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BRIEF COMMUNICATIONS

On the Synthesis and Structure of Resol Phenol-Formaldehyde Resins

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Abstract—Chemical structure of the SFZh-3013 standard resol phenol-formaldehyde resin was studied by the method of quantitative ^{13}C NMR spectroscopy.

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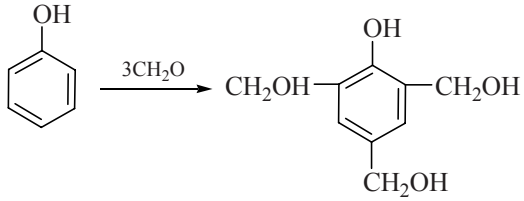
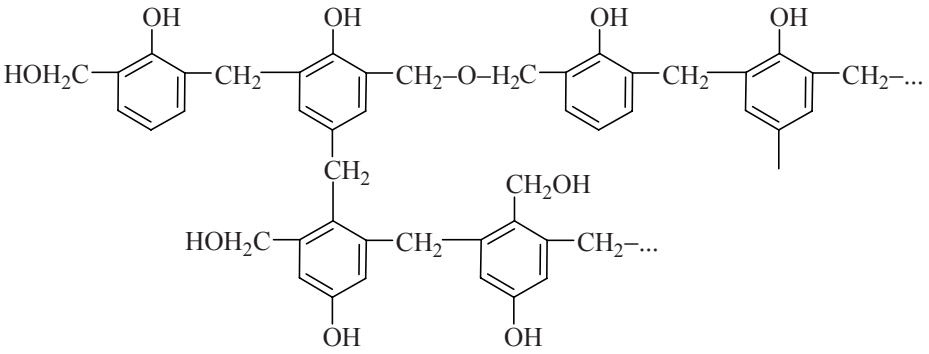
Resol phenol-formaldehyde resins (PFR) are widespread commercial synthetic polymers, which find wide application in production of various glued products: plywood, fiber boards, etc. According to the classical theory of the synthesis of resol resins [1–3], the reaction of phenol and formaldehyde in an alkaline medium proceeds in two stages: (1) synthesis of phenol alcohols:



(2) polycondensation of phenol alcohols with the formation of oligomers [scheme (1)].

As a result of the polycondensation phenol fragments combine with each other mainly through methyllene bridges. It has been shown [4] that aside from methylene bridges phenol nuclei can also combine with each other through the dimethylene ether groups $–CH_2–O–CH_2–$. It is pointed out that temperature of the process essentially affects the polycondensation rate [1–4].

To refine the mechanism of PFR stucturization, we have studied standard commercial PFR of the SFZh-



(1)

Distribution of carbon atoms in structural fragments of the copolymer of phenol with formaldehyde

Fragment	Relative content of carbon atoms		^{13}C chemical shift, ppm; assignment of signals [6]
	q, fraction	N[a]	
C=O	0.002	1.7	210–200; carbon atoms of carbonyl groups
C(O)O–	0.009	7.9	200–170; carbon atoms of quinoid, carboxylic, and ester groups
C_{ar}–O	0.110	96	164–145; carbon atoms of aromatic rings linked with oxygen atoms
$CH_{ar} + C_{ar}$	0.561	492	142–122; tertiary and quaternary carbon atoms of aromatic rings
$CH_{ar\ ortho}$	0.014	12	120–117; tertiary carbon atoms of aromatic rings located in the *ortho*-position to the C_{ar}-O fragment
CHO	0.019	17	80–70; carbon atoms of the aliphatic fragments =CHO–
CH_2O	0.175	154	69–60; carbon atoms of the aliphatic fragments –CH_2O–
CH_2	0.109	96	44–30; carbon atoms of the aliphatic fragments –CH_2–
f_a	0.685	600	Degree of the polymer aromaticity $f_a = I_{tot}/I_{arom.\ carbon\ atoms}$

[a] N is the number of carbon atoms per 100 aromatic rings.

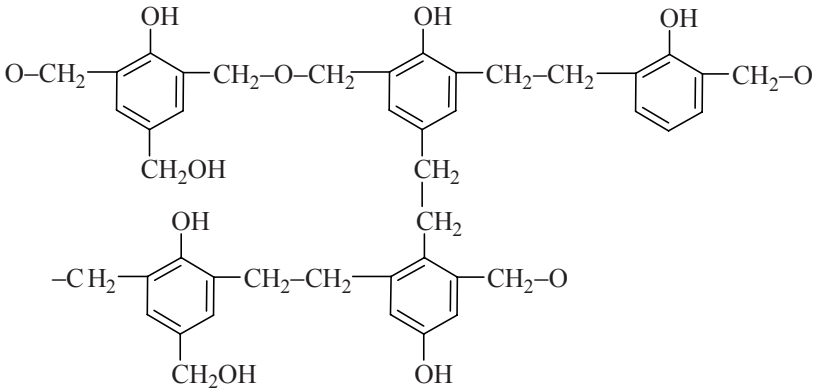
3013 resol type produced by "IlimBratskDOK" Joint-Stock Company.

The ^{13}C NMR spectra of the polymer were recorded on a VXR-500S Varian spectrometer with the noise decoupling from protons. The relaxation delay was 10 s, impulse –90°, a NaOD solution in D_2O. Working frequency was 125.5 MHz. The quantity of structural fragments is presented not only in fractions, but also per 100 aromatic rings (AR). Such normalization is allowable, as condensed aromatic rings are absent from the PFR structure. The relative error in the determination of the fraction of carbon atoms is 4.7%, the number of structural fragments per 1 AR calculated from the ^{13}C NMR spectra does not exceed 6.7% [5].

The analysis of the ^{13}C NMR spectrum of PFR has shown (the table), that the structure of the polymer under study differs from the structure presented in scheme (1). In particular, the presence of carbonyl groups of ketones and carboxy groups in the structure of condensation products was established. The presence of quinoid or quinonemethide fragments is not excluded, as is seen from the signals at 180–182 ppm and also from the fact that not 100 C_{ar}–O fragments, but 96 correspond to 100 AR. Furthermore, as a result of condensation reactions –CHO fragments are formed in a small amount (see the table) [6].

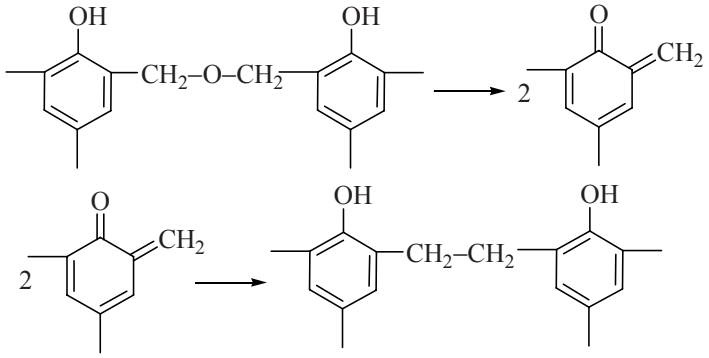
The main difference a the structure of the investigated polymer from the canonical structure [scheme (1)] consists in the fact that aromatic rings are connected not only by the methylene and –CH_2OCH_2– bridges, but also by the –CH_2–CH_2– ethylene bridges. Two groups of broadened resonance signals in the ^{13}C NMR spectrum at 44–38 and 38–30 ppm, which correspond to the resonance of carbon atoms of the methylene bridge and the –CH_2–CH_2– fragment, respectively, point to this fact [6]. The quantitative analysis of the spectrum leads to the following averaged structure of the copolymer (without taking into account minor structural units) [see scheme (2)].

The characteristic signals in the region of 120–117 ppm of tertiary carbon atoms located in *ortho*-position with respect to the phenolic hydroxyl testify that 12 *ortho*-positions per every 100 aromatic rings are not replaced. Apparently, the chain termination takes place at these rings.



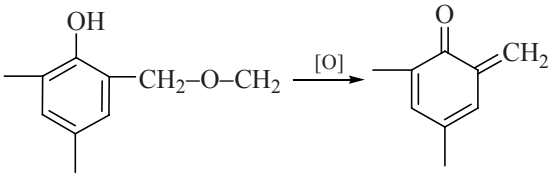
(2)

The monograph [7] notes that ethylene bridges between phenol PFR units can be formed on the dimerization of quinone methides, which, in turn, are generated at the thermal hardening of resols from resol dibenzylester fragments according to scheme (3).



(3)

As it is known, the amount of oxygen dissolved in an alkali, can reach the concentration of 8 mmol dm^{-3} for 1 N NaOH solution [8]. The occurrence of the oxidation reactions at elevated temperatures (boiling points of reaction mixtures) of the copolymer synthesis should not be excluded [9]. In this case quinone methides can be formed immediately from hydroxymethylphenols:



(4)

CONCLUSIONS

(1) It was shown that the copolymer resulted from the phenol-formaldehyde condensation, contains ethylene bridges, ketone and carboxy groups, and also quinone and quinone methide fragments apart from methylene bridges and ether bonds between phenol rings.

(2) The process of phenol-formaldehyde polycondensation in an alkaline medium proceeds by a mechanism differing from the canonical mechanism.

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