The Copolymerization of Vinylhydroquinone and Acrylonitrile by Tri-n-butylborane[1]

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ABSTRACT: Vinylhydroquinone (VHQ) was found to copolymerize with acrylonitrile (AN) by tri-n-butylborane (Bu_3B) in cyclohexanone at 35°C under nitrogen atmosphere. IR-, UV-, and NMR-spectral studies revealed that VHQ copolymerized in terms of vinyl polymerization. Monomer reactivity ratios for VHQ (M_1) and AN (M_2) were $r_1=0.46$ and $r_2=0.02$. Q and e values were also calculated; $Q_1=1.9$ and $e=-1.0$. These r and e values, which are similar to those for styrene (St), and other data suggest that VHQ behaves like St rather than as an inhibitor in the Bu_3B-initiated copolymerization. No homopolymerization occurred under the same conditions either under a nitrogen atmosphere or in the presence of oxygen. The reaction mechanism is also discussed.
KEY WORDS   Vinylhydroquinone / Copolymer / Acrylonitrile / Tri-n-butylborane / NMR / Reactivity Ratios / Q—e Value / Oxygen /

Polyhydroquinone is one of the best-studied redox polymers.[2-5] Cassidy and coworkers first prepared vinylhydroquinone (VHQ) from coumarin and tried to polymerize it thermally;[6,7] but, since hydroquinone is a free-radical or ionic inhibitor, they obtained oligomers only.[8,9] Therefore, the hydroxy groups of VHQ were protected with ester or other groups, such as acetate,[9] benzoate,[9] ethoxyethyl,[10] methoxy,[10,11] methoxymethyl,[12] etc.; the protective groups were removed after polymerization to get linear redox polymers which contained hydroquinone units in the polymer chains.[2-5] Similarly, Cassidy and coworkers published their studies on the copolymerization of the protected VHQ derivatives.[13,14]

OH
|
[benzene ring]—CH=CH₂
|
OH
VHQ
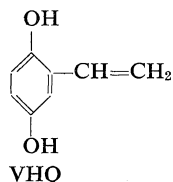
In the course of our research work on the polymerization and copolymerization of vinyl monomers by tri-n-butylborane (Bu_3B),[15-20] we showed that hydroquinone did not disturb the

polymerization of methyl methacrylate (MMA) by Bu_3B.[21] Minoura and Ogata reported that hydroquinone did not inhibit some free-radical polymerization systems.[22] Furukawa and coworkers indicated that hydroquinone showed cocatalytic effects on the polymerization of vinyl monomers with alkyl-cadmium initiators.[23,24]

Previously,[25] we reported the copolymerization of VHQ and MMA by Bu_3B in cyclohexanone. Our spectral study showed that VHQ was incorporated in the polymer chains. The purpose of the present paper is to describe some results of our further investigation on the Bu_3B-initiated copolymerization of VHQ and acrylonitrile (AN).

EXPERIMENTAL

Preparation of VHQ

VHQ was prepared from coumarin via o-cumaric acid and 2,5-dihydroxycinnamic acid by the method of Updegraff and Cassidy.[7]

o-Coumaric Acid. A solution of 32 g (1.4 mol) of sodium and 100 g (0.68 mol) of coumarin in 500 ml of abs ethanol was refluxed for 2 hr. After the mixture was diluted with 200 ml of water and most of solvent removed, it was neutralized with conc hydrochloric acid. The

raw product was recrystallized from water; yield: 85 g (82%); mp 207—208°C (lit.[26] 208°C).

2,5-Dihydroxycinnamic Acid. 140 g of sodium hydroxide and 80 g (0.5 mol) of coumaric acid were dissolved in 2.5 *l* of water and a slurry of 150 g of potassium persulfate in 800 m*l* of water added. The mixture was stirred for 24 hr. It was then neutralized with small amounts of conc hydrochloric acid until it was red to methyl orange. The mixture was extracted with ether for 24 hr. To the remaining solution was added 500 m*l* of conc hydrochloric acid and the extraction was continued for one week. After removal of ether, the product was treated with active carbon and recrystallized from water, yield: 20 g (20%); mp 207—208°C (lit.[7] 208°C).

VHQ. In a vacuum sublimation apparatus was placed 5 g (0.028 mol) of 2,5-dihydroxycinnamic acid. The acid was heated in an oil bath at 220°C and at 0.01 Torr for 1 hr. The crude sublimate was mixed with 50 m*l* of benzene and the mixture heated to boiling point. After filtration of the warm solution, the filtrate gave 1.15 g (30%) of VHQ on cooling; mp 110—111°C (lit.[7] 111°C).

Comonomers and Solvents

Commercial AN, MMA, styrene, 2-vinylpyridine, and organic solvents were dried and purified in the usual manner.

Initiator

Tri-*n*-butylborane (Bu₃B; Callery Chemical Co., USA.) was distilled under nitrogen; bp 108—110°C/20 mmHg.

Copolymerization

Typical Procedure. A solution of 0.344 g (2.53 mmol) of VHQ and 0.258 g (4.87 mmol) of AN in cyclohexanone was placed in a glass ampoule. After the atmosphere was replaced with nitrogen by the freeze-thaw method, 0.0071 g (3.5×10^{-2} mmol) of Bu₃B was added to the solution and the ampoule sealed. The ampoule was dipped in a thermostatted bath at 35°C. After 36 hr, the reaction was stopped by pouring the solution into 100 m*l* of *n*-hexane to precipitate the copolymer. The copolymer was reprecipitated three times from cyclohexanone-*n*-hexane. Conversions were 9—12%.

The composition of the copolymer was de-termined by elementary analysis.

Measurements

The IR spectra were recorded on a Hitachi Model EPI-G2 spectrophotometer. The NMR spectra were obtained on a JEOL Model 4H-100 instrument.

RESULTS AND DISCUSSION

Copolymerization

Copolymerizations of VHQ and AN by Bu₃B were carried out in cyclohexanone under nitrogen at 35°C. After a specified time, the reaction mixture was poured into an excess of *n*-hexane to give a white precipitate. The precipitate was reprecipitated three times from cyclohexanone-*n*-hexane. It was then filtered, washed with *n*-hexane, and dried *in vacuo* at temperatures not higher than 50°C. The results are summarized in Table I, together with those of other vinyl monomers, such as MMA and 2-vinylpyridine.[25]

The precipitate was characterized spectroscopically as follows. The IR spectrum showed a characteristic absoption band at 3400 cm⁻¹, assignable to hydroxy groups, while vinyl bands disappeared. When the precipitate was treated with ceric solution, a new band was found at 1660 cm⁻¹, assignable to quinone carbonyl groups, while the OH band disappeared. In the UV spectra, the λ_{max} values of VHQ, the precipitate, and its oxidized form were 326, 297, and 271 mμ, respectively. Figure 1 illustrates the NMR spectra of VHQ (I), the precipitate (II), and, for the purpose of comparison, a styrene—AN copolymer (III).[27] Characteristic signals of vinyl protons at $\delta = 4$—5 ppm in I were not found to any greater extent in II. Other peaks at $\delta = 6$—7 ppm (phenyl groups) and 1.75—3 ppm (methylene and methine groups) in II were seen at nearly the same positions as those in III, which suggests that the chemical structure of the precipitate is similar to that of the styrene—AN copolymer. From these spectral data, it may be assumed that the precipitate is a copolymer of VHQ and AN in terms of vinyl polymerization.

No homopolymerization of VHQ occurred under the same conditions both under nitrogen and in the presence of oxygen.

Table I. The copolymerization of VHQ and vinyl monomers[1,25]

| No.	Monomer[a] composition in feed, mmol		Solvent,[b] ml	Bu₃B concn, mmol	Time, hr	Conversion %	Main data of copolymers			
							η_{sp}/C,[c] dl/g	UV,[d] λ_{max}, mμ	IR[e] OH, cm^{-1}	Softening temp, °C
1	VHQ	3.12	10	3.5×10^{-2}	30	—	—	—	—	—
	—	—								
2	VHQ	3.70	15	3.5×10^{-2}	30	34.4	0.13	299	3400	140–145
	MMA	3.70								
3	VHQ	2.53	10	7.0×10^{-2}	37	15.1	0.19	296	3370	213–217
	AN	4.87								
4	VHQ	2.41	10	7.0×10^{-2}	37	4.7	0.07	297	3300	165–170
	VPy	4.85								

[a] VHQ, vinylhydroquinone; MMA, methyl methacrylate; AN, acrylonitrile; VPy, 2-vinylpyridine.
[b] Solvent, cyclohexanone.
[c] Determined in methanol at 25°C.
[d] In methanol at 25°C.
[e] KBr disk.
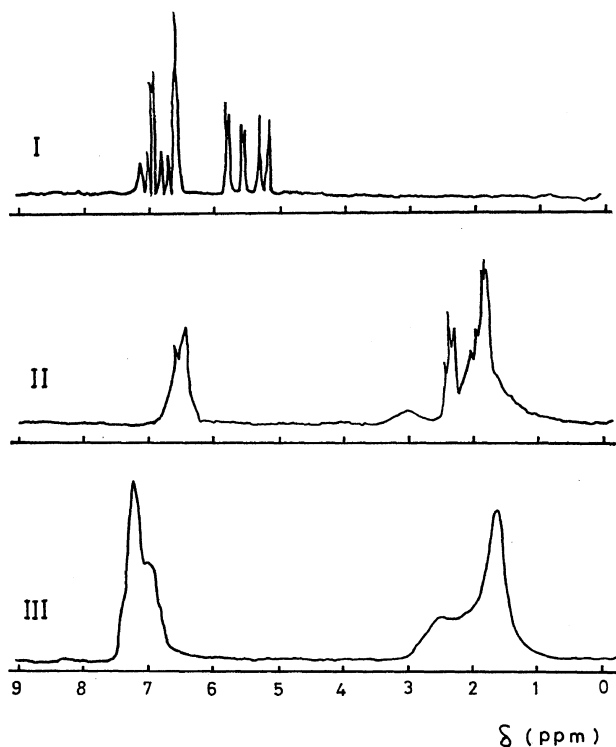
Figure 1. The NMR spectra of VHQ (I), VHQ—AN copolymer, St—AN copolymer (III):[27] I and II in CD₃OD, III in dichloromethane.[27]

Monomer Reactivity Ratios

In order to determine the monomer reactivity ratios of VHQ (M_1) and AN (M_2), copolymerizations were carried out by changing molar ratios in feed from $M_1/M_2 = 1/9$ to 6/4. The results are given in Table II. Elementary analyses indicate that considerable amounts of VHQ units were incorporated into polymer chains.

Monomer reactivity ratios were calculated by the Fineman—Ross method, using the method of least squares. They were found to be $r_1=0.46$ and $r_2=0.02$. It is interesting to note that these values are similar to those of styrene—AN copolymers as reported in the literature (Table III).

From the monomer reactivity ratios so obtained and the Q and e values of AN in the literature,[28] $Q=0.60$ and $e=1.2$, Q and e values of VHQ were calculated to be $Q_1=1.9$ and $e_1=-1.0$; the latter was also similar to that of styrene, $e=-0.8$.

On the Reaction Mechanism

Alkylboranes are known to initiate the free-radical polymerization of vinyl monomers in the presence of oxygen.[29,30] Although, in our experiments, the atmosphere was replaced with nitrogen, there could have been a trace of oxygen, or, there was enough oxygen and reaction

time during the addition of Bu_3B to the reaction mixture, to form borane peroxides. The initiation reaction of the copolymerization of VHQ and AN by Bu_3B is therefore assumed to involve free-radicals. As given in Figure 2, the plot of the monomer concentrations in feed *vs.* the monomer compositions in copolymers was similar to that of the ordinary free-radical polymerization.[31]

In the initiation reaction, it could be possible that the copolymerization of VHQ and AN by Bu_3B proceeds *via* a Bu_3B—VHQ complex:

Formation of the complex:

$$Bu_3B + VHQ \rightarrow complex \qquad (1)$$
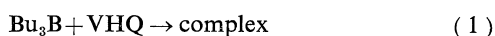
Formation of the active center:

Table II. The copolymerization of VHQ (M_1) and AN (M_2)[a]

No.	Monomer			Copolymer		
	Composition in feed, mol %		N contents, wt % calcd	Composition, mol %		N contents, wt % found
	M_1	M_2		m_1	m_2	
1	10.0	90.0	20.65	42.6	57.4	9.21
2	20.0	80.0	16.09	49.8	50.2	7.45
3	40.0	60.0	9.74	58.1	41.9	5.80
4	60.0	40.0	5.44	62.5	37.5	5.13

[a] Bu_3B, 7.0×10^{-2} mmol; solvent, cyclohexanone, 10 m*l*; reaction time, 15 hr; temp, 35°C.
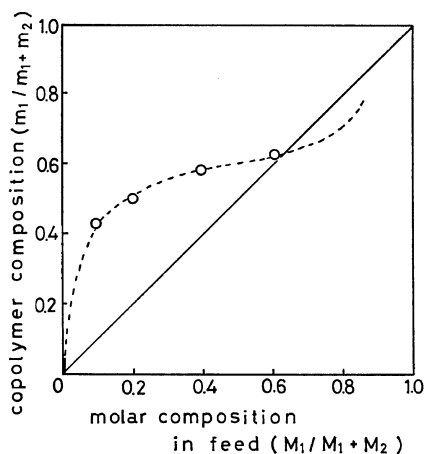
Figure 2. Plot of copolymer composition (m_1/m_2) *vs.* momomer composition in feed (M_1/M_2) in the Bu_3B-initiated copolymerization of VHQ (M_1) and AN (M_2).

Table III. Monomer reactivity ratios of VHQ and vinyl monomers

No.	Initiators[a]	Temp, °C	Monomers[b]		Solvents[c]	Monomer reactivity ratios		Ref
			M_1	M_2		r_1	r_2	
1	Bu_3B	35	VHQ	AN	CHN	0.46	0.02	This work
2	Bu_3B	30	St	AN	PE	0.70	0.07	22
3	Bu_3B	0	St	AN	PE	0.55	0.05	22
4	BPO	60	St	AN	—	0.40	0.04	28

[a] Bu_3B, tri-*n*-butylborane; BPO, benzoyl peroxide.
[b] VHQ, vinylhydroquinone; St, styrene; AN, acrylonitrile.
[c] CHN, cyclohexanone; PE, petroleum ether.

Complex → active center to initiate the
copolymerization (2)

Borsini and Cipolla found that the alkylborane-initiated polymerization of vinyl chloride is accelerated by electron-donating solvents, such as ether and pyridine,[32] and they assumed that the formation of the complex of alkylborane and these electron donors plays an important role in the acceleration.[32] We previously reported that pyridine shows cocatalytic effects in the Bu_3B-initiated polymerization of MMA in the presence of oxygen and proposed the following reaction mechanism:[15]

Bu_3B + pyridine → complex (3)

complex → radical to initiate the
polymerization (4)

In Step 1 (eq 1 or 3), VHQ or pyridine is assumed to behave as an electron donor. As previously reported,[16-20] MMA was found to be grafted by Bu_3B on to natural and synthetic polymers containing hydrophilic groups, such as amino and hydroxyl groups. They are fibers (e.g., cotton,[20] silk,[16] and wool[16]), proteins (e.g., albumin and casein[16]), solid blood components,[17,19] etc. Similarly, the initiation reaction of the copolymerization of VHQ and AN by Bu_3B could be explained by assuming the formation of the Bu_3B—VHQ complex; VHQ is assumed to behave as an electron donor, as in the case of pyridine (eq 3).

Participation of oxygen and/or AN in the formation of the complex could be possible; then, Bu_3B in eq 1 could be expressed in the term of (Bu_3B peroxides), and the Bu_3B—VHQ complex in term of (Bu_3B peroxides—VHQ), (Bu_3B—VHQ—AN), or (Bu_3B peroxides—VHQ—AN) complex. The participation of AN could be supported by the fact that the vinyl monomers which copolymerize with VHQ, such as AN, MMA, and 2-vinylpyridine (Table I), belong to those which have electron-accepting properties.

Sept 2 (eq 2) is assumed to involve free-radicals, as discussed above and as in the case of eq 4.

When the same procedures were repeated in the presence of air, no precipitates were obtained. This fact was quite different from the usual alkylborane-initiated polymerization of vinyl monomers, where the presence of oxygen is essential to the initiation step. This could be explained by assuming that (1) too much oxygen inhibits the polymerization as in the case of benzoyl peroxide and/or (2) VHQ was oxidized by the oxygen to yield a trace of the oxidized form of VHQ, a quinone, which inhibited the copolymerization, since benzoquinone is capable of inhibiting the Bu_3B—initiated polymerization.[31] Attemps were made to identify the oxidized form of VHQ by UV-spectroscopy, but in vain. Absorption of VHQ was too strong to distinguish it from that of the oxidized form of VHQ. However, the above assumption, i.e., the formation of the quinone type of VHQ, could be quite possible, because a trace of quinone is good enough to inhibit the polymerization.

Thus, we have just revealed that Bu_3B can initiate the copolymerization of VHQ and AN. However, the problem, why Bu_3B is incapable of initiating the homopolymerization of VHQ, remains unsolved. We assume that VHQ behaves like styrene rather than as an inhibitor under these conditions so far as Bu_3B-initiated polymerization and copolymerization are concerned. This assumption could be supported by the following experimental facts:

1) Monomer reactivity ratios and e value for VHQ are similar to those for styrene;

2) Styrene is a substantially less reactive and rather more inert monomer than AN, MMA, and vinyl acetate in the Bu_3B-initiated homopolymerization, although styrene copolymerizes with these monomers.

Further investigations on the reaction mechanism, especially those is the absence of oxygen, are now in progress.

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