

**Corresponding Member of
the Academy of Sciences of
the USSR M. M. KOTON,
I. V. ANDREEVA, A. I.
TURBINA,**

V. G. SINYAVSKII

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Abstract

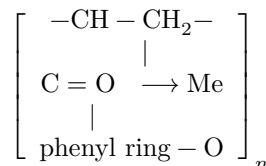
Full Text

Corresponding Member of the Academy of Sciences of the USSR M. M. KOTON,
I. V. ANDREEVA, A. I. TURBINA,
V. G. SINYAVSKII

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.

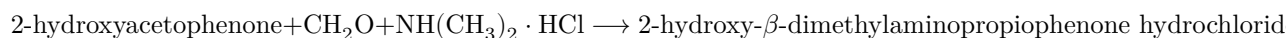
The presence of a chelating group in the monomer molecule, analogous to that contained in hydroxyketone dyes ⁽²⁾, makes it possible to obtain complex-forming polymers directly by polymerization and copolymerization of *o*-hydroxyphenyl vinyl ketone:



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



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.

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 $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ (pH 11.5), 4.2 mg-equiv/g.

Fig. 1. Dependence of the yield of poly-*o*-hydroxyphenyl vinyl ketone on time at $a-70^\circ$ (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. $67-68^\circ/1-2$ mm, n_D^{20} 1.5783. The content of double bonds, determined by hydrogenation over Pd/CaCO₃, 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.

Institute of High-Molecular-Weight Compounds
Academy of Sciences of the USSR

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