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## COPOLYMERIZATION OF VINYLHYDROQUINONE DIBENZOATE WITH ACRYLIC AND METHACRYLIC ACIDS\*

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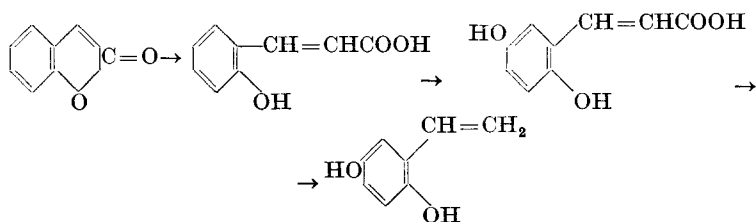
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THE ATTENTION of investigators has recently been attracted to the copolymerization of vinylhydroquinone derivatives with different vinyl monomers; the presence of units of vinylhydroquinone and its derivatives opens up wide possibilities. In the series of works by Cassidy and collaborators [1, 2, 4, 8] vinylhydroquinone was used to prepare crosslinked electron-exchange resins. Ushakov and his collaborators [3] found that vinylhydroquinone can be used to synthesize soluble high molecular weight inhibitors.

The purpose of the present work was the copolymerization of vinylhydroquinonedibenzoate (VHD) with acrylic (A) and methacrylic (MA) acids. These monomer pairs have not been described in the literature, and are of considerable interest.

The vinylhydroquinone was prepared on the scheme suggested by Cassidy [1]:



\* Vysoikomol. soyed. **6**: No. 10, 1799-1801, 1964.

Oxidation of the *o*-cumarinic acid was performed by the Elbs method, with potassium persulphate in an alkaline medium.

For the decarboxylation we heated dioxycinnamic acid at 220° and a residual pressure of 0.02 mm. After removing the benzene by recrystallization, the vinylhydroquinone had a melting point of 111°. The Schotten-Bauman method of benzylation was used, with benzoyl chloride in a strong alkaline medium at room temperature. The product VHD was purified by dissolving it in hot alcohol and precipitating it in water. It was dried in air for several days, and then over P<sub>2</sub>O<sub>5</sub> and in vacuum at room temperature.

After double distillation *in vacuo* the A and MA had the following refractive indices:  $n_D^{20}=1.421$  for the A and 1.431 for the MA.

The copolymerization of VHD with A and MA was performed in sealed Carius tubes in toluene with azobisisobutyronitrile in the amount of 1% by weight of the original monomer mix, at 60°. The O<sub>2</sub> was removed by washing three times in specially purified nitrogen.

The time required for the various different experiments ranged between 40 min and 2 hr. The copolymers separated were washed in toluene and ether, dissolved in dimethylformamide and precipitated, depending on the amount of VHD, in one of the following solvents: acetic acid, dichloroethane or petroleum ether. They were vacuum dried at 60°.

The extent of conversion was determined from the polymer yield. The composition of the copolymer was determined from elementary analysis.

The results given in Table 1 were used to calculate the relative activities ( $r_1$  and  $r_2$ ) using the Mayo and Lewis method [7]. They were as follows: for the pair A ( $r_1$ )-VHD ( $r_2$ ):  $r_1=0.44\pm0.13$ ;  $r_2=0.95\pm0.002$ ; for the pair MA ( $r_1$ )-VHD ( $r_2$ ):  $r_1=1.91\pm0.23$ ,  $r_2=0.91\pm0.25$ .

TABLE 1. RELATION BETWEEN THE COPOLYMER COMPOSITION AND THAT OF THE ORIGINAL MIXTURE OF MA AND A (M<sub>1</sub>) AND VHD (M<sub>2</sub>)

Number of mmoles in the original mixture		$\frac{M_1^0}{M_2^0}$	Copolymer, yield, %	Carbon concentration of copolymer, %	Copolymer composition, mole %		Number of mmoles in remaining mixture		$\frac{M_1}{M_2}$
$M_1^0$	$M_2^0$				$M_1^1$	$M_2^1$	$M_1$	$M_2$	
MA( $M_1$ )-VHD( $M_2$ )									
6.493	1.3619	4.7676	25.79	61.99	90.52	9.48	4.466	1.116	4.002
4.1314	1.9866	2.0796	13.39	64.5	83.6	16.4	3.259	1.844	1.766
1.0433	1.1324	1.0433	4.09	71.0	59.5	40.5	0.835	0.896	0.932
A( $M_1$ )-VHD( $M_2$ )									
8.7388	1.1485	7.6089	6.94	67.2	72.62	27.38	8.263	1.0465	7.895
6.5541	1.5796	4.1492	17.24	60.55	63.23	36.77	5.9095	1.2133	4.870
2.4056	2.4034	1.0001	23.80	72.00	50.75	49.25	1.8861	1.8203	1.007

For the pair VHD-A the relative reactivity of A to the VHD radical ( $1/r_2$ ) was 1.05.

The relative reactivity of VHD to the A radical ( $1/r_1$ ) is 2.4. For the pair VHD-MA the relative reactivity of MA to the VHD radical is 1.08, and that of the VHD monomer to the MA radical, 0.5.

TABLE 2. MONOMER ACTIVITY FACTORS

Monomers	$Q$	$e$
VHD*	1.61	0.05
Acrylic acid	1.58	1.0
Methacrylic acid	2.0	0.7
Styrene	1.0	-0.8

\* The  $Q$  and  $e$  values are the means calculated from the results of the copolymerization of VHD with A and MA.

Paired with MA, the VHD monomer is thus the less reactive component, while when paired with A it is more reactive; but the reactivity of the VHD radical is of the same order for A and MA.

To find the activity factors of the VHD i.e. its individual characteristics we used the  $Q$ - $e$  scheme suggested by Alfrey and Price [5]. It related  $Q$  the specific activity and  $e$  the polarity of the product of radical attachment to the relative activities ( $r_1$  and  $r_2$ ) as follows:

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] .$$

The  $Q$  and  $e$  values for A and MA were taken from the findings obtained in the copolymerization of these polymers with styrene by Chapin and collaborators [6].

$Q$  the specific activity of VHD was calculated from the data obtained for the copolymerization with A and found to be 1.43; the polarity  $e=0.06$ . From the figures obtained in the copolymerization of VHD with MA  $Q=1.80$  and  $e=0.04$ .

Table 2 shows the numerical  $Q$ - $e$  values for the monomers studied. On the basis of the  $Q$ - $e$  scheme used and taking account of the semi-quantitative nature of the scheme the following conclusions can be drawn.

The addition of the ester benzoate groups to styrene weakens the donor properties of the benzene ring as shown by the change in position in the  $Q$ - $e$  scheme ( $e$  moves from -0.8 to 0.05). The specific activity rises slightly. Substitution of the hydrogen of the double bond in the acrylic acid by a methyl group weakens the acceptor nature of the carboxyl group, and this changes the  $e$  value (for A  $e=1.0$ , and for MA  $e=0.7$ ), and slightly increases the specific of activity MA.

## CONCLUSIONS

(1) Vinylhydroquinonedibenzoate has been copolymerized with acrylic and methacrylic acid in the presence of azobisisobutyronitrile at 60°, and the relative activities determined.

(2) The activity factors have calculated on the  $Q-e$  scheme for vinylhydroquinonedibenzoate.

*Translated by V. ALFORD*

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## CONDUCTIVITY OF POLYMER FILMS AT HIGH FREQUENCIES\*

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WHEN the conductivity of films of the polymer complex tetracyanoethylene (TCE) on different metals was investigated, it was found that the capacitance and resistivity of these films depend on the frequency [1, 2] but the results are restricted to a small range of frequencies from 0 to 0.2 Mc/s. In the present work we have studied the conductivity of films in a frequency range of 0.5 to 200 Mc/s.

## EXPERIMENTAL

The specimens studied were a polymeric complex of TCE with silver, and also films of a metal-free polymer. The latter were prepared at two extreme temperatures, 300° which is the minimum for the formation of a metal-free polymer on mica, glass or quartz; and 500° where the film is no longer subject to total degradation, and may be more ordered than in the first case. The base used was mica 3 mm thick, the pieces being cut in such a way as to correspond exactly with the terminals of the  $Q$ -meters KV-1 and UK-1.

\* Vysokomol. soyed. **6**: No. 10, 1802-1805, 1964.