%; at 60°C, respectively 77.6> 60.7> 43.4> 39.5> 32.7%; at 80 °C - 71.0> 49.2> 32.9> 23.2> 18.0%; and at 100 °C - 57.7> 36.7> 20.9> 15.5> 12.3%. A similar trend is observed in the case of other oxides.

Mixed oligomers dissolve in alcohol, acetone, dimethylformamide, tricresol, etc. When interacting with hexamethylenetetramine at 180-200 °C, they are structured and turn into resite, which have a spatial structure. At the same time, they completely lose solubility in the above solvents and do not melt.

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