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Abstract

Full Text

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POLYMERIZATION OF *o*-HYDROXYPHENYL VINYL KETONE

Recently, polymers containing groups capable of forming intracomplex or chelate compounds with metal ions have been acquiring ever greater importance ([1]). Usually the indicated compounds are synthesized by means of various polymer-analogous transformations, which is a substantial drawback of this method.

The presence of a chelating group in the monomer molecule, analogous to that contained in hydroxyketone dyes ([2]), makes it possible to obtain complex-forming polymers directly by polymerization and copolymerization of *o*-hydroxyphenyl vinyl ketone:

$$\left[\begin{array}{c} -\mathrm{CH}-\mathrm{CH_2}- \\ | \\ \mathrm{C=O} \longrightarrow \mathrm{Me} \\ | \\ \text{phenyl ring} - \mathrm{O} \end{array}\right]_n$$

There is almost no information in the literature on the polymerization of substituted phenyl vinyl ketones, in particular hydroxy-substituted ones ([3]).

The aim of the present investigation was to study and select conditions for the radical polymerization of *o*-hydroxyphenyl vinyl ketone.

The monomer was synthesized according to the scheme

$$\text{2-hydroxyacetophenone} + \mathrm{CH_2O} + \mathrm{NH(CH_3)_2} \cdot \mathrm{HCl} \longrightarrow \text{2-hydroxy-}\beta\text{-dimethylaminopropiophenone hydrochlorid}$$

$$\text{2-hydroxy-}\beta\text{-dimethylaminopropiophenone hydrochloride} \xrightarrow{\text{distillation with steam}} \text{*o*-hydroxyphenyl vinyl ketone-}$$

Polymerization of *o*-hydroxyphenyl vinyl ketone was carried out in a nitrogen atmosphere by several methods: in solution, in bulk, and in suspension. The polymerization initiators were benzoyl peroxide and azobisisobutyronitrile.

At 75–80°, polymerization in bulk and in benzene solution is completed in 1–1.5 hours, and in suspension in 3–4 hours. The polymers are transparent light-yellow blocks or granules; after reprecipitation, white powders. Poly-*o*-hydroxyphenyl vinyl ketone dissolves in many orga-

organic solvents (benzene, acetone, pyridine, dimethylformamide) and dilute alkalis; it does not dissolve in methanol, carbon tetrachloride, or ether. The molecular weight, determined by the light-scattering method, is 125,000.

The values of the intrinsic viscosities of benzene solutions of the polymers and their melting temperatures are given in Table 1. From the data in Table 1 it is evident that, in the case of polymerization of *o*-hydroxyphenyl vinyl ketone, the usual dependence of the molecular weight (the value of $[\eta]$) on the polymerization method is observed.

Table 1

Polymerization method	$[\eta]$	M.p., °C
In benzene solution	0.23	165–175
In bulk	0.26	175–185
In suspension with emulsifier: polyvinyl alcohol	0.35	185–195
In suspension with emulsifier: $CaCO_3$	0.42	190–195

The kinetics of polymerization was studied by the dilatometric method. The dependence of the degree of polymerization on time was determined in benzene solution at a 1 M concentration of *o*-hydroxyphenyl vinyl ketone in the presence of 0.5 mol.% benzoyl peroxide at 70, 80, and 90°. The kinetic curves are shown in Fig. 1. The values of the reaction rate constants, activation energy, and pre-exponential factor are given in Table 2.

Table 2

Temp., °C	K, sec^{-1}	U_a, kcal/mol	K_0, sec^{-1}
70	$1.69 \cdot 10^{-4}$	17.5	$1.832 \cdot 10^{7}$
80	$3.61 \cdot 10^{-4}$	17.5	$1.832 \cdot 10^{7}$
90	$7.01 \cdot 10^{-4}$	17.5	$1.832 \cdot 10^{7}$

The IR spectra shown in Fig. 2 confirm the fact that polymerization proceeds only through the double bond. In the IR spectrum of the polymer the absorption bands characteristic of the vinyl bond (990 and 1580 cm^{-1}) disappeared, while the bands of the carbonyl and hydroxyl groups remained (respectively 1630 and 2500–3300 cm^{-1}) [(4)].

The presence of the theoretical quantity of carbonyl groups in the polymer was confirmed by determination through their oximation.

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Fig. 2. IR spectra of the monomer (1) and polymer (2)

Figure 1: Fig. 2. IR spectra of the monomer (1) and polymer (2)

Products of copolymerization of *o*-hydroxyphenyl vinyl ketone with methyl methacrylate (in benzene solution) and with divinylbenzene (by bead polymerization) were also obtained. The copolymer with divinylbenzene (DVB) has ion-exchange properties: appearance—transparent light-yellow beads; size 0.25-0.5 mm; crosslinking, 2.0% DVB; static exchange capacity (s.e.c.) in 1 N NaOH, 5.6 mg-equiv/g; s.e.c. in 0.1 N $Cu(NH_3)_4SO_4$ (pH 11.5), 4.2 mg-equiv/g.

Fig. 1. Dependence of the yield of poly-*o*-hydroxyphenyl vinyl ketone on time at *a*—70° (1), 80° (2), and 90° (3)

Experimental Part

Synthesis of *o*-hydroxyphenyl ketone. By condensation of *o*-hydroxyacetophenone, paraform, and dimethylamine hydrochloride in propanol solution, hydrochloride of *o*-hydroxydimethylaminopropiophenone was obtained in 72% yield. On steam distillation of the latter, *o*-hydroxyphenyl vinyl ketone is obtained in up to 50% yield. The monomer was purified by double distillation in vacuo in a nitrogen atmosphere. B.p. 67-68°/1-2 mm, n_D^{20} 1.5783. The content of double bonds, determined by hydrogenation over $Pd/CaCO_3$, is 99.2%.

Polymerization of *o*-hydroxyphenyl vinyl ketone. Polymerization in solution and in bulk was carried out in a nitrogen atmosphere by conventional methods at various concentrations of monomer and initiator. Benzene solutions of the polymers were precipitated into petroleum ether.

Granular copolymerization of *o*-hydroxyphenyl vinyl ketone was carried out: a) by the usual procedure, using polyvinyl alcohol as stabilizer, b) in a 10% solution of sodium chloride with calcium carbonate as stabilizer, according to the procedure ([5]).

Fig. 2. IR spectra of the monomer (1) and polymer (2)

The IR spectra were recorded on a Japanese spectrophotometer of the Nippon-Bunko company, model D-301, with a NaCl prism in the region from 4000 to 660 cm^{-1}. Oximation was carried out by treating the polymer in a solution of boiling pyridine with hydrochloric acid hydroxylamine.

As a result of the work carried out, conditions for the radical polymerization of *o*-hydroxyphenyl vinyl ketone were studied and selected. The kinetics of polymerization of *o*-hydroxyphenyl vinyl ketone was investigated, and the activation energy of the polymerization process was calculated (17.5 kcal/mol). The presence of a chelate grouping in the polymer unit opens the possibility of using the polymers and copolymers as complex-forming agents with metals.

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