

Vinylhydroquinone. III. Copolymerization of Vinylhydroquinone and Vinyl Monomers by Tri-*n*-butylborane*

S. IWABUCHI, K. KOJIMA, T. NAKAHIRA, M. UEDA,
M. KOBAYASHI, and M. IWAKURA,
*Department of Applied Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba, Japan*

Synopsis

The copolymerization of vinylhydroquinone (VHQ) and vinyl monomers, e.g., methyl methacrylate (MMA), 4-vinyl-pyridine (4VP), acrylamide (AA), and vinyl acetate (VAc), by tri-*n*-butylborane (TBB) was investigated in cyclohexanone at 30°C under nitrogen. VHQ is assumed to copolymerize with MMA, 4VP, and AA by vinyl polymerization. The following monomer reactivity ratios were obtained (VHQ = M_1): for MMA/VHQ/TBB, $r_1 = 0.62$, $r_2 = 0.17$; for 4VP/VHQ/TBB, $r_1 = 0.57$, $r_2 = 0.05$; for AA/VHQ/TBB, $r_1 = 0.35$, $r_2 = 0.08$. The Q and e values of VHQ were estimated on the basis of these reactivity ratios as $Q = 1.4$ and $e = -1.1$, which are similar to those of styrene. This suggests that VHQ behaves like styrene rather than as an inhibitor in the TBB-initiated copolymerization. No homopolymerization was observed either under nitrogen or in the presence of oxygen. The reaction mechanism is discussed.

INTRODUCTION

Cassidy et al.¹⁻⁴ and Manecke et al.⁵⁻⁷ prepared a large number of the redox polymers containing hydroquinone/quinone systems in polymer chains. Most of the polymers were synthesized carrying protective groups on the hydroxy groups of hydroquinone units, because hydroquinone is a well-known ionic or radical inhibitor;⁸ the protective groups were removed afterwards.

In a previous paper,⁹ we briefly reported the alkylborane-initiated copolymerization of an unprotected hydroquinone, 2-vinyl-1,4-hydroquinone (VHQ), and methyl methacrylate (MMA) in cyclohexanone at 30°C. Tri-*n*-butylborane (TBB) was found to be capable of initiating the copolymerization of VHQ and MMA. Copolymers were also obtained from VHQ and acrylonitrile (AN).¹⁰ This paper furnishes some additional information on the copolymerization behavior of VHQ.

* Dedicated to Professor Yoshio Iwakura on the occasion of his 60th birthday.

EXPERIMENTAL

Materials

Vinylhydroquinone (VHQ) was prepared from coumarin via *o*-coumaric acid and 2,5-dihydroxycinnamic acid by the method of Updegraff and Cassidy.¹¹ Commercial methyl methacrylate (MMA), 4-vinylpyridine (4VP), acrylamide (AA), vinyl acetate (VAc) and cyclohexanone were dried and purified in the usual manner. Commercial TBB, (*n*-C₄H₉)₃B (Callery Chemical Co., U.S.) was distilled under nitrogen; bp 108–110°C/20 mm Hg.

Copolymerization

Copolymerizations were performed at 30°C as previously described.^{9,10} The composition of the copolymers was estimated on the basis of elementary analysis or by means of ultraviolet spectroscopy.

Measurements

The infrared spectra were recorded on a Hitachi Model EPI-G2 spectrophotometer, the ultraviolet and visible spectra on a Hitachi Model EPS-3T spectrophotometer, and the NMR spectra on a JEOL Model 4H-100 instrument.

Viscosities of the copolymers were determined at 30°C with a modified Ubbelohde viscometer.

RESULTS

Copolymerization of VHQ and MMA by Tri-*n*-butylborane (TBB)

Previously, the copolymer of VHQ and MMA was characterized by infrared spectroscopy.⁹ In the ultraviolet spectra, the λ_{\max} values of VHQ and the copolymer were found to be 326 and 299 nm, respectively. After the copolymer was treated with a ceric solution, the λ_{\max} value of the oxidized product was shifted downfield to 270 nm. Figure 1 shows the NMR spectra of VHQ (I), of the copolymer (II), and of a copolymer of styrene and MMA (III). Characteristic signals of vinyl protons at 4–5 τ in I disappeared in II, while those of phenyl protons at 3–4 τ remained in II. Ito and Yamashita¹² assigned characteristic signals of a styrene–MMA copolymer at 6.4–6.8 and 7.1–7.4 τ to methoxy protons and those at 7.9 τ to methylene and methine groups (III). Analogously, new signals in II at 6.3–6.5 and 6.8–6.9 τ can be assigned to methoxy protons and those near 7.7 τ to methylene/methine protons. In general, II was similar to III; this suggests that the chemical structure of the VHQ–MMA copolymer is similar to that of the styrene–MMA copolymer. From these spectral data, the VHQ–MMA copolymer may be regarded as a vinyl copolymer.

Table I presents a series of copolymerizations of MMA (M_1) and VHQ (M_2) at various molar ratios of the monomers in feed $M_2/(M_1 + M_2)$.

TABLE I
Copolymerization of VHQ and MMA by TBB^a

Expt. no.	Monomer composition in feed, mole-%		Time, hr	Conversion, %	Copolymer composition, mole-%		Characteristics of copolymer	
	MMA (M_1)	VHQ (M_2)			MMA (m_1)	VHQ (m_2)	UV λ_{\max} , nm ^b	$[\eta]$, ^c dl/g
201	20.0	80.0	24	1.5	44.7	55.3	297	0.15
202	40.0	60.0	24	7.6	56.8	43.2	298	0.15
203	60.0	40.0	24	11.5	65.2	34.8	298	0.11
204	80.0	20.0	20	14.4	77.1	22.9	298	0.17
205	90.0	10.0	15	11.4	82.4	17.6	300	0.33

^a Solvent, 10 ml cyclohexanone; temperature, 30°C; TBB, 4.0×10^{-5} mole.

^b Solvent, methanol.

^c Solvent, methanol for Nos. 201-204; tetrahydrofuran for No. 205.

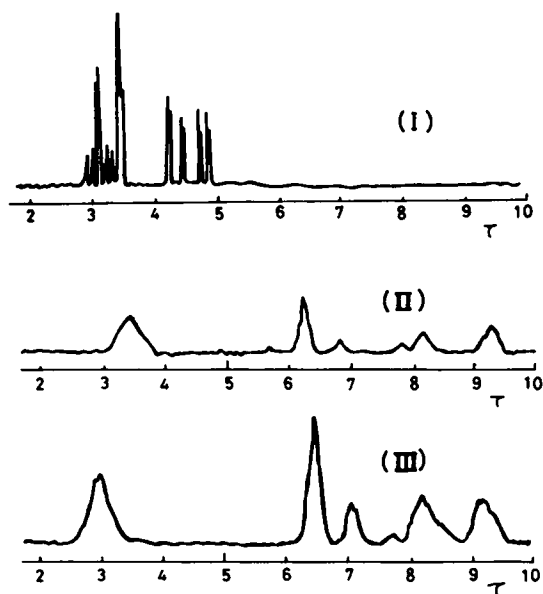


Fig. 1. NMR spectra of (I) VHQ, (II) VHQ-MMA copolymer and (III) St/MMA copolymer.¹² I and II in CD_3OD , and III in CDCl_3 .

Monomer reactivity ratios were calculated from the data of Table I by using the Fineman-Ross method.¹³ The following values were obtained: $r_1 = 0.62$ and $r_2 = 0.17$. The Q and e values¹⁴ of VHQ were also estimated to be $Q = 1.0$ and $e = -1.2$ on the basis of the reactivity ratios so obtained, and the values of MMA in the literature ($Q = 0.74$ and $e = 0.40$).¹⁵

Copolymerization of VHQ and 4VP by TBB

VHQ was copolymerized with 4VP by TBB in cyclohexanone under the same conditions as those for the VHQ-MMA-TBB system (Table II).

TABLE II
 Copolymerization of VHQ and 4VP by TBB^a

Expt. no.	Monomer composition in feed, mole-%		Time hr	Conver- sion, %	Copolymer composition, mole-%		Copolymer λ_{\max} , nm ^b
	4VP (M_1)	VHQ (M_2)			4VP (m_1)	VHQ (m_2)	
301	30.0	70.0	23	7.5	64.3	35.7	295
302	61.0	39.0	23	4.3	73.2	26.8	297
303	82.0	18.0	23	6.3	78.7	21.3	298
304	90.0	10.0	23	13.2	84.6	15.3	299

^a Solvent, 10 ml cyclohexanone; temperature, 30°C; TBB, 4.0×10^{-4} mole.

^b Solvent, methanol.

The precipitates obtained were reprecipitated from methanol/ether. The products were characterized by infrared, NMR, and ultraviolet spectroscopy. These spectral data supported our assumption, namely, that the products may be assumed to be vinyl copolymers. Q and e values as well as monomer reactivity ratios were obtained from the data of Table II as follows (VHQ = M_2): $r_1 = 0.58$ and $r_2 = 0.05$; $Q_2 = 1.2$ and $e_2 = -1.5$ (based upon the literature values,¹⁵ $Q_1 = 0.82$ and $e_1 = -0.20$).

Copolymerization of VHQ and AA by TBB

VHQ and AA were copolymerized by TBB in cyclohexanone at 30°C under the same conditions as those for the VHQ-MMA-TBB and VHQ-4VP-TBB systems. Our spectral studies revealed that the products were vinyl copolymers. Table III shows the results of the copolymerization. Monomer reactivity ratios were estimated by the Fineman-Ross method¹³ (VHQ = M_2): $r_1 = 0.35$ and $r_2 = 0.08$. Q and e values of VHQ were found to be $Q_2 = 1.6$ and $e_2 = -0.6$ on the basis of the literature values¹⁵ for AA ($Q_1 = 1.18$ and $e_1 = 1.30$).

 TABLE III
 Copolymerization of VHQ and AA by TBB^a

Expt. no.	Monomer composition in feed, mole-%		Time, hr	Conver- sion, %	Copolymer composition, mole-%		Characteristics of copolymer	
	AA (M_1)	VHQ (M_2)			AA (m_1)	VHQ (m_2)	UV λ_{\max} , nm ^b	$[\eta]$, dl/g ^c
401	20.3	79.8	45	2.6	50.0	50.0	295	0.16
402	39.0	61.0	45	3.9	52.9	47.1	296	0.09
403	59.8	40.2	15	6.2	63.3	36.7	296	
404	80.2	19.8	8	8.1	67.1	32.9	299	
405	90.0	10.0	6	13.9	80.6	19.4	299	0.09

^a Solvent, 10 ml cyclohexanone; temperature 30°C; TBB, 1.60×10^{-4} mole.

^b Solvent, methanol.

^c Solvent, methanol for Nos. 401 and 402; water for No. 405.

Copolymerization of VHQ and VAc by TBB

No copolymerization occurred when VHQ and VAc were treated under the same conditions although VAc homopolymerizes with alkylborane initiators.^{16,17} VAc was also inert in the TBB-initiated grafting onto cotton¹⁸ and silk.¹⁹ The question why VHQ and VAc gave no copolymer will be discussed in the next section.

Q and e Values for the Systems VHQ-Vinyl Monomer-TBB

The Q and e values for the systems VHQ-MMA-TBB, VHQ-4VP-TBB, and VHQ-AA-TBB, together with those for the system VHQ-AN-TBB¹⁰ are summarized in Table IV. The mean values for VHQ were estimated to be $Q = 1.4$ and $e = -1.1$.

DISCUSSION

Figure 2 shows plots of the molar ratios of VHQ (M_2) in feed versus the composition of VHQ in copolymer (m_2); the values were taken from Tables I-III. The curve so obtained was similar to that for the ordinary free-radical copolymerization.^{20,21} This suggests that the TBB-initiated copolymerization of VHQ and vinyl monomers proceeds via a free-radical mechanism. It is known that alkylboranes can initiate the polymerization of vinyl monomers in the presence of oxygen and the reaction involves free radicals.^{16,17,22-26} Our results are in agreement with these facts.

However, in the copolymerization of VHQ and vinyl monomers by TBB, no polymerization was observed in 10 days when the atmosphere was not replaced with nitrogen. This might be incompatible with the fact that the presence of oxygen is essential to the alkylborane-initiated polymeriza-

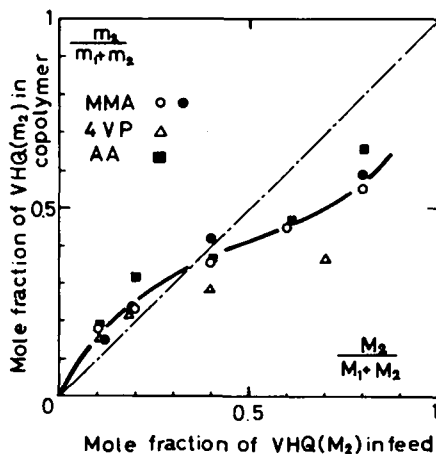


Fig. 2. Plot of copolymer composition vs. monomer composition in feed in the TBB-initiated copolymerization of vinyl monomers (M_1) and VHQ (M_2): (○, ●) MMA; (Δ) 4VP; (■) AA.

TABLE IV
Monomer Reactivity Ratios and Q and e Values for the Systems VHQ-Vinyl Monomers-TBB

Run no.	Monomers ^a		Reactivity ratios		Used ^b		Found		Average	
	M ₁	M ₂	r_1	r_2	Q_1	e_1	Q_2	e_2	Q_2	e_2
200	MMA	VHQ	0.62	0.17	0.74	0.40	1.0	-1.2		
300	4VP	VHQ	0.58	0.05	0.82	-0.20	1.2	-1.5		
400	AA	VHQ	0.35	0.08	1.18	1.30	1.6	-0.6	1.4	-1.1
100 ^c	AN	VHQ	0.46	0.02	0.60	1.20	1.9	-1.0		

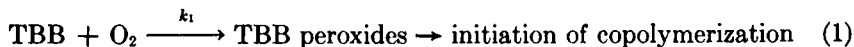
^a Monomers: MMA, methyl methacrylate; VHQ, vinylhydroquinone; 4VP, 4-vinylpyridine; AA, acrylamide; AN, acrylonitrile.

^b Data cited by Brandrup and Immergut.¹⁸

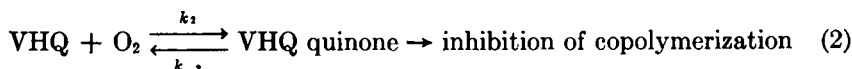
^c Data of Iwabuchi et al.¹⁰

tion of vinyl monomers.^{16,17,22-26} Why does VHQ copolymerize with vinyl monomers under nitrogen only? Why not in the air? This could be explained by assuming the following three points.

(1) TBB had enough time and oxygen to form its peroxides which are necessary for the initiation step, even under nitrogen atmosphere, before it was added to the reaction mixture with a microsyringe;



(2) VHQ was oxidized by the oxygen to yield a trace of the oxidized form of VHQ, a quinone, which inhibits the copolymerization, since benzoquinone is capable of inhibiting the TBB-initiated polymerization.^{27,28}



(3) Oxygen reacts with TBB much faster than with VHQ; i.e., $k_1 \gg k_2$.

Assumption (3) is quite acceptable, because TBB burns in the air and VHQ is stable under the same conditions. Thus, reaction (1) is assumed to proceed predominantly to give copolymers under nitrogen, while the presence of excess oxygen seems to cause the formation of vinyl quinone, so that no polymerization takes place in the air.

As Table IV shows, the Q and e values for the systems VHQ-vinyl monomer-TBB were found to be $Q = 1.4$ and $e = -1.1$, which are similar to those for styrene (St). The values suggest that VHQ behaves like St rather than like an inhibitor in the TBB-initiated copolymerization. This could be supported by assumption (3), because oxygen would be consumed much faster for the copolymerization than for the oxidation of VHQ. St is substantially less reactive than acrylonitrile (AN), MMA, VAc, etc., in the polymerization initiated by alkylboranes.^{16,17} Furthermore, Furukawa and co-workers revealed that vinyl monomers such as AN and MMA which have large positive e values exhibit higher reactivities.^{16,17} This suggests that VHQ is much less reactive than St, since VHQ has a larger e value. It would be therefore understandable that VHQ gave no homopolymer under these conditions.

As mentioned above, VHQ did not copolymerize with VAc, which homopolymerizes in the presence of alkylboranes.^{16,17} This finding is reasonable in the light of the above consideration. It is well known¹⁵ that, in the free-radical copolymerization of VAc (M_1) and St (M_2) by azobisisobutyronitrile (AIBN), $r_1 = 0.01$ and $r_2 = 55$; i.e., St homopolymerizes first and, after St has been almost consumed, VAc begins to react to give block copolymer. However, no copolymer was obtained from St and VAc by TBB under these conditions. This is quite natural, since St is very inert in the TBB-initiated polymerization.^{16,17} Analogously, the above experimental result with the VHQ-VAc-TBB system could be explained by assuming that VHQ behaves like St in the TBB-initiated copolymerization.

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