Poly(benzimidazole) Synthesis by Direct Reaction of Diacids and Tetramine

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ABSTRACT: A convenient method for the synthesis of certain poly(benzimidazoles) of high molecular weights has been developed. These polymers were prepared readily by direct polycondensation of activated dicarboxylic acids with 3,3′-diaminobenzidine tetrahydrochloride using phosphorus pentoxide/methanesulfonic acid (PPMA) as condensing agent and solvent. Polycondensation of aromatic dicarboxylic acids containing phenyl ether structures with tetramine proceeded very quickly, was completed within 80 min at 140 °C, and produced poly(benzimidazoles) with inherent viscosities up to 5.8 dL/g. The synthesis of 2-substituted benzimidazoles by the reaction of *o*-phenylenediamine with carboxylic acids in PPMA was studied in detail to demonstrate the feasibility of the reaction for polymer formation. The thermogravimetry of the aromatic poly(benzimidazoles) showed 10% weight loss in air and nitrogen at 470 and 540 °C, respectively.

Introduction

Poly(benzimidazole) (PBI) is one candidate for high-temperature/flame-resistant fibers and fabrics and also shows promise as a reverse osmosis membrane in graphitization to high-strength, high-modulus fibers for composites and in high-temperature adhesives.

A number of synthetic routes for producing PBI have been developed and reviewed in detail.[1,2] The routes widely employed in the synthesis of PBI are represented by melt polymerization of tetramine with dicarboxylic acid diphenyl esters and by solution polymerization of tetramine hydrochloride with dicarboxylic acids or their derivatives in poly(phosphoric acid) (PPA) as a reaction medium. Recently, a series of rigid-rod polymers such as PBI, poly(benzothiazole) (PBT), and poly(benzoxazole) (PBO) has been prepared by the latter method.[3]

In the preceding communications,[4,5] we show that phosphorus pentoxide/methansulfonic acid (PPMA) in a weight ratio of 1:10 as a substitute for PPA is a very useful dehydrating agent for the preparation of diaryl sulfones and polyketones by direct polycondensation of various dicarboxylic acids with diaryl compounds. In order to expand the preparative utility of this method, it was applied to the synthesis of 2-substituted benzimidazoles (**3**). We have found that compounds **3** were conveniently prepared from *o*-phenylenediamine (**1**) and carboxylic acids (**2**) in the presence of PPMA.

This article describes a successful synthesis of PBI by direct polycondensation of various dicarboxylic acids with 3,3′-diaminobenzidine tetrahydrochloride using PPMA as condensing agent and solvent.

Experimental Section

Materials. The reagent PPMA was prepared according to the reported procedure.[6] Various reagent-grade substituted benzoic acids (**2**), aliphatic carboxylic acids (**2**), aliphatic dicarboxylic acids (**5**), and *o*-phenylenediamine (**1**) were used as received.

3,3′-Diaminobenzidine tetrahydrochloride monohydrate (**4**) was prepared from benzidine in four steps by the reported procedure.[7] Crystallization from 4 N hydrochloric acid solution yielded faint brown needles.

Anal. Calcd for $C_{12}H_{14}N_4 \cdot 4HCl \cdot H_2O$: C, 38.12; H, 5.33; N, 14.82. Found: C, 38.5; H, 5.2; N, 15.4.

4,4′-Oxybis[benzoic acid] (**6a**), 3,3′-(*p*-phenylenedioxy)bis[benzoic acid] (**6b**), and 4,4′-(*p*-phenylenedioxy)bis[benzoic acid] (**6c**) were prepared through oxidation of the corresponding dimethyl compounds with potassium permanganate in pyridine–water. These dicarboxylic acids were purified by recrystallization from acetic acid. **6a**: mp 337 °C (by DTA) (lit.[8] 331–333 °C). **6b**: mp 312 °C (by DTA) (lit.[9] 305–313 °C). **6c**: mp 333 °C (by DTA) (lit.[9] 331–333 °C, from dioxane).

2-Substituted Benzimidazoles (3): General Procedure. A mixture of *o*-phenylenediamine (**1**) (2.5 mmol) and the carboxylic acid **2** (2.5 mmol) in the reagent PPMA (6 mL) was stirred at 100 °C for 30 min. The solution was poured into ice water (300 mL) and neutralized with sodium carbonate. The product was filtered, washed with water, and dried. The products were virtually pure (IR, ^{1}H NMR spectra and TLC ethyl acetate, or *n*-hexane/ethyl acetate 1:1).

4,4′-Bis(2-benzimidazolyl)diphenyl ether (**8c**) was prepared from dicarboxylic acid **6c** and **1** as described above. The yield was 94%. It was recrystallized from ethanol to give white needles, mp 380 °C (by DTA). The IR spectrum (KBr) showed absorptions at 3300–2700 (imidazole ring), 1600 (C=N), and 1240 cm^{-1} (C—O—C).

Anal. Calcd for $C_{26}H_{18}N_4O$: C, 77.60; H, 4.51; N, 13.92. Found: C, 77.4; H, 4.7; N, 14.1.

Polymer Synthesis. Two typical examples of the polymerization follow.

a. Polymer 7d from 5d and 4. 3,3′-Diaminobenzidine tetrahydrochloride monohydrate (**4**) (0.378 g, 1.0 mmol) was stirred in PPMA (5 mL) for 1.5 h at 120 °C under nitrogen to effect dehydrochlorination. Sebacic acid (**5d**) (0.202 g, 1.0 mmol) was then added to this solution. The mixture was stirred for 5 h at this temperature. The extremely viscous solution that resulted was diluted with methanesulfonic acid. This hot polymer solution was poured into an aqueous sodium hydroxide solution. The fibrous polymer was collected, washed with hot water, and heated under reflux in water for 2 h. The polymer was dried in vacuo at 180 °C for 2 days. The yield was essentially quantitative. The inherent viscosity of the polymer in concentrated sulfuric acid was 0.94 dL/g, measured at a concentration of 0.2 g/dL at 30 °C. The IR (KBr) spectrum exhibited absorptions at 3250–2750 (imidazole ring) and 1620 cm^{-1} (C=N).

Anal. Calcd for $(C_{22}H_{24}N_4 \cdot H_2O)_n$: C, 72.90; H, 7.23; N, 15.45. Found: C, 72.3; H, 6.3; N, 15.8.

b. Polymer 9a from 6a and 4. Polymer **9a** was prepared from **6a** and **4** at 140 °C as described above (dehydrochlorination time, 1 h; polycondensation time, 20 min). The polymer, obtained in near quantitative yield, has the inherent viscosity of 3.63 dL/g in methanesulfonic acid (0.2 g/dL at 30 °C). The IR spectrum (KBr) showed absorptions at 3300–2750 (imidazole ring) and 1600 cm^{-1} (C=N, C=C).

Anal. Calcd for $(C_{26}H_{16}N_4O \cdot 4H_2O)_n$: C, 66.09; H, 5.12; N, 11.86. Found: C, 66.3; H, 4.9; N, 11.8.

Results and Discussion

Model Reaction. The synthesis of 2-substituted benzimidazoles (**3**) by the reaction of *o*-phenylenediamine **1** with carboxylic acids (**2**) in PPMA has not been reported so far. Therefore, we first studied the reaction of **1** with benzoic acid (**2a**) in PPMA to determine if the method gave the desired model compounds in high enough yield to give promise as a polymer-forming reaction. The reaction was performed by dissolving the **1** and **2a** in PPMA

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Scheme I

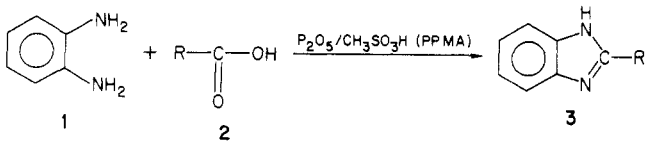


Table I
Preparation of 2-Substituted Benzimidazoles 3[a]

		product	
no.	acid(R-COOH)	no.	yield, %
2a	C_6H_5	3a	93
2b	p-ClC_6H_4	3b	91
2c	p-$NO_2C_6H_4$	3c	50[b,c]
2d	p-$CH_3OC_6H_4$	3d	96[d]
2e	o-HOC_6H_4	3e	30[e]
2f	m-$CH_3C_6H_4$	3f	97
2g	o-ClC_6H_4	3g	97
2h	n-C_4H_9	3h	85
2i	n-C_5H_{11}	3i	91
2j	n-C_6H_{13}	3j	95
2k	n-C_7H_{15}	3k	96
2l	c-C_6H_{11}	3l	97

[a] Reaction temperature, 100 °C; reaction time, 30 min. [b] Reaction time, 10 h. [c] Anal. Calcd for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56. Found: C, 65.4; H, 4.2; N, 17.6. Mp 323 °C (by DTA). [d] Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.7; H, 5.5; N, 12.6. Mp 231 °C (by DTA). [e] Recrystallized yield.

Table II
Effect of Amount of PPMA on Polycondensation[a]

amt of PPMA, mL	polymer η_{inh}, dL/g[b]
3	0.78
5	0.94
7	0.87
10	0.75

[a] Polycondensation was carried out with 1 mmol of each monomer (4 and **5d**) at 120 °C for 5 h. [b] Measured at a concentration of 0.2 g/dL in concentrated sulfuric acid at 30 °C.

and heating at various temperatures. After the reaction was complete, the solution was poured into ice water, and the crude product was filtered. These preliminary experiments revealed that the condensation was completed in 30 min at 100 °C and 6 mL of PPMA was found to be enough for the reaction on a 2.5 mmol scale.

On the basis of these results, various benzimidazoles (**3**) were prepared (Scheme I). The data summarized in Table I indicate that PPMA acts as both a very strong condensation agent and a solvent and gives good yields of benzimidazoles **3** under milder conditions compared to those using PPA. Furthermore, the reactivity of substituted benzoic acid was increased with electron-donating groups and decreased with electron-withdrawing ones. These observations suggest that active intermediates are acylium ions $XC_6H_4C{=}O^+$ rather than carboxylic sulfonic acid anhydrides because the reaction involving the rate-controlling formation of an acylium ion is markedly stabilized by resonance electron-donating substituents. When o-hydroxybenzoic acid (**2e**) was used as the carboxylic acid moiety, a formation of ester was observed as a side product. The structures of benzimidazoles **3** were confirmed by elemental analyses, IR, ^1H NMR spectra, and melting points.

Polymer Synthesis. In order to determine the optimal conditions for the polycondensation, the polycondensation of 3,3′-diaminobenzidine tetrahydrochloride monohydrate (**4**) and sebacic acid (**5d**) was studied. The polycondensation was performed with 1 mmol of each monomer at 120 °C for 5 h under nitrogen. Table II lists the effect of the amount of PPMA on the polycondensation. Five milliliters of PPMA was found to be appropriate for the reaction on a 1.0 mmol scale.

Table III
Effect of Reaction Temperature on Polycondensation

reaction conditions[a]		
temp, °C	time, h	polymer[b] η_{inh}, dL/g
100	5	0.60
120	5	0.94
140	0.5	0.87
140	1	1.28
140	1.5	2.27

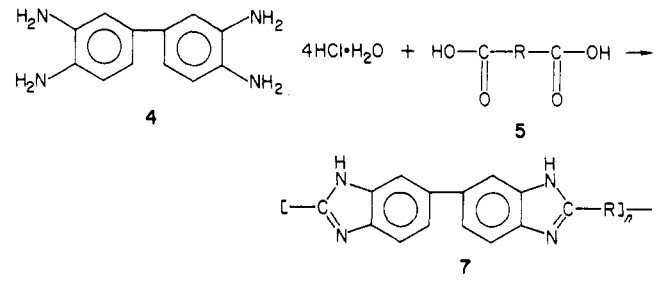
[a] Polycondensation was carried out with 1 mmol of each monomer (4 and **5d**) in 5 mL of PPMA. [b] Measured at a concentration of 0.2 g/dL in concentrated sulfuric acid at 30 °C.

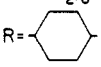
Table IV
Preparation of Aliphatic and Alicyclic Poly(benzimidazoles) in PPMA

		reaction conditions[a]		polymer	
no.	dicarboxylic acid, HOOC-R-COOH	time, h	temp, °C	no.	η_{inh}, dL/g[b]
5a	$-(CH_2)_5-$	10	120	7a	0.21
5b	$-(CH_2)_6-$	10	120	7b	0.45
5c	$-(CH_2)_7-$	5	120	7c	1.49
5d	$-(CH_2)_8-$	8	120	7d	3.34
5e	$-(CH_2)_{10}-$	2	120	7e	1.36
5f	t-1,4-cyclohexanediyl	1.6	140	7f	4.43[c]

[a] Polycondensation was carried out with 1 mmol of each monomer in 5 mL of PPMA. [b] Measured at a concentration of 0.2 d/dL in concentrated sulfuric acid at 30 °C. [c] In methanesulfonic acid (0.2 g/dL at 30 °C).

Scheme II



a, R = $-(CH_2)_5-$; b, R = $-(CH_2)_6-$; c, R = $-(CH_2)_7-$; d, R = $-(CH_2)_8-$; e, R = $-(CH_2)_{10}-$; f, R = 

The effect of the reaction temperature on the inherent viscosity of the resulting polymer was examined over the temperature range 100–140 °C because cyclization was incomplete at temperatures lower than 100 °C and methanesulfonic acid begins to decompose at temperatures higher than 150 °C. The results are shown in Table III. The inherent viscosity increased with increasing temperature, and the polycondensation at 140 °C gave polymer with an inherent viscosity as high as 2.27 dL/g in 1.5 h.

On the basis of these studies, direct polycondensation of various aliphatic and alicyclic dicarboxylic acids (**5**) with tetramine **4** was carried out in PPMA for several hours at 120–140 °C (Scheme II).

The results are summarized in Table IV. The polycondensation proceeded in homogeneous solution and gave quantitative yields of polymer (**7**) with inherent viscosities up to 3.34 dL/g. The polycondensation of pimelic (**5a**) or suberic acid (**5b**) with tetramine **4** yielded low molecular weight polymers. It seems that some side reaction such as a cyclization of these acids occurred.[10] Next, the synthesis of aromatic poly(benzimidazole) from isophthalic

Scheme III

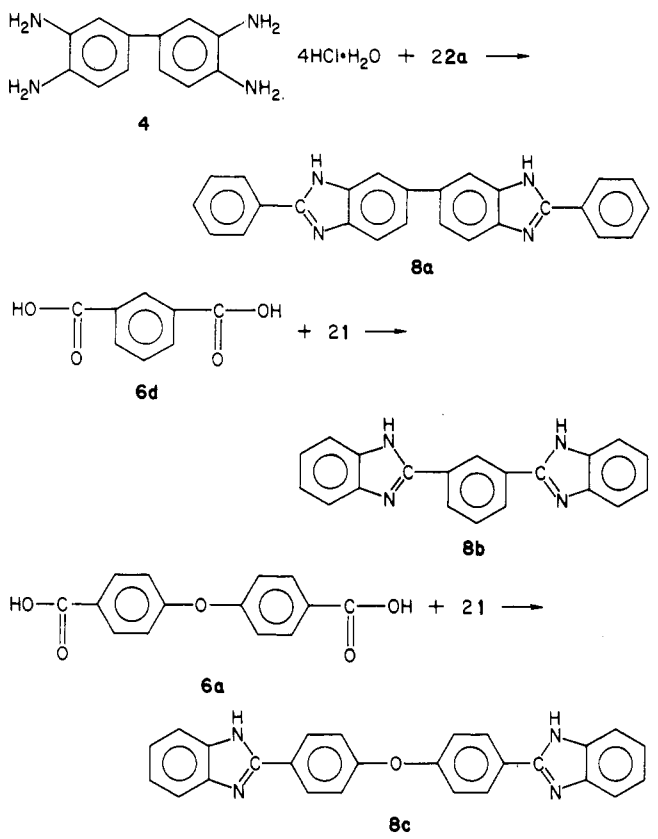


Table V
Preparation of Bis(benzimidazoles) in PPMA[a]

bis(benzimidazole)	temp, °C	yield, %
8a	100	95
8b	140	29
8c	100	94

[a] Condensation was carried out with 1 mmol of each monomer in 5 mL of PPMA for 3 h.

acid (**6d**) was tried. However, a black-colored product having rather low molecular weight was obtained in low yield. Model compound work was then performed again. The reaction of tetramine **4** with **2a** and that of **6d** with **1** were studied (Scheme III). The former reaction afforded the model compound 2,2′-diphenyl-5,5′-bibenzimidazole (**8a**) in quantitative yield. The model compound, 2,2′-*m*-phenylenebis[benzimidazole] (**8b**), was prepared in only 29% yield even at 140 °C with the latter reaction. The low reactivity of **6d** is associated with electron-withdrawing substituents meta to the carboxylic group. Even if one of the two carboxylic groups reacts with diamine **1**, the formed benzimidazole ring is protonated by methanesulfonic acid to form the imidazolium ion, which is a strong electron-withdrawing group. These substituent effects are disadvantageous for the formation of the acylium ion. From the determination of these structural effects in the

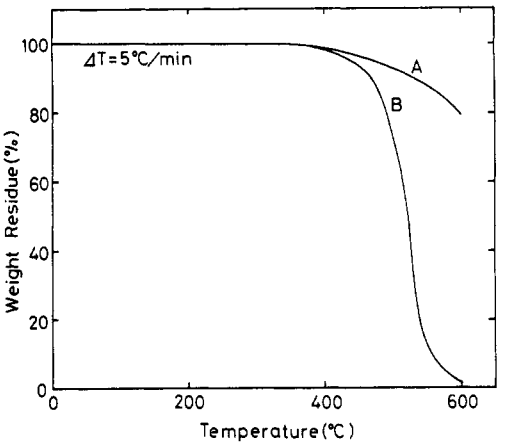
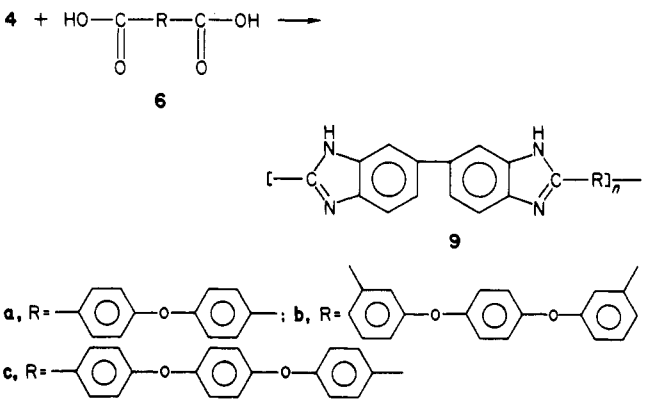


Figure 1. TG curves of poly(benzimidazole) **9a**: (A) in nitrogen; (B) in air.

Scheme IV



aromatic dicarboxylic acids, 4,4′-oxybis[benzoic acid] (**6a**) was chosen. The condensation of **6a** with **1** proceeded smoothly, as would be expected, to give a desired product, 4,4′-bis(2-benzimidazolyl)diphenyl ether (**8c**) in excellent yield. These results are shown in Table V.

As polymer-forming aromatic dicarboxylic acids, 3,3′-(*p*-phenylenedioxy)bis[benzoic acid] (**6b**) and 4,4′-(*p*-phenylenedioxy)bis[benzoic acid] (**6c**) were prepared. Synthesis of the aromatic poly(benzimidazoles) (**9**) was performed under conditions similar to those described for preparation of the aliphatic poly(benzimidazoles) (**7**). The results are summarized in Table VI. The polycondensation proceeded rapidly and was completed within 80 min at 140 °C (Scheme IV). Aromatic poly(benzimidazoles) containing *p*-phenyl ether linkages of high molecular weights could be obtained quite readily in PPMA.

Polymer Characterization. The polymers were defined as poly(benzimidazoles) by comparing their IR spectra with those of model compounds. The IR spectra exhibited characteristic absorptions at 3250–2750 and 1620 cm^{-1} due to the benzimidazole ring and C=N stretching. Elemental analyses also supported the formation of the expected polymers.

Table VI
Preparation and Thermal Stability of Aromatic Poly(benzimidazoles)

			polymer[a]		decomp temp, °C[c]	
no.	dicarboxylic acid HOOC-R-COOH	time, min	no.	η_{inh}, dL/g[b]	in air	in N_2
6a	#a	20	**9a**	3.63	465	540
6b	#b	80	**9b**	0.94	440	500
6c	#c	30	**9c**	5.84	470	540

[a] Polycondensation was carried out with 1 mmol of each monomer in 5 mL of PPMA at 140 °C. [b] Measured at a concentration of 0.2 g/dL in methanesulfonic acid at 30 °C. [c] 10% weight loss temperature observed by TG.

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(BCQ) = 0.9 ± 0.3 and r_2 = 0.02 ± 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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