0.5 mm. X-ray diffractograms of mesophases were obtained on samples obtained by quenching the polymer melts with a dry ice/acetone mixture. Annealing of polymers was conducted in a vacuum oven preheated to a desired temperature. Afterward, the annealed samples were slowly cooled to room temperature in the vacuum oven.

Acknowledgment. We gratefully acknowledge the financial support of this research by the Korea Science and Engineering Foundation. The helpful comments made by Dr. Robert Ausubel on the manuscript is gratefully acknowledged.

Registry No. NO_2/H (copolymer), 107514-81-8; NO_2/H (SRU), 107556-07-0; NO_2/Cl (copolymer), 107514-82-9; NO_2/Cl (SRU), 107556-06-9; NO_2/Br (copolymer), 107514-83-0; NO_2/Br (SRU), 107556-04-7; NO_2/CH_3 (copolymer), 107514-84-1; NO_2/CH_3, 107556-09-2; NO_2/C_6H_5 (copolymer), 107514-85-2; NO_2/C_6H_5 (SRU), 107556-10-5; Br/H (copolymer), 107514-86-3; Br/H (SRU), 95978-14-6; Br/Cl (copolymer), 107514-87-4; Br/Cl (SRU), 95935-11-8; Br/Br (copolymer), 107514-88-5; Br/Br (SRU), 107556-05-8; Br/CH_3 (copolymer), 107514-89-6; Br/CH_3 (SRU), 107556-08-1; Br/C_6H_5 (copolymer), 107514-90-9; Br/C_6H_5 (SRU), 95935-16-3.

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Polymerization Behavior of 7,7-Dicyanoquinone Methide as an Acceptor Monomer

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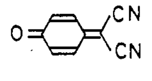
ABSTRACT: The electron affinity of 7,7-dicyanoquinone methide (CQM) was estimated by the charge-transfer band method to be 2.36 eV. It was found that CQM copolymerizes alternatingly with styrene (St) or *p*-methoxystyrene in benzene at 60 °C in the presence of α,α'-azobis(isobutyronitrile) (AIBN). Terpolymerizations of the CQM–maleic anhydride (MAnh)–St, CQM–*p*-chloranil (PCA)–St, and CQM–2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)–St systems in benzene at 60 °C in the presence of AIBN gave nearly alternating copolymers of CQM with St, CQM with St, and DDQ with St, respectively. These results of the terpolymerization plainly exhibit a relative polymerizability between a pair of acceptor monomers, suggesting that these four acceptor monomers may be arranged in the following order of relative polymerizability as acceptor monomer: MAnh < PCA < CQM < DDQ. This order, except for PCA, agrees with that of their electron-accepting character. In addition, several parameters of the reactivity of these acceptor monomers in their alternating copolymerizations with St were estimated by means of the π-electron LCAO MO method and were compared with experimental results, allowing us to suggest an idea about a rate-determining state in their alternating copolymerization.

Introduction

Previously it has been pointed out that highly electron-accepting quinodimethane and quinone compounds such as 7,7,8,8-tetracyanoquinodimethane (TCNQ),[1] 2,5,7,7,8,8-hexacyanoquinodimethane,[2] 11,11,12,12-tetracyanonaphthoquinodimethane (TNAP),[2] 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$),[3] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[4] 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ),[5] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[6] are alternatingly and almost spontaneously copolymerizable as an acceptor monomer with donor monomers such as styrene (St) and vinyloxy compounds. In addition, *p*-benzoquinone bis(benzenesulfonimide) (QBS), with a highly electron-accepting property, was reported to exhibit a similar polymerization behavior.[7]

7,7-Dicyanoquinone methide (CQM), prepared originally by Hyatt,[8] was considered to be an interesting compound, intermediate between TCNQ and *p*-benzoquinone, because its chemical structure has oxygen and dicyanomethylene carbons at the exocyclic 7 and 8 positions, but its polymerization has not yet been studied.

In this work were investigated the polymerization behavior of CQM, its copolymerizations with St and *p*-methoxystyrene (MeOSt), and the terpolymerizations of St, CQM, and a second acceptor monomer such as maleic anhydride (MAnh), *p*-chloranil (PCA), and DDQ; its electron-accepting character was also measured. In addition, the reactivity of CQM, MAnh, PCA, and DDQ as acceptor monomers in their alternating copolymerizations with St was estimated by means of the π-electron linear combination atomic orbital (LCAO) molecular orbital (MO) method to get some idea about a rate-determining state in the alternating copolymerization.



CQM

Experimental Section

Materials. CQM was prepared from 1,4-cyclohexanedione and malononitrile according to the method of Hyatt.[8] MAnh was purified from the commercial product by subliming it in the presence of phosphorous pentoxide, and it was used immediately. Commercial DDQ was recrystallized from a mixture of benzene and chloroform (1/4 by volume) and then sublimed. PCA was purified by treating its benzene solution with calcium carbonate and then recrystallizing from benzene. MeOSt was prepared from anisole and acetyl chloride according to the method of Overberger

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et al.[9] St and benzene were purified from commercial products by the conventional methods. 2,2'-Azobis(isobutyronitrile) (AIBN) and hexamethylbenzene (HMB) were purified from commercial products by recrystallization from ethanol.

Charge-Transfer Absorption Band for the CQM-HMB, PCA-HMB, CQM-St, and CQM-MeOSt Systems. Absorption spectra of the charge-transfer transition for the CQM-HMB, PCA-HMB, CQM-St, and CQM-MeOSt systems were taken in benzene at room temperature. The concentrations of the solutions employed were as follows: [CQM] = [HMB] = 2×10^{-2} mol/L for the CQM-HMB system, [PCA] = [HMB] = 1×10^{-2} mol/L for the PCA-HMB system, and [CQM] = 2×10^{-2} mol/L and [St] = [MeOSt] = 0.2 mol/L for the CQM-St and CQM-MeOSt systems.

Determination of the equilibrium constant, K_{CT}, and molar absorption coefficient, ϵ_{CT}, for the charge-transfer complex between CQM and MeOSt was carried out in benzene at 10, 20, and 29 °C according to the Benesi-Hildebrand equation.[10] The wavelength at which the absorbance was measured was 508 nm. The concentrations of the solutions employed were as follows: [CQM] = 2.0×10^{-3} mol/L and [MeOSt] = 0.3-1 mol/L. The path length of the cell employed was 0.5 cm.

Polymerization Procedure. For copolymerization, given amounts of CQM and a comonomer such as St and MeOSt, 3 or 5 mg of AIBN, and 2 mL of benzene were placed in an ampule, which was degassed completely by the freeze-thaw method (repeated 3 times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and opened. 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.

For terpolymerization, given amounts of CQM, St, and a second acceptor monomer such as MAnh, PCA, and DDQ, 3 mg of AIBN, and 2-5 mL of benzene were placed in an ampule. For the CQM-MAnh-St system, isopropyl ether was employed as precipitant. The rest of the procedure was similar to that mentioned above for the copolymerization.

Polymer Characterization. Polymer composition was established by elemental analysis. The molecular weight ($\bar{M}_n$) of the polymers was determined without correction by gel permeation chromatography (GPC) using standard polystyrene as reference and tetrahydrofuran (THF) as eluent.

^{1}H NMR measurement for the copolymers of CQM with St and with MeOSt was carried out in chloroform-*d* with tetramethylsilane as internal standard.

Instrumentation. Instruments for UV-vis and ^{1}H NMR spectral determination were Jasco UVIDEC-430B and Hitachi R-600, respectively. Elemental analysis and GPC were performed on Yanagimoto CHN Corder Model MT-2 and Toyo Soda Model HLC-803D with a series of four columns, Toyo Soda G4000H, G3000H, G2500H, and G2000H.

Results and Discussion

Electron-Accepting Character. The electron-accepting character (electron affinity (EA)) of CQM was estimated by means of a charge-transfer transition band method. The charge-transfer transition between CQM and HMB was observed in benzene at room temperature to be at 504 nm, as shown in Figure 1. The charge-transfer transition between PCA and HMB was measured at 510 nm, as also shown in Figure 1. From a well-known relationship,[10] $\hbar\nu_{\mathrm{CT}} = \mathrm{IP} - \mathrm{EA} + C$, where ν_{CT} refers to the absorption maximum (in wavenumbers) of the charge-transfer transition band, $\hbar$ to Plank constant, EA to the electron affinity of the acceptor compound, IP to the ionization potential of the donor compound, and C to the Coulomb energy of the charge-transfer transition[11] (C being taken as constant in an analogous charge-transfer complex), the EA value of CQM could be estimated numerically to be 2.36 eV on the basis of the EA value of 2.48 eV[12] for PCA and the charge-transfer transition band of 510 nm between PCA and HMB. It is concluded therefore that CQM is weaker in electron-accepting character than PCA. The EA values of MAnh and DDQ used as a second acceptor monomer in this work were reported to be 1.33 and 3.13 eV,[12] respectively. Therefore, the electron-accepting character of the acceptor compounds was placed in the following order: MAnh ≪ CQM < PCA ≪ DDQ.

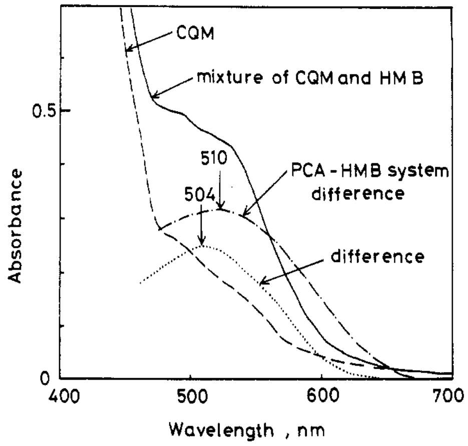


Figure 1. UV-vis spectra of a mixture of CQM with HMB in benzene at room temperature: (—) spectrum of a mixture of CQM with HMB; (---) spectrum of CQM; (···) difference spectrum between the above two spectra, corresponding to that of the complex. (-·-) difference spectrum between PCA and a mixture of PCA with HMB. Concentration of solutions employed are [CQM] = [HMB] = 2.0×10^{-2} mol/L for the CQM-HMB system and [PCA] = [HMB] = 1.0×10^{-2} mol/L for the PCA-HMB system.

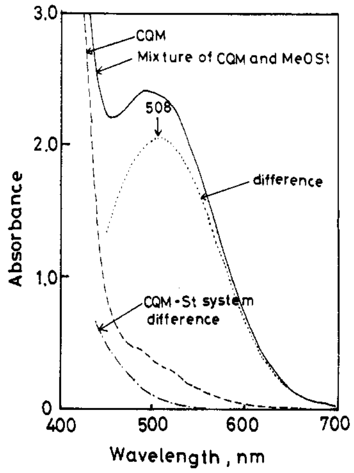


Figure 2. UV-vis spectra of a mixture of CQM with MeOSt in benzene at room temperature: (—) spectrum of a mixture of CQM with MeOSt; (---) spectrum of CQM; (···) difference spectrum between the above two spectra, corresponding to that of the complex. (-·-) Difference spectrum between CQM and a mixture of CQM with St. Concentrations of solutions employed are [CQM] = 2.0×10^{-2} mol/L and [MeOSt] = [St] = 0.2 mol/L.

Charge-Transfer Transition Band for the CQM-St and CQM-MeOSt Systems. Addition of St to CQM in benzene causes a CQM solution to tinge red, as shown Figure 2, where the difference spectrum between the mixture and CQM appears only as an end absorption. Addition of MeOSt to CQM in benzene causes a CQM solution to turn from orange to red, as shown Figure 2, where the difference spectrum between the mixture and CQM exhibits an absorption maximum at 508 nm. Both these difference spectra can be explained in terms of the electron-donating character of St and MeOSt, MeOSt being a stronger donor than St. Figure 3 shows the Benesi-Hildebrand plots for the CQM-MeOSt system at 10, 20, and 29 °C, which give K_{CT} values of 0.14, 0.12, and 0.11,

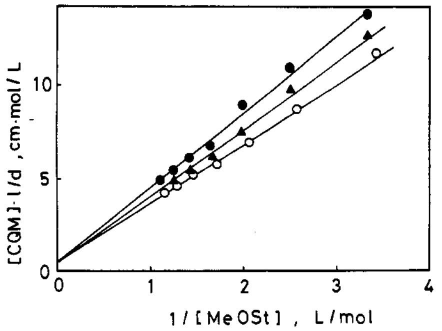


Figure 3. Benesi–Hildebrand plots for the CQM–MeOSt system at (○) 10, (▲) 20, and (●) 29 °C. Concentrations of solutions employed are [CQM] = 2.0×10^{-3} mol/L and [MeOSt] = 0.3–1 mol/L. Benzene was used as solvent. The wavelength of measurement is 508 nm; l and d are cell length (in cm) and absorbance due to complex, respectively.

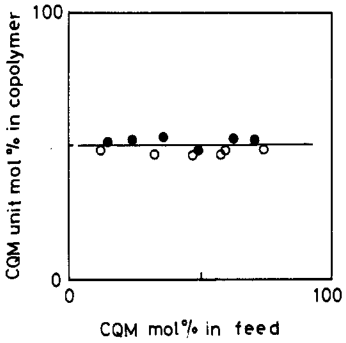


Figure 4. Composition diagram of the copolymerizations of CQM with St (●) and with MeOSt (○).

respectively, and the ϵ_{CT} value of 2270. These K_{CT} values are less than unity, similar to those of the alternating copolymer systems[1-7] between electron-accepting quinodimethane and quinone compounds and styrenes.

Copolymerizations of the CQM–St and CQM–MeOSt Systems. Although CQM is not homopolymerizable with any type of initiator, it is alternatingly copolymerizable with donor monomers such as St and MeOSt and free radical initiators such as AIBN. When this copolymerization was carried out without the initiator at 60 °C for 80 h, no polymeric material was obtained and the monomers were recovered in quantitative amounts.

Table I summarizes the results of the copolymerizations of CQM with St and with MeOSt, and Figure 4 shows their composition diagrams. Both copolymerizations in benzene proceeded without precipitation. The copolymers were obtained as a white powder. The copolymer compositions were found to be constant regardless of monomer feed ratios. The experimental values are in good agreement with the calculated ones for the copolymer composed of equimolar amounts of acceptor (CQM) and donor (St or MeOSt) monomers. The molecular weight of the copolymers of the CQM–St and CQM–MeOSt systems was measured by GPC to be 1400–6500 and 5800–10600, respectively, corresponding to degrees of polymerization of 5–25 and 20–27 based upon a basic unit containing both a donor and an acceptor monomer unit. Apparently these copolymers are not polymeric but oligomeric. The copolymers of DDQ with St (η_{sp}/C = 0.055–0.07 dL/g in chloroform at 30 °C)[6] and of QBS with St ($\bar{M}_n$ = 7000, determined by GPC),[7] were reported to be similarly very low while alternating copolymers of St with TCNQ [(η) = 0.407 dL/g in *N,N*-dimethylformamide (DMF) containing 0.1 wt % LiCl at 30 °C),[1] St with TNAP (η_{sp}/C = 0.2–0.4 dL/g in DMF at 30 °C)[2], St with $TCNQF_4$ (η_{sp}/C = 0.2–0.3 dL/g in DMF containing 0.1 wt % LiCl at 30 °C),[3] and St with TMCQ (η_{sp}/C = 0.1–0.4 dL/g in benzene at 30 °C)[4] have high molecular weights, indicating that CQM, QBS, and DDQ, with heteroatoms at the exocyclic 7 and 8 positions, should be much more reluctant to propagate in alternating copolymerization with St than quinodimethanes, with carbon atoms at the exocyclic 7 and 8 positions.

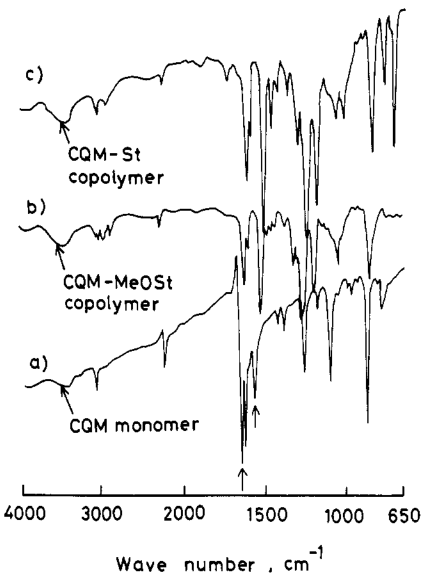


Figure 5. IR spectra (KBr disk method) of (a) CQM monomer, (b) the copolymer of CQM with MeOSt, and (c) the copolymer of CQM with St.

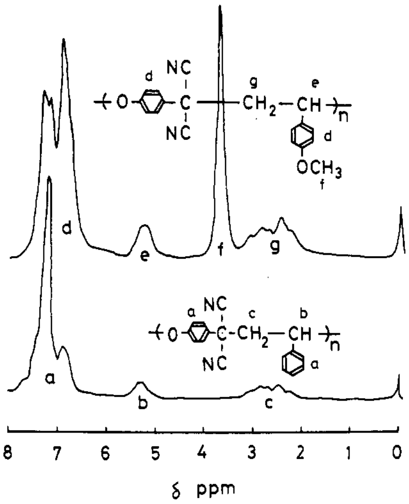


Figure 6. ^{1}H NMR spectrum of the copolymers of CQM with (a) St and (b) MeOSt in chloroform-*d* at 30 °C.

Figure 5 illustrates IR spectra of the CQM monomer and the copolymers of CQM with MeOSt and CQM with St. The CQM monomer shows absorptions at 1640 cm^{-1} due to the stretching vibration of the carbonyl group and at 1520 cm^{-1} due to that of the exocyclic carbon–carbon double bond, but both absorptions disappear in the copolymers. On the other hand, absorption peaks due to the ether linkage are observed at 1240 cm^{-1} for the copolymer of CQM with St and at 1260 cm^{-1} for the copolymer of CQM with MeOSt. The ^{1}H NMR spectra of the copolymers of CQM with St and MeOSt are shown in Figure 6, where the absorption peaks can be assigned to the respective protons of the chemical structure illustrated. The methine and methylene protons of the St and MeOSt monomer units of the copolymer appearing in the 5.3 and 2.6 ppm regions, respectively, were found to be much more subject to deshielding than the corresponding ones of

Table I
Copolymerizations[a] of CQM with Styrene and with *p*-Methoxystyrene in Benzene at 60 °C

run no.	monomer feed, mg: CQM	monomer feed, mg: comonom	amt of CQM, mol %	time, h	convrsn, %	copolym comp, mol %: N	copolym comp, mol %: CQM	$\bar{M}_n/10^3$ [b]
				Styrene				
1[c]	46.7	99.4	25.4	80	0			
2	53.8	206.8	14.8	47	22.9	10.97	51.4	6.5
3	53.8	108.9	24.6	43	24.7	11.13	52.3	5.6
4	49.2	57.8	36.2	87	18.9	11.34	53.3	4.3
5	53.4	36.8	49.2	109	28.1	10.40	48.0	4.2
6	51.9	20.8	62.5	183	28.2	11.17	52.6	1.5
7	77.5	21.8	70.4	183	35.3	11.19	52.6	1.4
				p-Methoxystyrene				
8	29.7	187.0	12.0	4.5	11.8	9.22	47.7	6.0
9	30.2	54.3	32.3	17	44.0	8.97	46.3	10.7
10	60.3	59.0	46.8	17	44.0	8.96	46.2	6.7
11	119.4	75.4	57.6	7.5	28.9	8.98	46.5	6.6
12	80.8	47.2	59.5	18	58.8	9.34	48.4	6.6
13	118.9	35.8	74.0	17	15.1	9.31	48.0	5.8

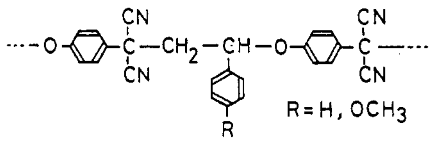
[a] Solvent, 2 mL; AIBN, 5 mg for CQM-St system, 3 mg for CQM-MeOSt system. [b] Determined by GPC (standard polystyrene) with THF as elvent. [c] Without AIBN.

Table II
Terpolymerizations[a] of CQM–MAnh–St, CQM–PCA–St, and CQM–DDQ–St Systems in Benzene at 60 °C

run no.	monomer feed in mg: CQM	monomer feed in mg: second acceptor	monomer feed in mg: St	monomer feed in mol %: CQM	monomer feed in mol %: second acceptor	monomer feed in mol %: St	time, h	polym yield, mg	convrsn, %	anal.: H	anal.: C	anal.: N	anal.: Cl	terpolymer comp, mol%: CQM	terpolymer comp, mol%: second acceptor	terpolymer comp, mol%: St	$\bar{M}_n/10^3$ [b]
								Second Acceptor: MAnh									
1	31.0	21.6	123.1	12.4	13.8	73.8	35.5	31.5	17.9	4.70	77.17	10.79		50.0	3.9	46.1	7.5
2	30.6	57.2	247.2	6.2	18.5	75.3	35.5	57.5	17.2	4.52	76.26	11.29		53.3	5.1	41.6	9.4
3	20.5	63.1	223.4	4.5	22.1	73.5	21.5	20.3	6.6	4.95	76.42	11.57		54.7	3.1	42.2	6.5
4	20.1	79.8	153.3	5.3	33.7	61.0	22.0	13.3	5.3	4.69	75.95	10.36		47.4	9.1	43.5	5.0
								Second Acceptor: PCA									
5	30.3	30.8	237.0	7.5	4.8	87.7	36.0	39.5	13.3	4.37	74.15	10.14	5.37	49.0	4.4	46.6	7.6
6	19.6	24.7	258.4	4.6	3.7	91.7	51.0	48.8	16.1	4.81	74.51	10.41	1.56	48.6	1.5	49.9	6.0
7	14.5	35.1	200.3	4.3	6.6	89.1	41.0	8.5	3.4	3.79	71.24	9.59	4.18	43.7	4.2	52.1	6.0
8	18.7	39.4	189.2	5.7	7.7	86.7	41.0	21.2	8.6	4.30	73.63	10.10	5.36	49.4	5.0	45.5	10.5
								Second Acceptor: DDQ									
9	39.0	36.9	100.1	18.2	11.8	70.0	15.0	36.7	20.9	2.14	57.75	8.86	19.39	5.1	46.9	48.0	22.0
10	30.2	20.3	105.2	14.9	6.9	78.2	12.5	14.9	9.6	2.42	58.24	8.89	19.06	7.8	43.5	48.7	6.3
11	29.3	38.0	101.4	14.1	12.6	73.3	12.5	42.0	24.9	2.46	60.53	9.00	19.27	8.1	44.2	47.7	19.5
12	4.0	19.7	115.0	17.7	6.0	76.3	12.5	35.6	20.4	2.48	58.70	8.78	19.26	6.7	43.9	49.4	15.5

[a] AIBN, 2 mg; solvent, 3 mL for run no. 1–4, 6, and 9–12, 4 mL for run no. 5, and 5 mL for run no. 7 and 8. [b] Determined by GPC with THF as elvent.

homopolymers of St and MeOSt, generally appearing in the 1–2 ppm region.[13] Presumably, the deshielding arises from electron withdrawal by the neighboring oxygen atom and the dicyanomethylene group when the St and MeOSt monomer units are sandwiched between the CQM monomer units in the copolymer. In the cases of alternating copolymers of TCNQ with St and of DDQ with St the methine and protons of the St unit were observed in the 3–4 ppm region (3 H)[1] and at 6.2 (1 H) and 4–5 ppm (2 H),[6] respectively. Consequently it is reasonable to expect that the methine carbon with the proton at 5.3 ppm (1 H) is directly combined with the oxygen of the CQM unit and the methylene carbon with the proton at 2.6 ppm (2 H) is combined with dicyanomethylene of the CQM unit, as shown in the following structure:



It was concluded therefore that CQM copolymerizes with St and MeOSt in an alternating fashion as well as electron-accepting quinodimethane and quinone compounds[1-7] and CQM reacts at its exocyclic carbon and oxygen sites.

Terpolymerizations of the CQM–MAnh–St, CQM–PCA–St, and CQM–DDQ–St systems were carried out to give an estimation of the polymerizability as an acceptor monomer among CQM, MAnh, PCA, and DDQ. The terpolymerizations proceeded in a homogeneous state. The terpolymers of all systems were obtained as white powder. Table II summarizes the results of those terpolymerizations and Figure 7 shows their triangular composition diagrams, where all terpolymers of the three systems are considered as nearly alternating copolymers of CQM with St, CQM with St, and DDQ with St. It is thought that these terpolymers are always composed of about 50 mol % of the St monomer unit regardless of monomer feed ratios and that the sum of CQM and the second acceptor monomer (MAnh, PCA, or DDQ) is also about 50 mol %, though one acceptor monomer is predominantly incorporated into the terpolymers while another acceptor monomer is incorporated in only small amounts. Consequently, these results of the terpolymerizations plainly exhibit a relative polymerizability between pairs of acceptor monomers. The three terpolymerization system allowed us to say that CQM is

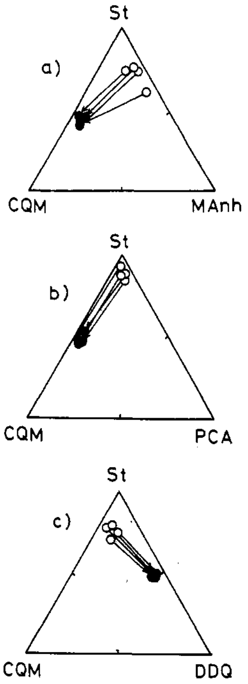


Figure 7. Triangular composition diagrams of the terpolymerization for (a) CQM–MAnh–St, (b) CQM–PCA–St, and (c) CQM–DDQ–St systems: (○) feed composition; (●) terpolymer composition. Arrows show change in composition from the feed to the terpolymer obtained.

Table III
Values[a] of Energy Difference (ΔE) between Quinonid Ground and Benzenoid Excited States, Localization Energy (L_β), Resonance Stabilization Energy (ΔE_{rs} and $\Delta E'_{rs}$), and Frontier Electron Density (fr)

	DDQ	PCA	CQM	QBS	TCNQ
$\Delta E, -\beta$	0.65	0.65	0.37	0.31	0.17
$L_\beta, -\beta$	2.32	2.33	o: 1.41 c: 2.00	1.41	1.06
ΔE_{rs},[b] $-(\Delta\beta)^2/\beta$	0.92	0.85	o: 0.87 c: 1.07	1.42	1.07
$\Delta H'_{rs}$,[c] $-(\Delta\beta)^2/\beta$	0.76	0.75	o: 0.78 c: 0.70	0.89	0.70
fr	0.35	0.39	o: 0.31 c: 0.47	0.49	0.41

[a] Calculated by using the Hückel parameters described by Coppinger and Bauer.[15] Since some Hückel parameters were not described in their literature, the values of Streitwieser[25] were employed: $\alpha + 0.5\beta$, $\alpha + 0.5\beta$, and $\alpha + 2.0\beta$ for the Coulomb integral of nitrogen, sulfur, and chlorine, respectively, and 1.85β, 0.37β, 1.10β, 0.93β, 0.4β, 0.9β, and 0.93β for the exchange integral of C≡N, C—Cl, C═N, S═O, N—S, C—N, and S—C, respectively. [b] Resonance stabilization energy due to π-conjugation between the polymeric radical with the St terminal unit and an acceptor monomer. [c] Resonance stabilization energy due to π-conjugation between the polymeric radical with an acceptor monomer terminal unit and St monomer.

much more reactive than MAnh for the CQM–MAnh–St system, CQM is much more reactive than PCA for the CQM–PCA–St system, and CQM is much less reactive than DDQ for the CQM–DDQ–St system. In addition, it was reported previously that PCA is much more reactive than MAnh for the terpolymerization of the MAnh–PCA–St system.[14] Therefore, it is certain that these four acceptor monomers can be arranged in the following order in relative reactivity: MAnh < PCA < CQM < DDQ. On the other hand, they are placed in a somewhat different order for their electron-accepting character: MAnh (1.33 eV) < CQM (2.36 eV) < PCA (2.48 eV) < DDQ (3.13 eV).

Previously, the terpolymerizations of the QBS–MAnh–St, QBS–PCA–St, QBS–TMCQ–St, and QBS–TCNQ–St systems were studied to obtain the following order of the polymerizability as acceptor monomers involved: MAnh < PCA < TMCQ < QBS < TCNQ.[7] The order of the polymerizability also did not always agree with that of the electron-accepting character of the same group of acceptor monomers: MAnh ≃ TMCQ < QBS < PCA < TCNQ. PCA was considered to be somewhat extraordinary, being not as reactive as can be expected from its electron-accepting character. The stability of a quinonoid compound may be estimated by the energy difference between its quinonoid ground and benzenoid excited states by means of the π-electron LCAO MO method.[15] Then it was pointed out that the extraordinarily low reactivity of PCA likely arises from its extra stability as a quinonoid compound due to the oxygen atoms at the 7 and 8 positions.

The electron-accepting order in both studies is in good agreement with the polymerizability order if PCA is excluded. However, it is not reasonable that only PCA is extraordinary among MAnh, CQM, PCA, and DDQ. DDQ also is a quinone with the oxygen atoms at the exocyclic 7 and 8 positions, like PCA. The energy difference (ΔE) between quinonoid ground and benzenoid excited states was calculated by means of π-electron LCAO MO method to be 0.65_β for both DDQ and PCA, implying that the extent of increase in the stability as a quinonoid compound is the same for both PCA and DDQ. However, since DDQ is very much stronger in electron-accepting character than PCA, the increase in reactivity of DDQ expected from its much stronger electron-accepting character was considered to be so much greater than that of PCA as to overcome the decrease of the reactivity due to the stability as quinonoid compound. Anyway we would like to mention that the reactivity of quinodimethane compounds as acceptor monomers is primarily dependent upon their electron-accepting character, even though there are some exceptions, such as PCA.

The reactivity of the electron-accepting quinodimethane and quinone compounds in their alternating copolymerization was estimated by means of the π-electron LCAO MO method in order to get some idea about a rate-determining state in the alternating copolymerizations. The following parameters have been proposed to be meaningful as a measure of reactvity in radical copolymerization: frontier electron density (fr),[16-18] localization energy (L_β),[19,20] and resonance stabilization energy (ΔE_{rs} and $\Delta E'_{rs}$)[21,22] due to π-conjugation between the polymeric radical with the St terminal unit and an acceptor monomer and between the polymeric radical with an acceptor monomer terminal unit and St monomer. The values of these parameters calculated for DDQ, PCA, CQM, QBS, and TCNQ are summarized in Table III. Two different values for the CQM are obtained with respect to its two different exocyclic atoms in Table III, suggesting that CQM reacts with a radical preferentially at the exocyclic carbon atom to yield a radical at its oxygen atom. The relative reactivities of acceptor monomer among DDQ, PCA, CQM QBS, and TCNQ on the basis of the parameters are placed in the following order: DDQ = PCA < CQM < QBS < TCNQ for ΔE and L_β, DDQ = PCA < TCNQ < CQM < QBS for fr and ΔE_{rs}, and TCNQ < DDQ ≃ PCA < CQM < QBS for $\Delta E'_{rs}$. None of the reactivity orders calculated is in agreement with the order of reactivity obtained from the experimental terpolymerizations.

In general, it is said in a conventional radical copolymerization that copolymerization reactivity is explained well in terms of L_β, ΔE_{rs} and $\Delta E'_{rs}$, indicating that the reactivity is determined mainly by the resonance stabilization (general reactivity) of a resulting polymeric radical in cross propagation of the copolymerization. In other words, a rate-determining transition state in a conventional copolymerization should be much closer to a reaction product than a reacting species. This discrepancy in the reactivity order between the observed and calculated allows us to mention that a rate-determining transition state in an alternating copolymerization is different from that in a conventional radical copolymerization. In previous studies of alternating terpolymerizations among donor–donor–common acceptor monomers[23] and among acceptor–acceptor–common donor monomers,[24] it was pointed out that monomer reactivity is controlled much more by the polar effect of the monomer and much less by the general reactivity (resonance stabilization) effect than the corresponding one of a conventional random radical copolymerization and furthermore that the polar effect is reasonably related to an interaction somewhat equivalent to Coulomb force type of an interaction taking place between donor and acceptor monomers within the dative bond structure of the charge-transfer complex.[24] It may be concluded therefore in an alternating copolymerization that a rate-determining transition state is a state close to the reacting species in which a new covalent bond is not yet formed between a polymeric radical and a coming monomer, and a Coulomb type-like polar interaction between reacting species plays an important role in the rate determination even though its mechanism has not been demonstrated in a concrete form yet.

Anyway, when the extraordinary reactivity of PCA due to its high stabilization as the quinonoid form is taken into account, the relative reactivity of the acceptor monomers obtained in the terpolymerization experiments might be regarded as agreeing with their electron-accepting properties. It was concluded therefore that the reactivity in alternating copolymerization is controlled primarily by the polarity of the acceptor monomer. In the case of PCA, the general reactivity (resonance stabilization) of a monomer should be taken into consideration in alternating copolymerization, but the extent of its contribution is presumed to be much less than that in a conventional random radical copolymerization.

Registry No. CQM, 83928-83-0; MAnh, 108-31-6; PCA, 118-75-2; DDQ, 84-58-2; (CQM)(St) (copolymer), 107455-30-1; (CQM)(MeOSt) (copolymer), 107455-31-2; (CQM)(MAnh)(St) (copolymer), 107455-32-3; (CQM)(PCA)(St) (copolymer), 107455-33-4; (CQM)(DDQ)(St) (copolymer), 107455-34-5; St, 100-42-5; MeOSt, 637-69-4.

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Cationic Polymerization of Nitrogen-Containing Electron-Rich Vinyl Monomers by Electrophilic Olefins and Their Cyclobutane Cycloadducts

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ABSTRACT: The major pathways for the reactions of very electron-rich N-containing olefins with several electrophilic olefins were studied. *N*-Ethyl-3-vinylcarbazole (**1**), *N*-vinylcarbazole (**2**), and *p*-(dimethylamino)styrene (**3**) undergo kinetic cyclobutane formation with an electrophilic olefin without a leaving group, methyl β,β-dicyanoacrylate (**4**), and with one with a weak β-leaving group, tetracyanoethylene (**5**). The third electrophilic olefin, β,β-dicyanovinyl chloride (**6**), has a strong β-leaving group and readily initiates the cationic polymerization of **1** and **2** and oligomerization of **3**. If an excess of donor olefin is used, **4**, **5**, and **6** all initiate cationic homopolymerization of **1** and **2**, while **3** only leads to oligomers, as it does with conventional Brønsted initiators. Cationic initiation by their own cyclobutane adducts is observed for the very electron-rich monomers **1** and **2**. Postcyanovinylation of the formed polymers by the electrophilic olefins occurs. We can conclude that incorporation of a β-leaving group enhances the initiating ability of electrophilic olefins and that *N*-carbazyl and *N*-ethyl-3-carbazyl are overall the most effective donor substituents favoring cationic homopolymerization.

Introduction

In earlier work we showed that electrophilic olefins could be used to initiate cationic homopolymerization of electron-rich vinyl monomers.[1,2] Electrophilic tri- and tetrasubstituted olefins initiated cationic homopolymerization of very electron-rich vinyl monomers, in particular *N*-vinylcarbazole, through the intermediacy of zwitterionic tetramethylene intermediates.

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