Thermal stability of the aromatic poly(benzimidazoles) (**9**) was conducted by thermogravimetry (TG). The samples were cured for 0.5 h at 300 °C in nitrogen and subsequently subjected to TG, with representative curves shown in Figure 1. The degradation temperature for 10% weight loss was 465 °C in air and 540 °C in nitrogen, respectively. TG data are listed in Table VI.

In summary, our studies indicate that poly(benzimidazoles) with high molecular weights are readily prepared by direct polycondensation of tetramine **4** with various activated dicarboxylic acids in PPMA as both condensing agent and solvent. This method is advantageous to the formation of poly(benzimidazoles) because of the rapidity and simplicity of the reaction and milder reaction conditions compared to conventional methods.

Acknowledgment. We are indebted to Sadao Kato for elemental analyses.

Registry No. 1, 95-54-5; **3a**, 716-79-0; **3b**, 1019-85-8; **3c**, 729-13-5; **3d**, 2620-81-7; **3e**, 6504-13-8; **3f**, 6528-83-2; **3g**, 3574-96-7; **3h**, 5851-44-5; **3i**, 5851-46-7; **3j**, 5851-48-9; **3k**, 5851-49-0; **3l**, 36947-70-3; 4, 7411-49-6; **7a** (copolymer), 99166-53-7; **7a** (SRU), 70502-60-2; **7b** (copolymer), 99166-54-8; **7b** (SRU), 26917-31-7; **7c** (copolymer), 99166-55-9; **7c** (SRU), 50867-43-1; **7d** (copolymer), 99166-56-0; **7d** (SRU), 25035-65-8; **7e** (copolymer), 99212-99-4; **7e** (SRU), 99166-49-1; **7f** (copolymer), 99166-57-1; **7f** (SRU), 99166-50-4; **8a**, 15179-41-6; **8b**, 29914-81-6; **8c**, 18509-48-3; **9a** (copolymer), 99166-58-2; **9a** (SRU), 32109-44-7; **9b** (copolymer), 99166-59-3; **9b** (SRU), 99166-51-5; **9c** (copolymer), 99166-60-6; **9c** (SRU), 99166-52-6; *p*-$MeOC_6H_4CO_2H$, 100-09-4; *o*-$HOC_6H_4CO_2H$, 69-72-7; $C_6H_5CO_2H$, 65-85-0; *p*-$ClC_6H_4CO_2H$, 74-11-3; *p*-$NO_2C_6H_4CO_2H$, 62-23-7; *m*-$CH_3C_6H_4CO_2H$, 99-04-7; *o*-$ClC_6H_4CO_2H$, 118-91-2; $CH_3(CH_2)_3CO_2H$, 109-52-4; $CH_3(CH_2)_4CO_2H$, 142-62-1; $CH_3(CH_2)_5CO_2H$, 111-14-8; $CH_3(CH_2)_6CO_2H$, 124-07-2; P_2O_5, 1314-56-3; CH_3SO_3H, 75-75-2; cyclohexanecarboxylic acid, 98-89-5.

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Polymerization Behavior of 7,8-Bis(butoxycarbonyl)-7,8-dicyanoquinodimethane

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ABSTRACT: 7,8-Bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) was found to exhibit an intermediate electron-accepting character between tetracyanoquinodimethane (TCNQ) and tetrakis(alkoxycarbonyl)quinodimethane (TACQ), as expected from their chemical structures. However, BCQ copolymerizes with styrene (St) in a random fashion ($r_1(\mathrm{BCQ}) = 0.9 \pm 0.3$ and $r_2 = 0.02 \pm 0.02$ at 60 °C) and with *p*-methoxystyrene as the stronger donor monomer in an almost alternating fashion, whereas the two latter monomers copolymerize with St alternatingly and spontaneously. BCQ also was found to be homopolymerizable with free radical and anionic initiators, even with very weak basic solvents such as acetone, acetonitrile, etc. The polymerization with butyllithium was found to be of living-like type to afford polymers with molecular weight >2 000 000. The polymerization with triethylamine was studied. Some physical properties of polyBCQ were measured, such as the solution viscosity–molecular weight relationship, the solubility for solvents, the glass transition temperature, UV light sensitivity, and gas permeability.

Previously preparation and polymerization of 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane (ACQ) with ethoxy (ECQ) and methoxy groups (MCQ) as the alkoxy group had been briefly reported independently by Hall et al.[2] and some of us[1] in 1982. On the basis of the chemical structure, ACQ was expected to exhibit just an intermediate nature in physical and chemical properties between 7,7,8,8-tetracyanoquinodimethane (TCNQ)[3,4] and 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes with methoxy (TMCQ)[3,5] and ethoxy (TECQ)[6] groups as the alkoxy group. On the other hand, ACQ also was expected to have properties different from those of TCNQ, TMCQ, and TECQ, compounds with all the same substituents at the 7 and 8 positions, because ACQ has two different substituents at the 7 and 8 positions.

In this work we studied the polymerization behavior of 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) as a representative of ACQ and also some physical properties of its high polymer because BCQ was found to be prepared with more ease than other ACQ monomers and because its polymer is more soluble in many conventional organic solvents.

Experimental Section

Preparation of BCQ. Sodium cyanide (22.40 g, 0.457 mol) was dissolved in 36 mL of water, and then 54 mL of ethanol and 74 mL of 1,4-dioxane were added. Into the solution was added 20.0 g of *p*-xylylene dichloride, and the mixture was stirred at room temperature for 2 days. Then the reaction mixture was poured into about 600 mL of water to give a white crystalline material, which was washed repeatedly with water and dried under reduced pressure. *p*-Xylylene dicyanide (17.2 g) melting at 97–98 °C (lit.[7] mp 98 °C) was obtained in 98% yield.

Commercial sodium hydride (60% in oil) (7.8 g) was washed twice with hexane and dried reduced pressure to obtain 6.5 g (0.27

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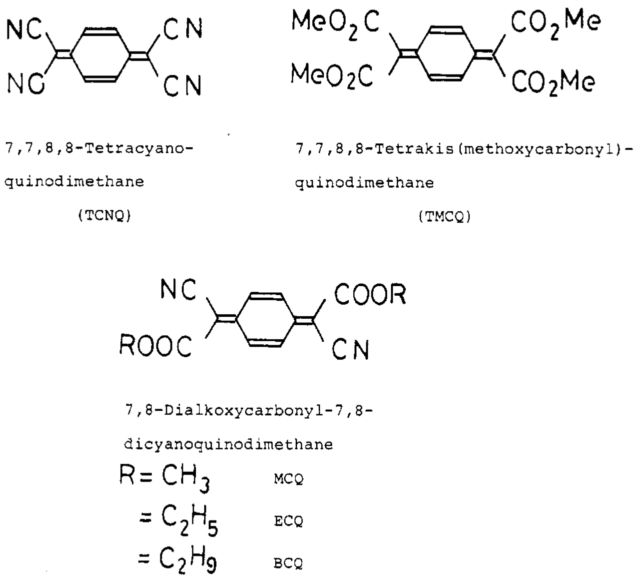
Chart I



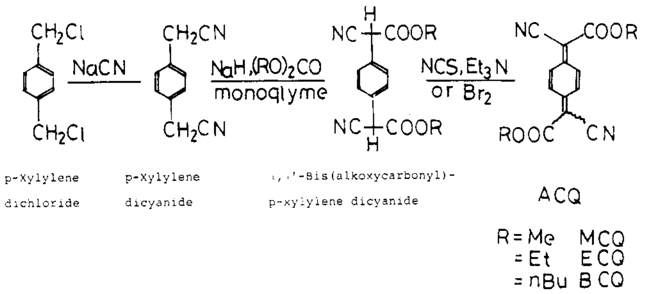
7,7,8,8-Tetracyanoquinodimethane (TCNQ)

7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane (TMCQ)

7,8-Dialkoxycarbonyl-7,8-dicyanoquinodimethane

R = CH_3 MCQ
= C_2H_5 ECQ
= C_2H_9 BCQ

Scheme I
Preparation of 7,8-Bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane (ACQ)



mol) of sodium hydride in the powder state, to which 20 mL of 1,2-dimethoxyethane was added under nitrogen. Into this mixture were added dropwise 9.00 g (0.058 mol) of *p*-xylylene dicyanide and 22.25 g (0.128 mol) of butyl carbonate in 80 mL of 1,2-dimethoxyethane, and the resulting mixture was stirred at room temperature for 1 day. The reaction mixture was placed under reduced pressure to remove the solvent. To the residue obtained was introduced sufficient acetic acid to acidify the mixture, and an additional 100 mL of water was added. The mixture was extracted twice with 100 mL of chloroform. The combined extracts were washed well with water, dried over anhydrous sodium sulfate, and placed under reduced pressure to remove chloroform. The residue obtained as an oil was recrystallized from methanol to give 15.7 g of α,α'-bis(butoxycarbonyl)-α,α'-dicyano-*p*-xylene in the powder state, melting at 69.5–72.0 °C: 76% yield; IR (KBr) 1750, 2250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 6 H), 1.52 (m, 8 H), 4.20 (t, 4 H), 4.75 (s, 2 H), 7.54 (s, 4 H).

α,α'-Bis(butoxycarbonyl)-α,α'-dicyano-*p*-xylene (1.0 g, 0.0028 mol) was dissolved in 20 mL of acetonitrile under nitrogen and the solution was cooled to 0 °C. *N*-Chlorosuccinimide (0.96 g (0.0054 mol) was added to the solution kept at 0 °C, the solution was stirred for 10 min, and then 0.36 mL (0.0025 mol) of triethylamine was added. After a few minutes, yellow crystals precipitated and were filtered out. The crystalline product obtained was washed well with cold isopropyl ether and then recrystallized from isopropyl ether mixed with a small amount of acetic acid to obtain 0.42 g of 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane as yellow needles: 42% yield; IR (KBr) 2220, 1710, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 6 H), 1.51 (m, 8 H), 4.32 (t, 4 H), 7.45 (dd, 2 H), 8.45 (dd, 2 H). Anal. Calcd for $C_{20}H_{22}O_4N_2$: N, 6.27; C, 67.77; N, 7.90; O, 18.06. Found: H, 6.21; C, 67.70; N, 7.88.

Polymerization Procedure. In the case of the free radical polymerization, given amounts of BCQ, a comonomer if copolymerization was carried out, a radical initiator such as azobis(isobutyronitrile) (AIBN), and a solvent containing a very small amount of acetic acid, e.g., 10 mL of chloroform with two drops of acetic acid, were placed in an ampule, which was degassed well by the freeze–thaw method and sealed. It was set in a bath thermostated at 60 °C for the time of polymerization and unsealed. The reaction mixture was poured into an excess mixture of isopropyl ether and hexane (1:1 by volume) to deposit a polymeric product that was washed repeatedly with isopropyl ether. Then the product was dissolved again in a small amount of methylene chloride, and the resulting solution was poured into an excess mixture of isopropyl ether and hexane to deposit a polymeric product for purification. The product was dried under reduced pressure until a constant weight.

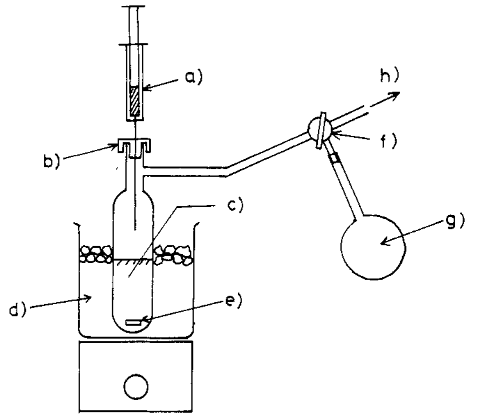


Figure 1. Outline of ampule used for the polymerization: (a) syringe (1 mL) containing the initiator solution; (b) rubber septum; (c) monomer solution; (d) ice–water bath; (e) magnetic stirrer; (f) three-way cock; (g) argon reservoir; (h) vacuum pump.

In the case of the anionic polymerization, an ampule with a lateral tubing and a septum rubber stopper at the top was used as shown in Figure 1. Given amounts of BCQ and the solvent were placed in the ampule, the apparatus was degassed by the freeze–thaw method, and argon gas was introduced. Then the ampule was set in a thermostated bath, and after a while a given amount of an anionic initiator in the solvent was injected by means of a syringe. After the time of polymerization, the reaction mixture was poured into excess isopropyl ether to deposit the polymeric product, which was dissolved again in a small amount of methylene chloride, and the resulting solution was poured into excess isopropyl ether for purification. The polymeric product obtained was washed repeatedly with isopropyl ether and dried until a constant weight under reduced pressure. When the yellow color of the monomeric BCQ had faded, i.e., when the polymerization was complete, an aliquot of the reaction mixture was diluted with tetrahydrofuran and the solution was subjected to gel permeation chromatography to measure the molecular weight of the polymer formed. The residual reaction mixture was poured into an excess of isopropyl ether to deposit a polymeric product that was purified by the dissolution–precipitation method. When BCQ was dissolved in an even weakly basic solvent, polymerization took place immediately and the yellow color of the monomeric BCQ faded very soon.

In the case of cationic polymerization, the procedure was carried out similarly to the above-mentioned case of anionic polymerization.

Results and Discussion

Electron-Accepting Character of BCQ. The electron-accepting character of BCQ was measured by means of the charge-transfer complex method by using an empirical relationship[8] between the electron affinities of the acceptors and the energy of intermolecular charge-transfer absorption (ν_{CT}) for the corresponding complexes with a given donor such as hexamethylbenzene (HMB). The solvent used was benzene. *p*-Chloranil (PCA) was employed as a reference acceptor compound, which was reported to have an electron affinity of 2.48 eV.[9] Table I summarizes the results of the intermolecular charge-

Table I
Electron-Accepting Character of ACQ, Including Other Related Quinodimethanes, MAnh, and PCA

	MAnh	TMCQ	TECQ	ACQ Me	ACQ Et	ACQ Bu	PCA	TCNQ
V[a]		−0.83		−0.65				−0.20
λ_{max}^{CT}(HMB)								
nm		<440–550[b]		500	497	496	516	594
eV				2.16[c]	2.10[c]	2.07[c]	2.48[d]	2.87[d]
λ_{max}^{CT}(DMA)								
nm	422		457					
eV	1.33[d]		2.27[e]					

[a] By cyclovoltammetry. In CH_3CN Ag/As$^+$. [b] λ_{max} of CT band overlapped with absorption of TMCQ and TECQ. [c] Calculated by using the equation $h\nu_{CT}$ = IP − EA + C and 2.48 eV for *p*-chloranil.[9] [d] Cited from literature.[9] [e] Calculated by using the equation $h\nu_{CT}$ = IP − EA + C and 1.33 eV for MAnh.[9]

Table II
Homopolymerizations[a] of BCQ Initiated by Various Catalysts at 0 °C

run no.	catalyst [I]	[BCQ]/[I]	solvent, mL	time, h	$\bar{M}_n/10^4$ [e]
1	Et_3N	103	$CHCl_3$, 5	1.0	9.5
2	Et_3N	103	$(CH_2Cl)_2$, 5	1.0	35.0
3	Et_3N	100	toluene, 10	1.0	21.5
4	Proton Sponge[b]	102	$CHCl_3$, 5	1.0	10.6
5	pyrrolidine	108	$CHCl_3$, 5	1.25	5.6
6	pyridine	93	$CHCl_3$, 5	0.5	no polym
7	Ph_3P	101	$CHCl_3$, 5	1.0	no polym
8	TPP-Al[c]	59	CH_2Cl_2, 5	56	10.1
9	BuLi	106	toluene, 10	0.7	103.0
10	EtMgBr	6	toluene, 10	0.5	1.9
11	AIBN[d]	8	$CHCl_3$, 5	5.5	4.4
12	$BF_3{\cdot}Et_2O$	101	CH_2Cl_2, 5	1.0	no polym

[a] [BCQ] = 28 mM for run no. 1, 2, 4–8, 11, and 12 and [BCQ] = 14 mM for run no. 3, 9, and 10. [b] Proton Sponge: 1,8-bis(dimethylamino)naphthalene. [c] TPP–Al: 5,10,15,20-tetraphenylporphine-Et_2AlCl. Polymerization temperature was room temperature. [d] One drop of AcOH was added. [e] Determined by GPC. THF was the eluent.

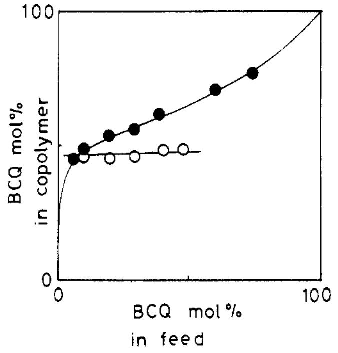


Figure 2. Copolymerization composition diagrams of BCQ with styrene (●) and *p*-methoxystyrene (○).

transfer absorption (λ_{max}^{CT}) and electron affinity of BCQ including TMCQ, TECQ, MCQ, ECQ, TCNQ, and PCA. It is apparent that ACQ is intermediate in electron-accepting character between TMCQ and TCNQ, as expected from the chemical structures.

Polymerization of BCQ with Various Initiators. Table II summarizes the results of the polymerizations of BCQ with various anionic, cationic, and free radical initiators. It is obvious that BCQ is homopolymerizable with anionic and free radical initiators but not polymerizable with cationic ones. On the other hand, TCNQ[3,4] and TECQ[6] were reported to be not homopolymerizable with any initiators, though they react as powerful electron-accepting monomers.

BCQ, which is just intermediate in electron-accepting character between TCNQ and TECQ, carries two different kinds of substituents such as cyano and butoxycarbonyl groups at the 7 and 8 positions, whereas TCNQ and TECQ have the same kind of substituents at the 7 and 8 positions. This difference for BCQ in substitution at the 7 and 8 positions is considered to be responsible for the high homopolymerizability.

Free Radical Copolymerization Behavior of BCQ. Table III summarizes the results of the copolymerizations of BCQ with styrene (St) and *p*-methoxystyrene (MeOSt), and Figure 2 shows their copolymerization composition diagrams. The copolymerization of BCQ with St was found to be really in random fashion because of the shape of the copolymerization composition curve and the fine

Table III
Copolymerizations[a] of BCQ with Styrene and Methoxystyrene in Chloroform at 60 °C

run no.	monom feed, mg: BCQ	monom feed, mg: comonom	amt of BCQ, mol %	time, min	yield, mg	conv %	anal. % H	anal. % C	anal. % N	copolym comp, mol % BCQ	$\bar{M}_n/10^4$ [b]
					Styrene						
1	68.7	319.3	5.9	22	12.0	3.1	6.04	71.10	5.81	45.0	45
2	50.2	131.9	10.1	20	13.4	7.4	6.26	73.25	6.05	49.0	20
3	86.1	106.0	19.3	32	23.9	12.5	6.55	72.17	6.31	53.8	23
4	121.1	85.8	29.4	25	22.1	10.7	6.34	70.88	6.42	56.1	29
5	121.1	57.4	38.4	25	18.8	10.5	6.26	71.94	6.68	61.7	36
6	201.4	39.7	59.9	30	48.2	20.0	6.67	70.19	7.05	70.9	25
7	202.5	20.9	74.0	40	27.3	12.2	6.60	69.64	7.26	77.0	46
					p-Methoxystyrene						
8	50.1	165.9	10.2	10	16.4	7.6	6.91	69.11	5.44	45.6	
9	85.0	126.4	20.3	13	18.7	8.8	6.69	70.80	5.40	45.0	6.4
10	112.6	101.5	29.6	10	7.5	6.0	6.00	70.85	5.46	45.9	7.4
11	81.1	44.9	40.6	10	8.4	8.4	6.34	69.17	5.62	48.3	4.7
12	122.0	50.1	48.0	20	26.1	15.2	6.48	69.65	5.63	48.4	5.2

[a] 10 mL of $CHCl_3$ containing 2 drops of acetic acid. (2 mg AIBN). [b] Determined by GPC. THF was the eluent.

Table IV
Spontaneous Homopolymerization[a] of BCQ in Various Solvents

solvent	$\Delta\nu_{OD}$[b]	$\bar{M}_n/10^4$[c]	$\bar{M}_w/\bar{M}_n$[c]
acetonitrile	49	410	1.72
acetone	64	455	1.94
THF	93	86	1.80
DMF	107	340	1.89
Me_2SO	141	360	1.76

[a] 5.5 mg BCQ; 1 mL of solvent; room temperature. [b] OD linkage frequency shift of MeOD-base hydrogen bonding.[12] [c] Determined by GPC with THF as eluent.

straignt lines for its Kelen–Tüdös and Fineman–Ross plots. The monomer reactivity ratios were obtained as $r_1 = 0.9 \pm 0.3$ (BCQ) and r_2 and 0.02 ± 0.02 (St) at 60 °C. The copolymerization of BCQ with MeOSt probably is in an alternating fashion, its Kelen–Tüdös plot giving no straight line. Only when the stronger donor monomer is used as the comonomer can BCQ perhaps copolymerize in an alternating fashion. On the other hand, TCNQ and TMCQ were reported to copolymerize with St alternatingly and spontaneously even though TMCQ is a weaker acceptor monomer than BCQ. This random behavior of the copolymerization of BCQ with St was thought to be closely associated with the homopolymerizability of BCQ, similarly being attributable to the lack of symmetry of BCQ in its substitution at the 7 and 8 positions. Monomer reactivity ratios of the copolymerization of BCQ with St allowed us to calculate the monomer reactivity parameters of BCQ such as Alfrey and Price's Q and e values to be 9.9 and +1.20, respectively. When these values were compared with values of maleic anhydride (Manh) ($Q = 0.23$, $e = 2.25$)[10] and ethyl α-cyanoacrylate ($Q = 2.14$, $e = 0.78$),[10] the electron affinity values do not coincide with e values between BCQ and Manh, BCQ having the higher electron affinity but the lower e value. On the other hand, BCQ seems to be in good agreement with ethyl α-cyanoacrylate, carrying a similar substitution situation at the terminal carbons. Presumedly the homopolymerizability of these monomers influences a determination of their monomer reactivity. Anyhow, it is obvious that BCQ, with two different substituents at the 7 and 8 positions, interestingly exhibits a quite different copolymerization reactivity from that of quinodimethane compounds with all the same substituents at the 7 and 8 positions such as TCNQ and TMCQ.

Polymerization of BCQ in Basic Solvents. When BCQ was dissolved in some conventional basic solvents, the solution changed rapidly from the yellow color to colorless, indicating a rapid conversion of the BCQ monomer to its polymer. The resulting colorless solution was added to excess tetrahydrofuran, and its tetrahydrofuran solution was subjected to gel permeation chromatography to determine the molecular weight of the product. Table IV summarizes the results of the polymerization of BCQ in five kinds of conventional basic solvents. As shown in Table II, most amine compounds except pyridine are capable of initiating the polymerization of BCQ in chloroform or toluene. Basicity of the basic compounds was reported[11] to be expressed in terms of the strength of the hydrogen bond formed between a proton–donating alcohol such as methanol-*d* and basic compounds. Pyridine is weaker in basicity ($\nu_{OH} = 168$ cm^{-1}) than triethylamine ($\nu_{OH} = 238$ cm^{-1}),[12] and pyridine is not capable of initiating the polymerization, but triethylamine is. Thus basicity apparently relates to the capability of initiating the polymerization of BCQ. However, even solvents such as acetonitrile and acetone, much weaker in basicity than pyridine, are capable of initiating the polymerization of BCQ, suggesting that some factors other than basicity also exert an influence on the initiation of the anionic polymerization of BCQ. The solvents for the polymerization of BCQ are limited to nonbasic solvents such as benzene, toluene, chloroform, and dichloromethane.

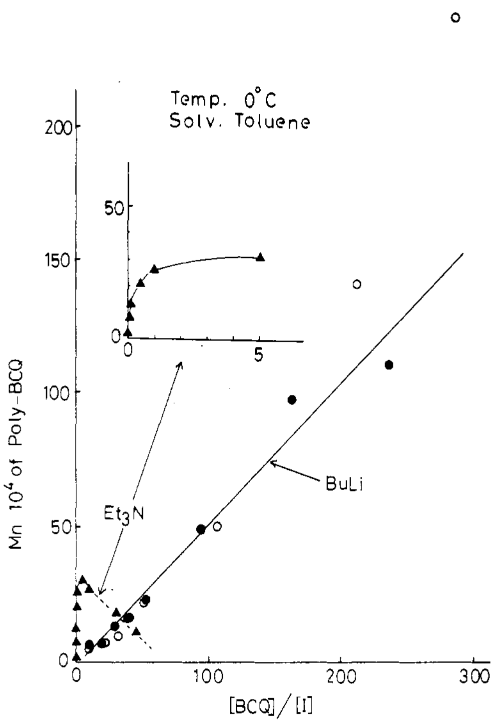


Figure 3. Relationships of the molecular weight of the polymer vs. the ratio of the concentration of monomer to initiator in polymerizations of BCQ with butyllithium and triethylamine: temperature of polymerization, 0 °C; solvent, toluene; monomer concentration, 10 mM; solution volume, 10 mL. (○) corresponds to run no. 1–8 and (●) to run no. 9–16 in Table V.

Polymerizations with Butyllithium and Triethylamine. A given amount (ca. 10 mL) of BCQ in toluene (with a concentration of 9 mM) was placed in the ampule of Figure 1. It was completely degassed by the freeze–thaw method, and argon gas was introduced. Into it was injected a fixed amount (0.2–0.01 mL) of butyllithium in toluene with a concentration of 0.04 mM or 0.8–0.3 mL of triethylamine in toluene with concentrations of 0.74 and 0.14 M by using a syringe, the volume of the initiator solution conceivably being small compared with the volume of the monomer solution so as to disregard a possible change in the monomer concentration. The ampule was set in an ice–water bath without stirring. After the yellow color of BCQ monomer disappeared (conceivably the polymerization being complete), the reaction mixture was poured into excess tetrahydrofuran, and the resulting solution was subjected to gel permeation chromatography to measure the molecular weight of the polymer produced. The molecular weight and the amount of the polymer obtained allowed us to calculate the number of moles of the polymer produced, which was divided by the mole number of the initiator used to obtain an initiator efficiency. Polymerization results with various amounts of butyllithium and triethylamine as initiator at an almost fixed concentration of BCQ as the monomer in toluene are summarized in Table V, and the relationships of the ratio of the concentration of the monomer to the initiator vs. the molecular weight of the polymers are shown in Figure 3.

In all experimental runs of butyllithium except run 8, the yellow color of the reaction systems disappeared within the time of polymerization of 0.5 h, suggesting that a

Table V
Homopolymerization[a] of BCQ with Butyllithium and Triethylamine in Toluene at 0 °C

run no.	[BCQ]/[initiator]	polym time, min	conv %	$\bar{M}_n/10^4$ [b]	efficiency (f)	$\bar{M}_w/\bar{M}_n$
			BuLi as Initiator			
1	10.0	15	100	5.0	0.71	
2	20.4	20	100	6.8	0.106	1.47
3	30.8	20	100	9.1	0.120	
4	40.7	20	100	16	0.090	
5	50.7	20	100	22	0.082	
6	106.0	30		50	0.075	
7	210.8	30	100	140	0.053	
8	285.5	60	(28.8)[c]	240	(0.012)	
9	10.1	10	100	5.2	0.069	
10	19.6	15	100	6.4	0.109	1.46
11	28.7	20	100	13	0.078	
12	39.6	20	100	16	0.088	
13	51.9	20	100	23	0.080	
14	94.1	30	100	49	0.068	
15	161.9	30	100	97	0.059	
16	235.9	30	100	110	0.076	
			Et_3N as Initiator			
17	0.012	30	100	1.95	0.0218	
18	0.050	30	100	7.1	0.0248	
19	0.100	30	100	12.5	0.0284	
20	0.494	30	100	20.5	0.0854	1.16
21	0.976	30	100	26.0	0.133	
22	5.04	60	100	30.0	0.595	
23	9.95	60	(86.6)[c]	26.8	(1.14)	
24	29.85	60	(40.3)[c]	17.4	(2.45)	
25	45.10	60	(21.5)[c]	10.6	(3.23)	
26	70.60	60	(11.4)[c]	4.3	(6.63)	

[a] [BCQ] = ca. 9 mM; conversion = 100%; 10 mL toluene. [b] Determined by GPC (standard polySt). [c] Yellow color remained within the time of polymerization. The polymer was obtained by precipitation and washing in nonsolvent.

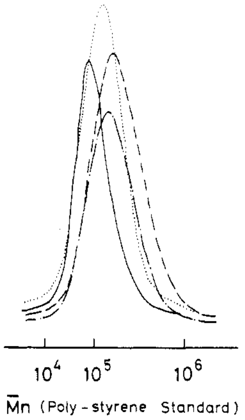


Figure 4. Gel permeation chromatogram of polyBCQs with additional monomer additions: Initiator, butyllithium; temperature of polymerization, 0 °C; solvent, toluene, concentration of the monomer solution, 8.13 mM; volume of the monomer solution at each addition, 7 mL. (1) The first polymerization at [BCQ]/[BuLi] = 21. (—) molecular weight ($\bar{M}_n$) of the polymer obtained was 9.1 × 10^4 and $\bar{M}_w/\bar{M}_n$ was 1.59. (2) After the first monomer addition. (···) $\bar{M}_n$ of the polymer obtained was 14.0 × 10^4 and $\bar{M}_w/\bar{M}_n$ was 1.76. (3) After the second addition. (-·-) $\bar{M}_n$ of the polymer obtained was 18.0 × 10^4 and $\bar{M}_w/\bar{M}_n$ was 1.79. (4) After the third addition. (---) $\bar{M}_n$ of the polymer obtained was 20.0 × 10^4 and $\bar{M}_w/\bar{M}_n$ was 1.83.

compelte conversion is reached rapidly. When a very small volume of the butyllithium solution was used, especially for experiments beyond the ratios of the concentration of the monomer to the initiator of 100, the polymerization was found to become slow and the reproducibility of the experiments to become poor. It is likely that the ratio of the concentration of the monomer to the initiator is linearly related to the molecular weight of the polymer produced. Initiator efficiencies of 0.1–0.05 were found; the low values and their scatter probably arise from an unrefined polymerization procedure and the fact that the experiments were not carried out in a vacuum system.

Next, the polymerization with additional monomer additions was carried out. BCQ (8.13 mmol) in 7 mL of toluene was polymerized with 0.39 mmol of butyllithium, and after the yellow color had disappeared, an aliquot of the polymerization mixture was taken out of the apparatus to determine the molecular weight of the polymer by gel permeation chromatography. Into the residual colorless polymerization mixture was added an additional 8.13 mmol of BCQ in 7 mL of toluene by means of a syringe. After the yellow color disappeared, the same procedure was carried out. On the whole, additional monomer was added three times. The experimental result is summarized in Figure 4, which shows apparently that the polymers, after all the monomer additions, exhibit one fairly sharp peak in their gel permeation chromatography, even though their peak widths become a little bit broader with each monomer addition, and that their peak positions move to the higher molecular weight side with each monomer addition, indicating that the polymeric species produced after the monomer has completely polymerized is still able to react with monomer molecules of the addition monomer to grow to a polymeric species with a higher molecular weight. It may be mentioned from these two results that the polymerization of BCQ with butyllithium is a living-like type.

In addition, the polymerization with triethylamine was studied because triethylamine was found to give a polymer with high molecular weight, as shown in table II. In the concentrated range of triethylamine, i.e., for BCQ: triethylamine ratios <5, it was found that the polymerization reaches completion within 0.5 h and the molecular weight of the polymers obtained increases with a decrease in the concentration of triethylamine in the monomer feed, as expected. However, in the more dilute range of triethylamine, i.e., for monomer:initiator ratios >6, the polymerization cannot be completed within an hour and the polymer obtained decreased in molecular weight with a decrease of the triethylamine concentration in the mono-

Table VI
Solubility of PolyACQ

polyACQ	soluble	swell	insoluble
polyBCQ, polyECQ	benzene, acetone, THF, $CHCl_3$, Me_2SO, DMF		MeOH, hexane, isopropyl ether (IPE)
polyMCQ	conc H_2SO_4	Me_2SO, DMF	benzene, acetone, THF, $CHCl_3$, MeOH, hexane, IPE

mer feed. In spite of the low concentration of triethylamine, the polymer with the lower molecular weight is produced, contrary to the general behavior of a living type of anionic polymerization. The calculated values of the initiator efficiency were found to increase extensively with the ratio of monomer to initiator. At the moment we could not give any mechanism for the polymerization with triethylamine, especially the decrease in the molecular weight of the polymer with a decrease in initiator concentration in the monomer feed.

Instead of triethylamine, pyrrolidine was employed as an initiator for studying the mechanism of initiation because in the experimental condition of high initiator concentration (i.e., [BCQ]/[I] ca. 10^{-3}) triethylamine gave a polymer of high molecular weight on the order of 10^4 while pyrrolidine afforded the formation of the 1:1 adduct. Into 10 g (140 mmol) of pyrrolidine in 20 mL of chloroform was dropwise added a solution of 51 mg (0.14 mmol) of BCQ in 3 mL of chloroform at room temperature for 15 min. The system changed from yellow to pink. The reaction mixture was placed under reduced pressure to remove chloroform and excess pyrrolidine, and the residual viscous oil was treated in elution chromatography using a silica gel column and chloroform as the eluent to give 48 mg of a pale pink viscous oil: IR (neat) 2260, 1750, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) as shown in Figure 5 with assignment of the peaks. It is obvious that the product is the 1:1 adduct. Therefore, it is conceivable that an electron-transfer reaction takes place between pyrrolidine and BCQ to give a zwitterion with pyrrolidinium ion and α-cyano-α-(butoxycarbonyl)benzyl anion as terminals. The latter anion is considered to be able to add the BCQ monomer. When excess pyrrolidone exists, it is conceivable that a number of the zwitterions could be formed, which would be readily subjected to a proton-transfer reaction with each other prior to the monomer addition reaction to give the 1:1 adduct. In the case of triethylamine, similar reactions were considered to take place to form a zwitterion with triethylammonium ion and α-cyano-α-(butoxycarbonyl)benzyl anion. Since this quaternary ammonium ion directly attaches no hydrogen ready to undergo a proton-transfer reaction, it was thought that the zwitterion would be able to add the BCQ monomer in preference to a termination reaction corresponding to the proton-transfer reaction in the reaction with pyrrolidine to give a polymer with molecular weight of ca. 10^4. Moreover, the electron-transfer reaction of triethylamine to BCQ as the first step of an initiator reaction was assumed to be able to take place only in the presence of a number of triethylamine molecules because of the very low initator effeiciency and the slow polymerization rate at the low initiator concentration.

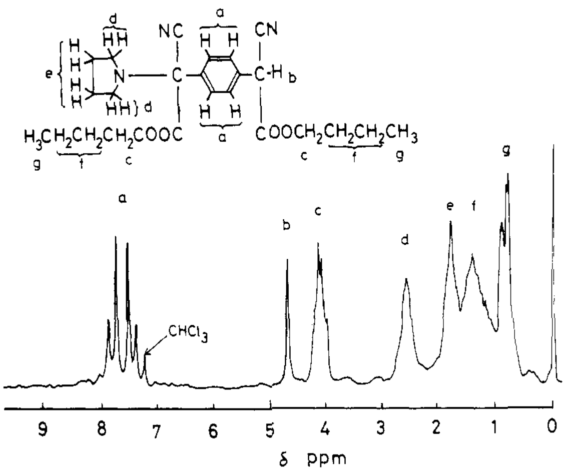


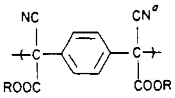
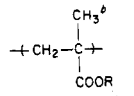
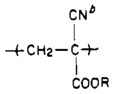
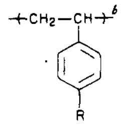
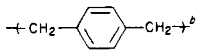
Figure 5. ^1H NMR spectrum of the 1:1 adduct of BCQ and pyrrolidine. Reaction condition: 0.14 mmol of BCQ and 140 mmol of pyrrolidine in chloroform at room temperature for 15 min.

It can be concluded that BCQ is homopolymerizable with free radical and anionic initiators and that polymerization with butyllithium is of a living-like type able to afford a polymer of molecular weight of several millions.

Some Physical Properties of PolyBCQ. The Mark–Houwink equation for polyBCQ in tetrahydrofuran was obtained. The polymer obtained with butyllithium was fractionated by means of fractional gel permeation chromatography to give four fractions for which the limiting viscosity number and the weight-average molecular weight were obtained from solution viscosity and light scattering measurements, respectively. The results are shown in Figure 6, where the α-index was found to be 0.63, indicating that this polymer chain is fairly flexible in solution even though it was expected to have a stiff nature from its chemical structure, i.e., carrying phenylene and tetrasubstituted ethylene groups in the backbone chain.

The solubility of polyBCQ, including polyMCQ and polyECQ, is summarized in Table VI. The glass transition temperature for polyBCQ, including polyMCQ and polyECQ, was measured by differential scanning calorimetery (DuPont Co.). The results are summarized in Table VII, including data for poly(alkyl methacrylate), poly(alkyl α-cyanoacrylate), poly(p-alkylstyrene), and poly(quinodimethane) for comparison. T_g's for polyACQs are constant at 108 °C independent of the alkoxy group, whereas T_g's for polymers of vinyl compounds such as poly(alkyl methacrylate), poly(alkyl α-cyanoacrylate), and poly(p-

Table VII
T_g of the PolyACQ, Poly(alkyl methacrylates), Poly(alkyl cyanoacrylates), Poly(alkylstyrenes), and Poly(p-xylylene)

R	 [a]	 $-\!\!\!+\!CH_2-\overset{CH_3}{\underset{COOR}{C}}\!+\!\!\!-$ [b]	 $-\!\!\!+\!CH_2-\overset{CN}{\underset{COOR}{C}}\!+\!\!\!-$ [b]	 [b]	 [b]
H				100	
Me	108	105	170	93	
Et	108	65	175	<78	~80
Bu (iBu)	108	20	(140)	6	

[a] By DSC, heating rate, 20 °C/min. [b] Cited from "Polymer Handbook".

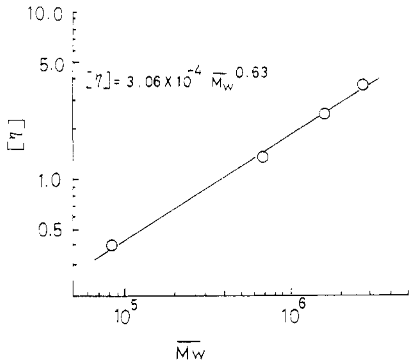


Figure 6. Relationship of solution viscosity (a) vs. molecular weight (b) for polyBCQ: (a) limiting viscosity number using Ubbelohde viscometer in tetrahydrofuran at 25 °C; (b) light scattering measurement.

Table VIII
Permeation Results[a]

T, °C	P_{O_2}	P_{N_2}	α
20	0.959	0.274	3.49
25	1.27	0.394	3.22
35	1.59	0.502	3.17

[a] P in 10^{-9} cm^3 (STP) cm/cm^2 s cmHg.

alkylstyrene) vary significantly depending upon the alkyl group. The difference in T_g dependence on substituent was thought to be attributable to the difference in the backbone chain structure. Poly ACQs exhibit higher T_g by ca. 30 °C than poly(quinodimethane). The difference was considered to arise from the fact that polyACQs carry many highly polar substituents, such as cyano and alkoxycarbonyl groups.

When polyBCQ in toluene was allowed to stand in a sealed ampule in a room for a long while, the solution changed from clear to yellow, indicating the regeneration of the BCQ monomer, probably via depolymerization with light irradiation. Therefore, photosensitivity of the depolymerization of polyBCQ with UV irradiation was investigated. A solution (10 wt %) of polyBCQ in 2-methoxyethyl acetate was cast on a metal plate to form a polyBCQ film of ca. 0.5-μm thickness. The coated late was heated at 100 °C for 0.5 h, exposed through a mask to a 200-W D_2 lamp with a distance of 5 cm, and then immersed in a mixture of methyl isobutyl ketone and isopropyl alcohol (35:65 by weight), followed by washing with isopropyl alcohol. PolyBCQ was found to be capable of forming patterns with the irradiation time of 2 min, whereas poly(methyl methacrylate) needed an irradiation time of 40 min, so the UV sensitivity of polyBCQ is 20 times as high as that of poly(methyl methacrylate). Moreover, the plate coated with a 0.5-μm polyBCQ film was dry-etched by means of a capacitance-coupled parallel-plate dry-etching apparatus (CF_4 gas, 0.2 torr gas pressure, 100-W power, 85-mm distance between electrodes, and 10 °C temperature of the electrode). A dry-etching rate for the polyBCQ film was found to be 15–18 nm/min, while the corresponding rate for poly(methyl methacrylate) film is 28 nm/min. Therefore, it can be mentioned that polyBCQ exhibits a high UV sensitivity and an anti-dry-etching character compared with poly(methyl methacrylate), suggesting that polyBCQ is one of the interesting possible materials for positive type resists. Oxygen and nitrogen gas permeability[14] was measured with a polyBCQ film with a thickness of 114 μm, prepared by the film-casting method of 3% polyBCQ solution in chloroform cast on a poly(tetrafluoroethylene) plate. The results are shown in Table VIII. The polyBCQ film was found to exhibit similar values of oxygen gas permeability and selective ratio in permeability of oxygen to nitrogen with ethylcellulose film.

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