Registry No. PBFP, 28212-50-2; PBCP, 90718-38-0.

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(27) As opposed to stiff rodlike molecules which unequivocally exhibit liquid crystal properties above some critical concentration.[13-15]
(28) Presently we are trying to model this crystallization process.
(29) It has been established by J. H. Magill, J. S. Lin, and J. M. Schultz (unpublished) that PBFP shows no discrete reflection above the $T(1)$ transition whenever bulk polymer is measured at 120 °C (i.e., above $T(1)$) (work conducted at Oak Ridge SAXS laboratory).

Polymerization Behavior of *p*-Quinone Bis(benzenesulfonimide) as an Acceptor Monomer

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ABSTRACT: The electron affinity of *p*-quinone bis(benzenesulfonimide) (QBS) was estimated from the charge-transfer band between QBS and hexamethylbenzene to be 2.17 eV. QBS was found to copolymerize alternatingly with styrene (St), acenaphthylene, *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether in benzene at 60 °C in the presence of α,α'-azobis(isobutyronitrile) (AIBN). However, QBS and vinyl acetate gave no polymeric product. Studies of terpolymerizations of the QBS–maleic anhydride (MAnh)–St, QBS–*p*-chloranil (PCA)–St, QBS–7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ)–St, and QBS–7,7,8,8-tetracyanoquinodimethane (TCNQ)–St systems afforded the relative reactivity of the St complexes toward the polymer radical with the QBS–St complex terminal unit to be MAnh–St complex (1/30) < PCA–St complex (1/5) < TMCQ–St complex (1/1.18) < QBS–St complex (1) < TCNQ–St complex (1/0.01). This order, except for the PCA–St complex, follows that of the electron-accepting character of the acceptor monomers. Influence of the exocyclic heteroatom was discussed on the basis of the unusual reactivity, PCA–St complex exhibiting a much lower reactivity in comparison with the electron-accepting character of PCA.

Unsubstituted quinodimethane[1] is so reactive that it cannot be prepared as the monomer unless the reaction is carried out at −78 °C in toluene at very dilute concentration; otherwise it reacts immediately to give its polymer. Electron-accepting quinodimethane compounds with strong electron-withdrawing substituents become much less reactive and can be synthesized under ordinary conditions as crystalline materials, e.g., 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[2] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane,[3] and so on, and they are polymerizable as acceptor monomer.[3-5] Furthermore, *p*-benzoquinone is a stable, yellow, crystalline, electron-accepting compound and is conventionally useful as an inhibitor[6,7] and a retarder[8] for free radical polymerization. As one of various reaction paths[9] to account for this inhibition reaction, alkylation on both oxygens of *p*-benzoquinone was proposed to take place to yield ether bonding, implying a copolymerization of *p*-benzoquinone with monomers. Stronger electron-accepting *p*-benzoquinones with electron-withdrawing substituents such as *p*-chloranil (PCA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) are subject to copolymerization with a donor monomer in a more definite fashion as acceptor monomer.[10-13] Quinine diimine, prepared as a colorless crystalline compound by Willstätter and Mayer,[14] is expected to be an intermediate compound between *p*-benzoquinone and quinodimethane from the relationship of Coppinger and Bauer[15] between the stability of hetero *p*-benzoquiones and the electronegativity of their exocyclic atoms, carbon (2.50),[16] nitrogen (3.07),[16] and oxygen (3.50).[16] Unsubstituted *p*-quinone diimine is very susceptible to light and acid, especially in solution, and may undergo reactions such as hydrolysis and polymerization.[17] Adams and Nagarkatti[17] reported that *p*-quinone diimines carrying electron-withdrawing substituents such as acyl, alkylsulfonyl, and acrylsulfonyl groups at exocyclic nitrogen atoms become less susceptible to hydrolysis, being likely more convenient for studies of polymerization. The polymerization behavior of the quinone imides has rarely been

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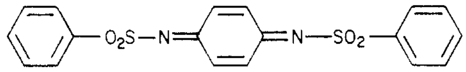
reported,[18] whereas the polymerization behavior of the electron-accepting quinodimethane and quinone derivatives has been studied in detail.[3-5,10-13,19-22]

In this work, *p*-quinone bis(benzenesulfonimide) (QBS)[17] was studied in detail in its polymerization behavior as an acceptor monomer. Furthermore, its electron-accepting character and reactivity as an acceptor monomer were compared with those of the electron-accepting monomers PCA, TCNQ, TMCQ, and maleic anhydride (MAnh).



Experimental Section

Materials. QBS was prepared from *p*-phenylenediamine and benzenesulfonyl chloride according to the method of Adams and Nagarkatti[17] and purified by recrystallization from ethyl acetate according to the procedure of Pinkus and Tsuji[23] (mp 164–166 °C) (lit.[23] mp 163–165 °C). The syn-type geometrical isomer of QBS was preferred in this work to the anti-type one because of its higher solubility in benzene and its higher yield. PCA was purified from the commercial product according to the procedure of Natsuume et al.[24] (mp 288.5–290 °C). TCNQ was prepared according to the method of Acker and Hertler[2] and purified by recrystallization from ethyl acetate and sublimation (twice) (mp 294–296 °C). TMCQ was prepared from TCNQ according to a modification of the method of Acker and Hertler[2] and recrystallized from a mixture of benzene and hexane. Commercial MAnh was recrystallized from chloroform and sublimed twice (mp 52.5–53.0 °C). α,α'-Azobis(isobutyronitrile) (AIBN) and hexamethylbenzene (HMB) were recrystallized from ethanol. Acenaphthylene was purified from the commercial product by recrystallization from methanol. Styrene (St), *n*-butyl vinyl ether (nBVE), isobutyl vinyl ether (iBVE), and vinyl acetate (VAc) were purified from commercial products by conventional methods. Phenyl vinyl ether (PhVE) was prepared from phenol and dibromoethane according to the methods of McElvain and Pinzón[25] and Fueno et al.[26] 2-Chloroethyl vinyl ether (CEVE) was prepared by the dehydrochlorination of 2,2′-dichloroethyl ether.[27] Benzene was washed with concentrated sulfuric acid and then water, dried over calcium chloride, refluxed over sodium metal for 5 h, and distilled at 80 °C. Chloroform was refluxed over calcium hydride for 7 h and distilled at 61.0 °C.

Charge-Transfer Complexation of QBS with St or HMB. Absorption spectra of the charge-transfer transition for the QBS–St and QBS–HMB systems were taken in benzene at room temperature. The concentrations of solutions employed were as follows: [QBS] = 1.82×10^{-3} mol/L and [St] = 0.96 mol/L for the QBS–St system and [QBS] = 1.0×10^{-2} mol/L and [HMB] = 0.1 mol/L for the QBS–HMB system.

Determination of the equilibrium association constant, K_{CT}, and the molar absorption coefficient, ϵ_{CT}, for the charge-transfer complex between QBS and St was carried out in benzene at 20 and 30 °C according to the Benesi–Hildebrand equation. The wavelength at which the absorbance was measured was 470 nm. The concentrations of the solutions employed were [QBS] = 2.0×10^{-3} mol/L and [St] = 0.3–2.7 mol/L. The path length of the cell employed was 0.5 cm.

Polymerization Procedure. For copolymerization, given amounts of QBS and comonomer (St, acenaphthylene, iBVE, nBVE, CEVE, PhVE, or VAc), 10 mg of AIBN, and 10 mL of benzene were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and opened. In the case of St or acenaphthylene as comonomer, the reaction mixture was poured into excess methanol to precipitate the copolymer. For purification, the copolymer obtained was dissolved again in a small amount of chloroform, and the resulting solution was poured into excess methanol to precipitate the copolymer, which was dried under reduced pressure. In the case of iBVE, nBVE, CEVE, PhVE, or VAc as comonomer, the reaction mixture was placed under reduced pressure to remove volatile materials. The residual material was dissolved in a small amount of dichloromethane, and the resulting solution was poured into excess isopropyl ether to precipitate the copolymer. The solvent and precipitant for the purification were dichloromethane and petroleum ether instead of chloroform and methanol, respectively.

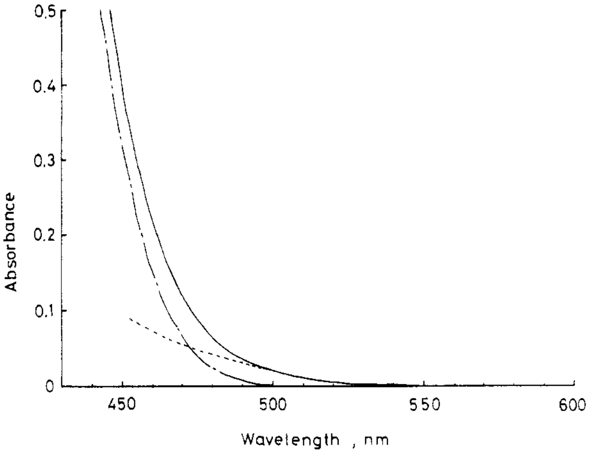


Figure 1. UV–vis spectra of a mixture of QBS with St in benzene at room temperature: (—) spectrum of a mixture of QBS with St; (-·-) spectrum of QBS; (---) difference spectrum, corresponding to that of the complex. Concentrations of solutions employed are [QBS] = 1.82×10^{-3} mol/L and [St] = 0.96 mol/L.

For terpolymerization, given amounts of QBS, St, and acceptor comonomer (MAnh, PCA, TMCQ, or TCNQ), 10 mg of AIBN, and 10 mL of benzene as solvent were placed in an ampule. For the case of the QBS–TCNQ–St system, chloroform was used as the solvent for the polymerization and *N,N*-dimethylformamide (DMF) as the solvent for the purification of the terpolymer. For the QBS–MAnh–St system, isopropyl ether was employed as precipitant. The rest of the procedure was similar to the above-mentioned copolymerization case for the QBS–St system.

Polymer Characterization. Polymer composition was established by elemental analysis. Molecular weight was determined in chloroform by vapor pressure osmometry. Solution viscosity was determined at 30 °C by using the Ostwald viscometer in chloroform, with the exception of the terpolymer of the QBS–TCNQ–St system, for which DMF containing 0.1 wt % lithium chloride was used.

^{1}H NMR measurement for the copolymer of QBS with St was carried out in chloroform-*d* with tetramethylsilane as an internal standard.

Instruments for Measurements. Instruments for ^{1}H NMR, IR, and UV–vis spectral determination were Varian A-60D, Jasco-A100, and Hitachi Perkin-Elmer Model 139 and Shimadzu Model UV-200, respectively. Knauer vapor pressure osmometer and Yanagimoto CHN CORDER Model MT-2 instruments were used for molecular weight determination and elemental analysis, respectively.

Results and Discussion

Charge-Transfer Absorption Band. Addition of St to QBS in benzene causes the yellow color of the QBS solution to deepen as shown in Figure 1, where the difference spectrum (broken line) between the mixture and QBS shows a broad absorption band in the range 450–550 nm, corresponding to the charge-transfer transition between QBS and St. St does not absorb any light at wavelengths longer than 400 nm. The wavelength of 470 nm was chosen for the determination of K_{CT} and ϵ_{CT} for the formation of the charge-transfer complex between QBS and St, taking into account that the absorbance may be attributed much more to the charge-transfer complex than to the individual component compounds. Figure 2 shows the Benesi–Hildebrand plots for the QBS–St system at 20 and 30 °C.[28] The linearity of the plots obtained suggests that the complex is composed of equimolar amounts of donor and acceptor components. Values of K_{CT} and ϵ_{CT} are summarized in Table I, together with the corresponding ones for the TCNQ–St,[4] TMCQ–St,[5] DDQ–St,[13]

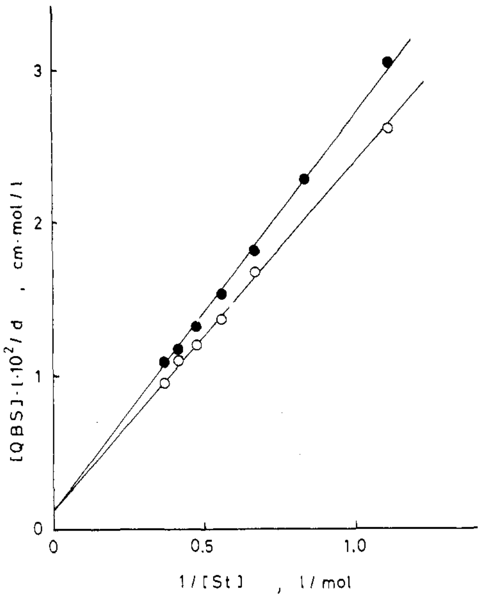


Figure 2. Benesi–Hildebrand plots for the QBS–St system. Temperatures of measurement are (○) 20 and (●) 30 °C. Concentrations of solutions employed are [QBS] = 2.0 × 10^{-3} mol/L and [St] = 0.3–2.7 mol/L. Benzene was used as solvent. The wavelength of measurement is 470 nm; l and d are cell length (in cm) and absorbance due to complex, respectively.

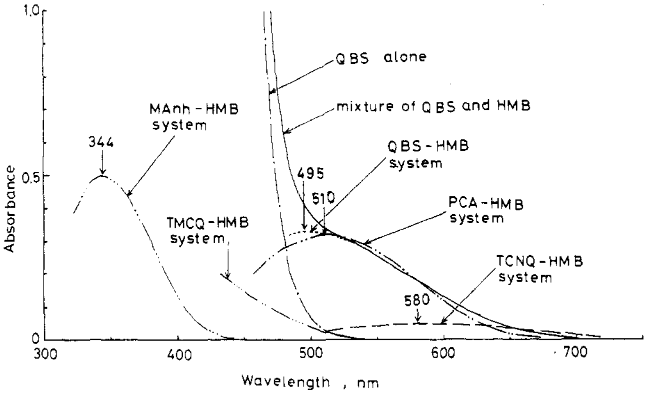


Figure 3. UV–vis spectra between HMB and various acceptor compounds in benzene at room temperature. Concentrations of solutions employed are [TCNQ] = 1.69 × 10^{-4} mol/L and [HMB] = 0.102 mol/L for the TCNQ–HMB system, [PCA] = 1.06 × 10^{-2} mol/L and [HMB] = 1.0 × 10^{-2} mol/L for the PCA–HMB system, [QBS] = 1.0 × 10^{-2} mol/L and [HMB] = 0.1 mol/L for the QBS–HMB system, [TMCQ] = 7.11 × 10^{-3}/L and [HMB] = 9.95 × 10^{-2} mol/L for the TMCQ–HMB system, and [MAnh] = 1.05 × 10^{-2} mol/L and [HMB] = 6.10 × 10^{-2} mol/L for the MAnh–HMB system, respectively.

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$)–St,[19] 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP)–St,[20] PCA–St,[21] and 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ)–St[29] systems. The K_{CT} values for all of these systems are similar and are less than unity.

The electron-accepting character (electron affinity (EA) of QBS was examined. The charge-transfer transition between QBS and HMB was measured in benzene at room temperature to be 495 nm as shown in Figure 3. HMB is a strong electron donor without polymerizability. From the well-known relationship[30] $h\nu_{CT} = \mathrm{IP} - \mathrm{EA} + C$ among the absorption maximum (ν_{CT}) in wavenumbers of the charge-transfer transition band, the EA of the acceptor monomer, and the ionization potential (IP) of the donor compound, the EA of QBS could be estimated numerically to be 2.17 eV on the basis of 2.48 eV[31] for the EA of PCA and the charge-transfer transition at 510 nm between PCA

Table I

Equilibrium Constants (K_{CT}) and Molar Absorption Coefficients (ϵ_{CT}) of Charge-Transfer Complex Formation between Various Acceptors and St

QBS–St[a]		TCNQ–St[b]		$TCNQF_4$–St[c]		TMCQ–St[a]		PCA–St[a]		DDQ–St[a]		TECQ–St[a]		TNAP–St[b]	
t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}	t, °C	K_{CT}
20	0.053	9	0.43	12.5	0.64	20	0.121	20	0.087	20	0.059	20	0.141	15	0.22
30	0.046	15	0.40	19.5	0.43	30	0.116	29.5	0.078	30	0.053	30	0.117	25	0.15
		25	0.36					40	0.065	39.5	0.049			35	0.10
$\epsilon_{CT}^{470} = 833$		$\epsilon_{CT}^{470} = 1900$		$\epsilon_{CT}^{570} = 2200$		$\epsilon_{CT}^{450} = 56$		$\epsilon_{CT}^{420} = 800$		$\epsilon_{CT}^{580} = 4200$		$\epsilon_{CT}^{440} = 88$		$\epsilon_{CT}^{532} = 17\,000$	

[a] Solvent benzene. [b] Solvent acetonitrile. [d] Solvent dichloromethane.

Table II
Copolymerization[a] of QBS with Styrene or Acenaphthylene in Benzene at 60 °C

run no.	monomer feed, mg QBS	monomer feed, mg comonomer	amt of QBS, mol %	time, h	polym yield, mg	conversn, %	anal.[d] % H	anal.[d] % C	anal.[d] % N	copolym comp, mol % QBS	$\bar{M}_n$[b]
					Styrene						
1[c]	390.0	208.8	33.4	168	0	0					
2	195.7	413.4	11.3	7.8	39.9	6.6	4.47	62.65	5.57	49.6	
3	194.4	165.0	24.1	11.4	62.5	17.4	4.65	62.77	5.41	48.9	7300
4	194.9	112.8	31.8	9	69.8	22.7	4.84	62.54	5.52	47.2	7600
5	388.9	113.0	48.1	23	30.9	6.2	4.41	63.92	5.82	51.1	
6	391.5	61.3	63.3	23.2	7.3	1.6	4.54	62.10	5.68	51.8	
7	333.3	34.7	72.1	9.1	9.1	2.5	4.57	62.28	5.34	51.8	
					Acenaphthylene						
8[c]	198.7	78.7	49.9	23.2	0	0					
9	195.3	404.3	16.0	2	42.8	7.1	4.15	66.40	5.43	51.6	7100
10	196.5	152.9	33.6	3	24.7	7.1	3.87	65.33	5.56	52.0	5100
11	388.4	157.0	49.3	5	73.9	13.5	4.24	66.05	5.39	51.5	6300
12	389.5	87.0	63.8	5.2	47.2	9.9	3.75	66.37	5.11	49.5	4500
13	389.2	64.9	70.3	6.6	31.3	6.9	3.68	67.05	5.43	51.6	4400

[a] Solvent, 10 mL; AIBN, 10 mg. [b] Determined by vapor pressure osmometry. Chloroform solvent. [c] Without initiator. [d] Calculated values for alternating copolymers: H, 4.53; C, 63.65; N, 5.70 (QBS–styrene system); H, 4.13; C, 66.89; N, 5.20 (QBS–acenaphthylene system).

and HMB, as shown additionally in Figure 3. It was concluded, therefore, that QBS is intermediate in electron-accepting character between PCA (EA = 2.48 eV)[31] and MAnh (EA = 1.33 eV).[31] Electron-accepting character was compared among TCNQ, PCA, QBS, and MAnh by means of their charge-transfer transition maxima with HMB, appearing at 580, 510, 495, and 344 nm, respectively, as shown additionally in Figure 3. The maximum for the TMCQ–HMB system was not observed because it overlaps seriously with the absorption of TMCQ alone. However, it exists certainly in the wavelength range below 450 nm, implying that TMCQ is weaker in electron-accepting character than QBS. Comparison between TMCQ and MAnh could not be carried out by this charge-transfer transition method. Therefore, the following order of the electron-accepting character of the acceptor compounds was found: TCNQ > PCA > QBS > TMCQ, MAnh.

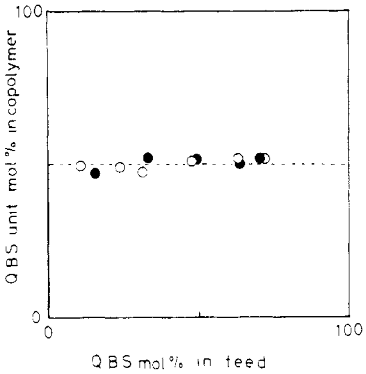


Figure 4. Composition diagram of the copolymerizations of QBS with St (○) and with acenaphthylene (●).

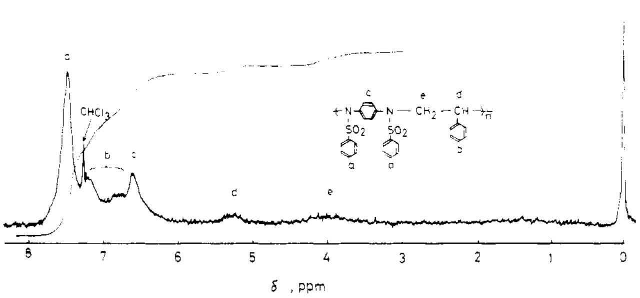


Figure 5. ^{1}H NMR spectrum of the copolymer of QBS with St in chloroform-d at 32 °C.

Copolymerization of QBS with Donor Monomers. First, as typical donor monomers St and acenaphthylene, which seems a stronger donor than St, were employed. The copolymerizations of QBS with St and acenaphthylene were attempted at 60 °C in benzene without initiator for 168 h (see run no. 1 in Table II) and 23.2 h (see run no. 8 in Table II), respectively. In both cases no polymeric material could be obtained, and only the starting materials were recovered in quantitative amounts. When a free-radical initiator such as AIBN was added, copolymers were obtained. Table II summarizes the results of the copolymerizations of QBS with St and acenaphthylene, and Figure 4 shows the composition diagrams of these copolymerizations. The copolymerizations proceeded in a homogeneous state. The copolymers, obtained as a white powder, were examined by elemental analysis and were found to have almost fixed amounts of carbon, hydrogen, and nitrogen regardless of monomer feed ratio. The found values are in good agreement with the calculated ones for the copolymers composed of equimolar amounts of each component monomers. The molecular weight of the copolymers obtained for the QBS–St and QBS–acenaphthylene systems were measured by vapor pressure osmometry in chloroform to be about 7000 and 400–7000, respectively, corresponding to degrees of polymerization of about 15 and 8–13, respectively, based upon an alternating structure of donor and acceptor units. The molecular weights of the copolymers obtained are very low, in contrast to alternating copolymers of St with TCNQ ([η] = 0.407 dL/g in DMF containing 0.1 wt % LiCl at 30 °C)[4], TMCQ (η_{sp}/C = 0.1–0.4 dL/g in benzene at 30 °C),[5] and PCA (η_{sp}/C = 0.19 dL/g in benzene, molecular weight 15 900).[11] In the IR spectra, the QBS monomer shows absorption at 1550 cm^{-1} due to the stretching vibration of the imide group but the QBS–St copolymer does not. The ^{1}H NMR spectrum of the copolymer of QBS with St is shown in Figure 5, where the absorption peaks were assigned to respective protons of the chemical structure illustrated. The methine and methylene protons of the St monomer unit of the copolymer appearing in the δ 5.2 and 4.0 region, respectively, were found to be much more subject to deshielding than the corresponding ones of homopolystyrene, generally appearing in the δ 1–2 ppm region.[32] Presumably, the deshielding arises from a powerful electron withdrawal by the neighboring benzenesulfonamide group when the St monomer unit is sandwished between QBS monomer units in the copolymer. In addition, an extreme broadness was observed in the

Table III
Reactions[a] of QBS with Vinyloxy Compounds in Benzene at 60 °C

monomer feed, mg							
QBS	vinyloxy compd	amt of QBS, mol %	polym yield, mg	conversn, %	anal. % S	copolym comp, mol % QBS	$\bar{M}_n$[b]
200.3	iBVE, 213.1	19.6	16.6	4.0	12.73	46.0	1650
203.0	nBVE, 208.6	20.1	21.2	5.2	13.36	51.7	1700
203.4	CEVE, 204.8	21.5	38.4	9.4	12.83	48.5	1700
202.8	PhVE, 206.0	23.4	11.7	2.9	12.16	46.1	1290
205.6	VAc, 219.6	17.3	0	0			

[a] Solvent, 10 mL; AIBN, 10 mg; time, 24 h. [b] Determined by vapor pressure osmometry. Chloroform solvent.

methine and methylene proton absorptions of the St monomer unit in the copolymer, presumably due to the influence of the quadrupole moment of the neighboring nitrogen nuclei and also due to the decrease in the flexibility of the main chain. It can be concluded, therefore, that QBS can copolymerize in an alternating fashion (cooligomerize) with St and acenaphthylene when free radical initiator is used, and QBS reacts at exocyclic nitrogen sites.

The copolymerizations between QBS and vinyl monomers with small positive e values such as methyl methacrylate (MMA), methyl acrylate (MA), and acrylonitrile (AN) were attempted with AIBN in benzene at 60 °C for 48. In no case was polymeric material obtained, and unreacted QBS was recovered in an almost quantitative amount, similarly to the reactions of PCA with those monomers.[11] Since QBS has a much lower electron-accepting character than $TCNQF_4$ and TCNQ, the gap in π-electron density between QBS and MMA was considered to be too small to undergo their charge-transfer complex formation and their further alternating copolymerization.

Table III summarizes the results of the copolymerizations of QBS with nBVE, iBVE, CEVE, PhVE, and VAc. The reaction products were obtained as white powders except in the case of VAc, in which no reaction took place and starting materials were recovered quantitatively. It is conceivable that VAc, which is the weakest donor monomer among the five vinyloxy monomer,[22] and QBS, the weak acceptor monomer, may not afford a sufficient gap in π-electron density to undergo charge-transfer complex formation and alternating copolymerization. It is evident from the composition data of the copolymers obtained that the copolymers are composed of equimolar amounts of QBS and donor comonomers, indicating the alternating copolymers. We point out that QBS, the weak acceptor monomer, cannot initiate the cationic polymerization of the vinyloxy compounds in benzene similarly to TECQ,[29] TMCQ,[5] and MAnh, whereas TCNQ and $TCNQF_4$, strong acceptor monomers, can initiate the cationic polymerization of a strong donor monomer such as nBVE and iBVE.[19,22] The results correspond well to the low electron-accepting character of QBS.

Terpolymerizations of the QBS–MAnh–St, QBS–PCA–St, QBS–TMCQ–St, and QBS–TCNQ–St Systems. Terpolymerizations of the QBS–MAnh–St, QBS–PCA–St, QBS–TMCQ–St, and QBS–TCNQ–St systems were carried out at 60 °C for a quantitative comparison in the polymerizability as an acceptor monomer among QBS, MAnh, PCA, TMCQ, and TCNQ. Benzene was used as a solvent for the polymerization except for the QBS–TCNQ–St system, in which chloroform was employed because TCNQ is very insoluble in benzene. Table IV summarizes the results of those terpolymerizations. The terpolymers of all systems were obtained as white powders and were always composed of about 50 mol % of the St monomer unit regardless of the monomer feed ratio, and thus the sum of the QBS and other acceptor monomer (MAnh, PCA, TMCQ, or TCNQ) unit was about 50 mol %. Consequently, the terpolymerization composition relationships of the QBS–MAnh–St, QBS–PCA–St, QBS–TMCQ–St, and QBS–TCNQ–St systems can be illustrated by their composition diagrams of binary copolymerizations between QBS and MAnh, between QBS and PCA, between QBS and TMCQ, and between QBS and TCNQ, shown in Figures 6–9, respectively. According to the complex mechanism treatment[33] the modified monomer reactivity ratios of the complexes were calculated to be $r_1(K_1/K_2)$ = 30 ± 20 and $r_2(K_2/K_1)$ = 0.1 ± 0.1 for the QBS–MAnh–St system (C_1 is QBS–St complex and C_2 is MAnh–St complex), $r_1(K_1/K_2)$ = 15 ± 10 and $r_2(K_2/K_1)$ = 0.2 ± 0.2 for the QBS–PCA–St system (C_1 is QBS–St complex and C_2 is PCA–St complex), $r_1(K_1/K_2)$ = 1.18 ± 0.1 and $r_2(K_2/K_1)$ = 0.15 ± 0.05 for the QBS–TMCQ–St system (C_1 is QBS–St complex and C_2 is TMCQ–St complex), and $r_1 \cdot (K_1/K_2)$ = 0.01 ± 0.01 and $r_2(K_2/K_1)$ = 45 ± 10 for the QBS–TCNQ–St system (C_1 is QBS–St complex and C_2 is

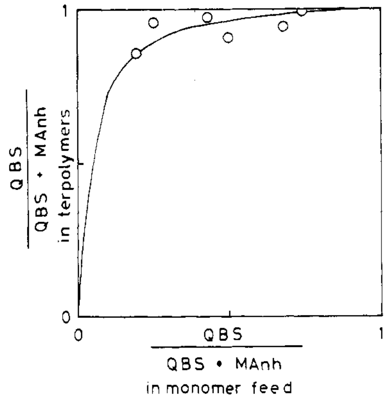


Figure 6. Composition diagram of the terpolymerization of QBS, MAnh, and St as binary copolymerization between QBS and MAnh. The line is calculated by using $r_1(K_1/K_2)$(QBS–St complex) = 30 and $r_2(K_2/K_1)$(MAnh–St complex) = 0.1.

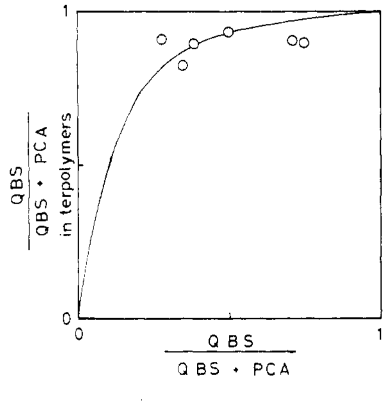


Figure 7. Composition diagram of the terpolymerization of QBS, PCA, and St as binary copolymerization between QBS and PCA. The line is calculated by using $r_1(K_1/K_2)$(QBS–St complex) = 15 and $r_2(K_2/K_1)$(PCA–St complex) = 0.2.

Table IV
Terpolymerizations[a] of the QBS–MAnh–St, QBS–PCA–St, QBS–TMCQ–St, and QBS–TCNQ–St Systems at 60 °C

run	monomer feed, mg			mol %			time,	polym	conversn,	anal.				terpolym comp, mol %			η_{sp}/C,[b]
no.	QBS	acceptor	St	QBS	acceptor	St	h	yield, mg	%	% H	% C	% N	% S	QBS	acceptor	St	dL/g
MAnh Acceptor																	
1	306.4	101.8	89.2	29.5	38.6	31.9	0.8	56.2	11.3	4.52	63.84	5.63		48.3	1.2	50.5	
2	485.0	58.0	87.7	46.7	22.0	31.3	0.8	21.8	3.5	4.29	63.28	5.68		49.3	3.0	47.7	
3	195.0	49.4	159.4	19.9	19.9	60.2	4.2	67.3	16.7	4.47	63.18	5.64		48.2	4.7	46.9	0.10
4	96.2	99.5	135.0	9.7	39.6	50.6	1.8	23.0	7.0	4.43	63.53	5.47		45.1	7.3	47.6	
5	199.4	150.0	58.8	19.8	58.6	21.6	3.0	17.4	4.3	4.33	63.31	5.70		49.7	2.2	48.1	0.04
6	589.7	51.3	67.5	56.6	19.4	24.0	3.5	11.0	1.6	4.14	63.65	5.74		49.6	0.3	50.1	0.04
PCA Acceptor																	
7	196.4	124.6	160.0	19.9	19.9	60.2	27.7	49.6	10.3	4.13	62.72	5.47		47.4	3.3	49.3	
8	188.9	306.1	88.5	18.9	48.2	32.9	26.2	12.6	2.2	5.03	62.46	5.36		46.0	4.6	49.4	
9	484.4	124.5	86.5	48.4	19.5	32.1	24.5	60.7	8.7	4.23	61.42	5.47		48.6	5.3	46.1	
10	592.5	126.6	95.8	51.7	17.3	31.0	23.9	82.1	10.1	4.18	61.40	5.46		48.6	5.6	45.8	0.07
11	100.7	120.7	420.5	5.5	10.3	84.2	23.9	47.8	7.4	4.37	61.64	4.94		41.0	8.8	50.2	0.05
12	183.7	188.2	103.0	21.3	34.3	44.3	29.7	46.8	9.9	4.39	62.16	5.32		45.8	5.3	48.9	0.04
TMCQ Acceptor																	
13	99.5	199.9	68.9	17.0	39.3	43.7	16.9	54.6	14.8	4.74	63.62	3.26		28.2	25.3	46.5	0.08
14	300.2	100.8	103.5	37.5	14.5	48.0	8.5	18.1	3.6	4.81	63.55	4.68		41.0	10.9	48.1	0.08
15	129.5	115.5	210.3	12.7	12.4	74.9	3.3	23.4	5.1	4.80	63.61	4.07		35.4	17.0	47.6	0.13
TCNQ Acceptor																	
16	131.6	48.6	148.7	17.0	11.9	71.1	1.1	22.5	6.8	3.98	76.90	17.28	0.77	1.9	47.7	50.4	0.26
17	263.8	51.9	112.8	33.8	12.6	53.6	1.3	21.1	4.9	4.08	76.42	16.87	1.15	2.9	46.6	50.5	0.21
18	369.0	50.6	82.0	48.0	12.5	39.5	1.7	17.8	3.5	4.03	76.26	16.78	1.43	3.6	46.3	50.1	0.21

[a] 10 mL of benzene and 10 mg of AIBN for the QBS–MAnh–St, QBS–PCA–St, and QBS–TMCQ–St systems and 10 mL of chloroform and 5 mg of AIBN for the QBS–TCNQ–St system. [b] Chloroform solvent for the QBS–MAnh–St (C = 0.2–0.3 g/dL), QBS–PCA–St (C = 0.3–0.6 g/dL), and QBS–TMCQ–St (C = 0.5 g/dL) systems and DMF containing 0.1 wt % LiCl for the QBS–TCNQ–St (C = 0.1 g/dL) system. t = 30 °C.

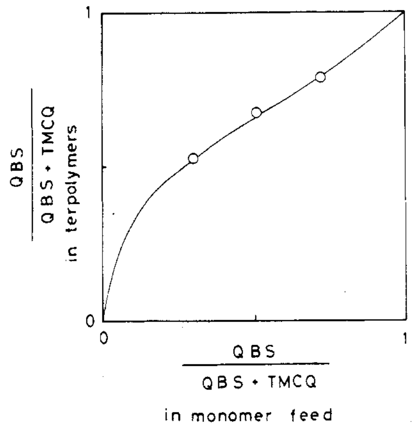


Figure 8. Composition diagram of the terpolymerization of QBS, TMCQ, and St as binary copolymerization between QBS and TMCQ. The line is calculated by using $r_1(K_1/K_2)$(QBS–St complex) = 1.18 and $r_2(K_2/K_1)$(TMCQ–St complex) = 0.15.

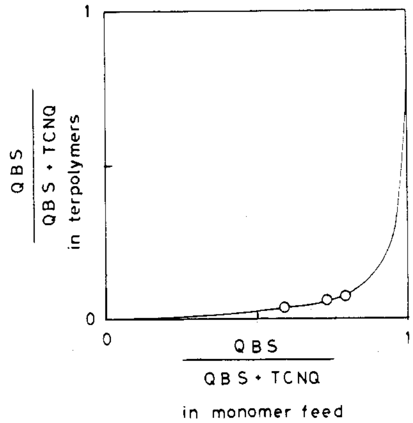


Figure 9. Composition diagram of the terpolymerization of QBS, TCNQ, and St as binary copolymerization between QBS and TCNQ. The line is calculated by using $r_1(K_1/K_2)$(QBS–St complex) = 0.01 and $r_2(K_2/K_1)$(TCNQ–St complex) = 45.

TCNQ–St complex), respectively. K_1 and K_2 refer to equilibrium constants for formation of complex 1 (C_1) and complex 2 (C_2), respectively. The reciprocals of the modified monomer reactivity ratios were compared as relative reactivity of the complexes toward the polymer radical with a given terminal complex unit. The order in relative reactivity of the MAnh–St, PCA–St, TMCQ–St, and TCNQ–St complexes toward the polymer radical with the QBS–St complex unit was obtained as MAnh–St complex (1/30) < PCA–St complex (1/5) < TMCQ–St complex (1/1.18) < QBS–St complex (1) < TCNQ–St complex (1/0.01). Previously, it was pointed out[19,20] from the alternating copolymerizations of those electron-accepting quinodimethane derivatives with St that reactivity of their St complexes is related intimately to an electron-accepting character, such as EA, of the quinodimethane derivatives. EA values of MAnh, QBS, PCA, and TCNQ were reported to be 1.33,[31] 2.17, 2.48,[31] and 2.88[31] eV, respectively. Although the EA value of TMCQ has not been reported yet, it is likely in the charge-transfer complexation profile as shown in Figure 3 that TMCQ is weaker in electron-accepting character than QBS. Thus, the order of electron-accepting character for the acceptor monomers is assumed to be MAnh, TMCQ < QBS < PCA < TCNQ and is in good agreement with the order of reactivity of their St complexes except for PCA. The PCA–St complex is regarded to be much less reactive than expected from the electron-accepting character of PCA in the above-mentioned relationship. Coppinger and Bauer[15] pointed out on the basis of the experimental data on the π–π* electron transition and the Hückel molecular orbital calculations that the stability of hetero p-benzoquinone compounds is related well to the energy difference between their quinoid ground state and benzenoid transition state. Increase in electronegativity of the exocyclic atom results in a decrease in the highest occupied bonding energy level

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and an increase in the lowest unoccupied antibonding level, leading to an increase in energy difference between ground and transition states and the large stability of the compound. Futhermore, it similarly exerts a great influence on the electron-accepting character of these compounds, ascertained with Fieser's reduction potential for the compounds. Consequently, the exocyclic atom of hetero p-benzoquinones affects not only the stability of their compounds, that is, the reactivity, but also their electron-accepting character. In the case of the PCA–St system, it is may be presumed that the exocyclic electronegative oxygen atom of PCA affects its stability of PCA more effectively than its electron-accepting character.

Registry No. Acenaphthylene, 208-96-8; butyl vinyl ether, 111-34-2; 2-chloroethyl vinyl ether, 110-75-8; phenyl vinyl ether, 766-94-9; isobutyl vinyl ether, 109-53-5; QBS, 1050-82-4; St, 100-42-5; MAnh, 108-31-6; PCA, 118-75-2; TMCQ, 65649-20-9; TCNQ, 1518-16-7.

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Ring-Opening Polymerization of 3-Methyloxetane: NMR Spectroscopy and Configurational Properties of the Polymer

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ABSTRACT: Poly(3-methyloxetane) was obtained at −78 °C by ring-opening polymerization of 3-methyloxetane, using a cationic initiator with a very stable counterion. The polymerization reaction was rapid and quantitative, suggesting that 3-methyloxetane is much more reactive than initially was suspected. The structure of the polymer was studied by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra show that the methine carbons present three peaks, which can be assigned to the isotactic, syndiotactic, and heterotactic triads. The chemical shift differences of these signals (0.017 ppm), much lower than those for poly(2-methyloxetane) (0.14), suggest that the vicinity of the oxygen atom to the methine carbon enhances the splitting of these carbons. Mean square dipole moments $\langle\mu^2\rangle$ of poly(3-methyloxetane) were determined as a function of temperature by means of dielectric constant measurements in cyclohexane. It was found that the value of the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where nm^2 is the mean square dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed, is 0.354 at 30 °C and its temperature coefficient is 2.7×10^{-3} K^{-1}. The experimental results were found to be in good agreement with theoretical results based on a 3 × 3 rotational state scheme. The theoretical analysis showed that the dielectric properties are not very sensitive to the stereochemical composition of the chains. The present study also indicates that all of the members of the polyoxetane series have a high degree of conformational randomness.

Introduction

The cationic ring-opening polymerization of oxetane (Ox)[1-3] and its derivatives 3-methyloxetane (MOx)[2,3] and 3,3-dimethyloxetane (DMOx)[2-4] was studied some time ago. The correlation between the reactivity and the monomer ring substitution was discussed from the viewpoint of the propagation rate constants and the corresponding activation parameters. However, a considerable discrepancy was observed in the kinetic results obtained by different authors. As far as we are aware, no additional work to that of ref 3 has been published on the reactivity of MOx.

The cationic polymerization of the oxetanes gives rise to chains of unusual interest to get a better understanding

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