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Abstract

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On the Structure of Copolymers of Acrolein with Vinyl Aryl Ethers

Recently, much attention has been given to high-molecular-weight compounds based on acrolein. In many papers, researchers discuss possible structures of polyacrolein and suggest that, along with other forms, chains consisting of condensed oxygen-containing rings may be formed (1-6).

Information on the structure of copolymers of acrolein with vinyl aryl ethers is entirely absent from the literature. It is known only that they react with one another with the formation of solid reaction products soluble, in contrast to polyacrolein, in organic solvents (7-9). The present work is devoted to the study of the structure of copolymers of acrolein with vinyl phenyl ether obtained under the influence of stannic chloride. As a result of the investigations carried out, interesting regularities were observed. Thus, with an equimolecular ratio of the initial reaction components, solid copolymers of the corresponding composition were obtained. Upon fractionation, copolymerization products are isolated which have different molecular weights, from 500 to 2000, and the same fractional composition. On this basis it may be assumed that alternation of units of both monomers occurs in the polymer chain. The absence of free aldehyde groups, demonstrated spectroscopically and chemically, suggests the presence of rings in the main chain of copolymers of acrolein and vinyl phenyl ether.

Investigation of the liquid products of the copolymerization reaction of acrolein with vinyl phenyl ether (constituting 60-70% of the weight of the reaction mass taken) showed that they contain no initial monomers, but consist mainly of a mixture of diene-synthesis adducts and products of their decomposition. Phenol (b.p. 180-181°, m.p. 39.5-40.5°) and an oily liquid with b.p. 112-116°/10 mm, n_D^{20} 1.5340, d_4^{20} 1.0760 were isolated; according to our assumptions, the latter contains 2-phenoxy-3,4-dihydropyran. Found: MR_D 50.84. $C_{11}H_{12}O_2$F. Calculated MR_D 50.02.

The independent synthesis of this compound, whose composition and properties were not known in the literature, was carried out by diene thermal condensation of acrolein with vinyl phenyl ether. Individual 2-phenoxy-3,4-dihydropyran was obtained with a purity of 99.9%, demonstrated by gas-liquid chromatography, with b.p. 115°/9 mm, n_D^{20} 1.5357; d_4^{20} 1.0950. MR_D found 50.08, calculated

50.02.

Found, %: C 74.43; H 6.94

$C_{11}H_{12}O_2$F. Calculated, %: C 74.97; H 6.87

These constants correspond to the characteristics of the above-mentioned substance isolated from the reaction mixture formed during the cationic polymerization of acrolein and vinyl phenyl ether. Investigation of the infrared spectra* of 2-phenoxy-3,4-dihydropyran obtained by independent synthesis and isolated from the reaction mixture formed— formed as a result of copolymerization, indicates the identity of their structure (Fig. 1).

The positions of the bands characteristic of the valence vibrations of all the principal bonds coincide for both products (curves 1 and 2). In the spectrum of individual 2-phenoxy-3,4-dihydropyran there are absorption bands at 1110, 1086, and 1040 cm^{-1}. In the IR spectrum of the substance isolated from the by-products of the copolymerization of acrolein with vinyl phenyl ether, in this absorption region there are, respectively, bands at 1114, 1090, and 1038 cm^{-1}. According to the available literature data, maxima in the interval 1124-1030 cm^{-1}, as well as the band at 1100 cm^{-1}, are assigned to C—O vibrations in the tetrahydropyran ring (10–12).

Thus, it may be considered proved that, in the cationic copolymerization of acrolein with vinyl phenyl ether, diene condensation of the starting monomers also takes place, in which acrolein plays the role of the diene and the vinyl ether of phenol the role of the dienophile.

The cyclic structure of the chains of copolymers of acrolein with vinyl aryl ethers is possible by virtue of the polymerization of the adducts of diene synthesis. To prove this assumption we carried out the polymerization reaction of 2-phenoxy-3,4-dihydropyran. The reaction was conducted by the cationic mechanism under the same conditions as the copolymerization of acrolein with vinyl phenyl ether.

Fig. 1. IR spectra: 2-phenoxy-3,4-dihydropyran obtained by the method of thermal diene synthesis (1), 2-phenoxy-3,4-dihydropyran isolated from the products of copolymerization of acrolein with vinyl phenyl ether (2), polymer of 2-phenoxy-3,4-dihydropyran (3), copolymer of acrolein with vinyl phenyl ether (4)

$$n\,\mathrm{HC({=}CH_2){-}CH{=}O} + n\,\mathrm{CH_2{=}CH{-}O{-}Ar} \longrightarrow \left[\mathrm{O}^{\text{six-membered ring}}_{\quad\mathrm{OAr}}\right]_n \longrightarrow$$

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* We express our gratitude to N. I. Shergina and N. I. Golovanova for assistance in measuring the IR spectra.

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⟶ cyclic polymer structures with OAr substituents [six-membered cyclic unit with OAr] cyclic term

where Ar =

$$C_6H_5; \quad C_6H_4{-}CH_3; \quad C_6H_3(R){-}CH_3.$$

As a result, a polymeric product was isolated in the form of a white powder, with m.p. 110-112°, molecular weight 1350 (viscometric), yield 90%, soluble in acetone, benzene, petroleum ether, and chloroform. The infrared spectra of the obtained poly-2-phenoxy-tetrahydropyri-

of pyran and the solid product of the cationic copolymerization of acrolein with vinyl phenyl ether show an almost complete coincidence of the principal absorption bands (Figs. 1, 3, 4).

In an analogous manner, the copolymerization of acrolein with homologs of vinyl phenyl ether—vinyl *o*-, *m*-, and *p*-cresyl ethers and vinyl thymol ether—was studied. Spectral investigations of the homopolymers obtained on the basis of 2-(*o*-, *m*-, *p*)-cresoxy-3,4-dihydropyran and 2-thymoxy-3,4-dihydropyran showed their identity with the spectra of copolymers of acrolein with the corresponding vinyl ethers and also confirmed the presence of tetrahydropyran rings in the copolymers.

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