be proportional to the crystallinity. However, in the actual polymer there exist some disorder in the crystalline region (which is obvious from the fact that the polyamides **3** of runs 1-6 have different melting temperatures from each other) and some order in the amorphous region nearby the crystalline region. The transition area would influence the separation factor (α), at least in a range of low crystallinity, resulting in a nonproportional relation between the chiral recognition ability and the crystallinity.

Conclusion

Optically active polyamides are easily obtained by the ring-opening polyaddition reaction of (−)-anti head-to-head coumarin dimer with diamines. The polyamides consisting of α,ω-alkanediamine with an even methylene number partially crystallize and show a chiral recognition ability, while the polyamides with an odd methylene number show neither crystallizability nor a chiral recognition ability. The superstructure of the crystalline part has not been clear yet, but the functional groups in the polyamides may exist in a regular conformation in the crystalline part, which play an important role on the chiral recognition ability.

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7-Phenyl-7,8,8-tricyanoquinodimethane: The First Unsymmetrical Electrophilic Quinodimethane

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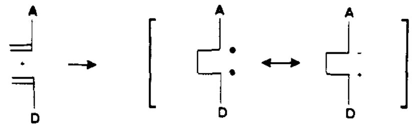
ABSTRACT: 7-Phenyl-7,8,8-tricyanoquinodimethane (1), the first unsymmetrical electrophilic quinodimethane, was synthesized successfully. The first reduction potential of 1 is −0.11 V by cyclic voltammetry. Title compound 1 can be homopolymerized with an anionic catalyst but does not homopolymerize with radical or cationic initiators. It copolymerized spontaneously and alternatingly with *p*-methylstyrene (MeSt), isobutyl vinyl ether, 2-chloroethyl vinyl ether, and *N*-vinylcarbazole at 60 °C. The propagation mode of the copolymerization for the 1–MeSt system will be discussed.

Introduction

We proposed the "bond-forming initiation theory"[1] to explain the spontaneous polymerizations of electron-rich olefins with electrophilic olefins. The inititating species is proposed to be a tetramethylene intermediate which may be either a zwitterion or a diradical



where A represents electron-accepting substituents such

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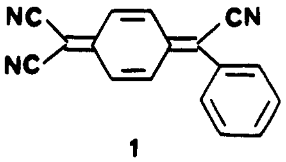
as cyano or ester groups and D represents electron-donating substituents such as alkoxy, dialkylamino, or carbazyl groups.

Electrophilic *p*-quinodimethanes also undergo spontaneous (co)polymerizations with electron-rich olefins. This field has recently been reviewed.[2,3] We have extended our initiation theory to these spontaneous reactions of electron-rich olefins with electrophilic *p*-quinodimethanes.[4] In this case, the expected initiating intermediate will be a *p*-phenylenetetramethylene, again either a zwitterion or diradical, depending on the terminal substituents. We have already reported the spontaneous copolymerization of 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane (ECQ) with *p*-methoxystyrene (MeOSt).[5] However, the study of spontaneous copolymerization of ECQ with MeOSt needed special experimental conditions because ECQ is too reactive.

The synthesis of an unsymmetrical quinodimethane, 7-phenyl-7,8,8-tricyanoquinodimethane (1), is now reported. This quinodimethane is expected to be less reactive. Moreover, due to its unsymmetric structure, it should give us some information about the mode of propagation: radical chain polymerization or radical coupling.



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Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were taken on a Bruker Model WM-250 Multinuclear FT spectrometer in chloroform-*d* with tetramethylsilane as internal standard. Infrared spectra were obtained with a Perkin-Elmer 983 grating infrared spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. All melting points were obtained from a Thomas-Hoover capillary melting poing apparatus and were uncorrected. Number-average molecular weights (M_n) were measured on Shodex GPC A-804 column, calibrated with polystyrene standards, with chloroform as eluent and a Spectra Physics UV detector at 254 nm.

Cyclic Voltammetry. Voltammetric measurement was carried out at room temperature in acetonitrile containing tetrabutylammonium perchlorate (0.1 mol/L) as supporting electrolyte. Ag/AgCl, glassy carbon, and platinum wire were used as reference, working, and counter electrodes, respectively. The scanning rate was 100 mV/s.

Monomer Synthesis Route 1. *p*-(Cyano(trimethylsiloxy)phenylmethyl)benzoyl Cyanide (3). A mixture of 4-benzoylbenzoyl chloride (2) (2.6 g, 10.6 mmol) (prepared by the reaction (82% yield) of 4-benzoylbenzoic acid with thionyl chloride), trimethylsilyl cyanide (4.21 g, 42.4 mmol), zinc iodide (50 mg), and benzene (5 mL) was refluxed for 24 h. The reaction mixture was placed under reduced pressure to remove the volatile materials, and the dark brown viscous residue was dissolved in 3 mL of benzene. The resulting solution was passed through a silica gel column with benzene as eluent. The pale-yellow elution band was collected to give 2.79 g (86% yield) of **3** as pale yellow viscous oil: IR (NaCl) ν CN 2220, CO 1680, CH 2950 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.15 (d, J = 7 Hz, 2 H), 7.76 (d, J = 7 Hz, 2 H), 7.48 (m, 2 H), 7.35 (m, 3 H), 0.17 (s, 9 H). Anal. Calcd for $C_{19}H_{18}N_2O_2Si$: C, 68.23; H, 5.43; N, 8.37; O, 9.57; Si, 8.40. Found: C, 68.11; H, 5.35; N, 8.43.

7-Phenyl-7,8,8-tricyanoquinodimethane (1). A mixture of **3** (1.10 g, 3.3 mmol), trimethylsilyl cyanide (0.72 g, 7.3 mmol), and pyridine (100 mg) was heated at 120 °C for 5 h. The mixture was placed under reduced pressure to remove volatile materials, and the dark brown residue was dissolved in 5.37 g (35.0 mmol) of phosphorus oxychloride at room temperature. To the resulting solution was added 3.54 g (45.4 mmol) of pyridine. The solution was stirred for 18 h at room temperature. The reaction mixture was poured into a large excess of ice water, extracted with 1,2-dichloroethane (100 mL × 2), and then dried over anhydrous magnesium sulfate. The filtrate was concentrated to 2 mL and passed through a silica gel column with 1,2-dichloroethane as eluent. The orange elution band and red elution band were collected separately. The orange elution band yielded 0.36 g (28.5% yield) of 1-(cyano(trimethylsiloxy)phenylmethyl)-4-(dicyanochloromethyl)benzene (**5**) as an orange viscous oil: IR (NaCl) ν CN 2241, CH 2950 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 4 H), 7.4 (m, 5 H), 0.17 (s, 9 H). The red elution band yielded a purple solid, which was recrystallized from a mixture of benzene and hexane (1:1 by volume) to give 0.2 g (21.5% yield) of 7-phenyl-7,8,8-tricyano-*p*-quinodimethane (**1**) (purple needles): mp 222–223 °C; IR (KBr) ν CN 2215, C=C 1580, 1554 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73 (dd, J = 9.8 and 1.8 Hz, 1 H), 7.56 (s, 5 H), 7.45 (dd, J = 9.8 and 1.8 Hz, 1 H), 7.42 (dd, J = 9.8 and 1.8 Hz, 1 H), 7.31 (dd, J = 9.8 and 1.8 Hz, 1 H); UV (CHCl$_3$) 434.7 (ϵ = 5.9 × 10^4) nm. Anal. Calcd for $C_{17}H_9N_3$: C, 79.99; H, 3.56; N, 16.45. Found: C, 80.20; H, 3.37; N, 16.43.

Monomer Synthesis Route 2. The synthesis of 4-(cyanophenylmethylene)cyclohexanone (**6**) is described in a related paper.[6]

1-(Dicyanomethylene)-4-(cyanophenylmethylene)cyclohexane (7). A mixture of **6** (1.64 g, 7.76 mmol), malononitrile (0.52 g, 7.8 mmol), β-alanine (0.1 g), acetic acid (0.1 mL), and benzene (30 mL) was stirred at reflux using a Dean–Stark water separator; 0.14 mL of water was collected. The reaction mixture was placed under reduced pressure to remove volatile materials, yielding a pale-brown solid as residue. The residue was washed with 5 mL of diethyl ether, filtered off, and dried under reduced pressure to yield 1.66 g (83% yield) of **7** as white needles: mp 155–156 °C; IR (KBr) ν CH 2971, CN 2231, 2209, C=C 1617, 1593 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.43 (m, 3 H) 7.29 (m, 2 H), 2.99 (s, 4 H), 2.77 (td, J = 6 and 1 Hz, 2 H), 2.66 (td, J = 6 and 1 Hz, 2 H). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.06; N, 16.20. Found: C, 78.97; H, 4.87; N, 16.16.

7-Phenyl-7,8,8-tricyanoquinodimethane (1). A mixture of **7** (0.26 g, 1.0 mmol), activated manganese oxide (1.04 g, 12 mmol), 3A molecular sieves (1.5 g), and 1,2-dichloroethane (10 mL) was heated under reflux for 2 h. The reaction mixture was filtered to remove insoluble materials, concentrated to 2 mL, and then passed through a silica gel column with 1,2-dichloroethane as eluent. The red elution band was collected to yield 0.36 g (28.5% yield) of **1** as a purple solid, which was recrystallized from a mixture of benzene and hexane to obtain purple needles identical in melting point, NMR spectrum, and IR spectrum with the material described above.

Other Materials. Commercial *p*-methylstyrene (MeSt) (bp 65 °C/20 mmHg), *tert*-butylstyrene (*t*-BuSt) (bp 65 °C/2 mmHg), and α-methylstyrene (α-MeSt) (bp 65 °C/20 mmHg) were washed with 2% sodium hydroxide aqueous solution and water, dried over anhydrous magnesium sulfate, stirred over calcium hydride at room temperature for 5 h, and distilled.

2-Chloroethyl vinyl ether (CEVE) (bp 109 °C) and isobutyl vinyl ether (IBVE) (bp 82 °C) were stirred over calcium hydride at room temperature for 12 h and distilled. *N*-Vinylcarbazole (NVCz) was recrystallized from hexane.

Commercial 7,7,8,8-tetracyanoquinodimethane (TCNQ) was purified by recrystallization from acetonitrile. 7,8-Dicyano-7,8-diphenylquinodimethane (CPQ) was prepared according to the method described by Brandt et al.[7]

Acetonitrile (bp 82 °C), chloroform (bp 61 °C), and 1,2-dichloroethane (bp 83 °C) were refluxed over calcium hydride for 24 h and distilled. Commercial toluene was washed with concentrated sulfuric acid and water, dried over calcium chloride, refluxed over sodium metal for 12 h, and distilled at 109 °C. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Butyllithium (Aldrich Co.) was used without further purification. Boron trifluoride etherate was distilled under nitrogen at reduced pressure. Tetrabutylammonium perchlorate was dried at 160 °C for 10 h under reduced pressure.

Preparation of Model Compounds and Alternating Copolymers. α,α-Dicyano-4-(dicyanomethyl)bibenzyl (8). Compound **8** was prepared according to literature procedure.[8] A solution of TCNQ (50 mg, 0.25 mmol) and trifluoroacetic acid (30 mg) in toluene (30 mL) was irradiated for 67 h under nitrogen with a 450-W medium-pressure mercury lamp at a distance of 5 cm through a Pyrex filter at room temperature. The solvent was then removed in vacuo at 40 °C. The residue was chromatographed on silica gel using benzene as eluent. The second pale-yellow elution band was collected; the solvent was evaporated under reduced pressure to give 50 mg of a pale-yellow solid residue, which was recrystallized from a mixture of benzene and hexane (1:1 by volume) to give 39.4 mg (54% yield) of **8** as white needles: mp 164-165 °C (lit.[8] mp 164-165 °C); ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 2 H), 5.15 (s, 1 H), 7.1-7.4 (m, 5 H), 7.62 (s, 4 H); IR (KBr) ν CN 2250 cm^{-1}. Anal. Calcd for $C_{19}H_{12}N_4$: C, 77.01; H, 4.09; N; 18.90. Found C, 77.03; H, 4.06; N, 18.91. ^{13}C NMR spectral data are shown in Table V.

α,α-Dicyano-α'-methyl-4-(dicyanomethyl)bibenzyl (9). Compound **9** was prepared as a viscous oil in 76% yield from TCNQ and ethylbenzene in a process similar to that for **8**: IR (NaCl) ν CN 2250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.71 (d, J = 7.1 Hz, 3 H), 3.46 (q, J = 7.1 Hz, 1 H), 5.13 (s, 1 H), 7.06 (dd, J = 1.4 and 7.7 Hz, 2 H), 7.28 (dd, J = 1.4 and 7.7 Hz, 2 H), 7.41 (d, J = 8.6 Hz, 2 H), 7.53 (d, J = 8.6 Hz, 2 H), 7.36 (s, 1 H). Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.56; N, 18.04. Found: C, 77.36; H, 4.64; N, 18.00. ^{13}C NMR spectral data are shown in Table V.

α,α-Dicyano-α',α'-dimethyl-4-(dicyanomethyl)bibenzyl (10). Compound **10** was prepared as pale-yellow needles in 53% yield from TCNQ and isopropylbenzene in a process similar to that for **8**: mp 147~148 °C; IR (KBr) ν CN 2250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 5.12 (s, 1 H), 7.1-7.5 (m, 9 H). Anal. Calcd for $C_{21}H_{16}N_4$: C, 77.75; H, 4.98; N, 17.26. Found: C, 77.69; H, 4.81; N, 17.50. ^{13}C NMR spectral data are shown in Table V.

Alternating Copolymer of TCNQ with α-MeSt (11). TCNQ (90.8 mg, 0.45 mmol), α-methylstyrene (54.3 mg, 0.46 mmol), and acetonitrile (12 mL) were placed in an ampule, which was degassed completely by the freeze-thaw method (repeated 3 times), filled with nitrogen, and sealed. The mixture was heated at 60 °C for 70 h. The copolymer was precipitated twice in excess methanol and washed with methanol. The dried copolymer (128.2 mg, 88.4% yield) was obtained as a pink powder. The molecular weight determined by gel permeation chromatography (GPC) was 9200 (M_n). Anal. Calcd for $(C_{21}H_{14}N_4)_n$: C, 78.24; H, 4.39; N, 17.37. Found: C, 78.51; H, 4.32; N, 17.18. ^{13}C NMR spectral data are shown in Table VI.

Alternating Copolymer of TCNQ with t-BuSt (12). The composition in feed and copolymer, reaction condition, and molecular weight of the copolymer are summarized in Table III. ^{13}C NMR spectral data are shown in Table VI.

Alternating Copolymer of CPQ with MeSt (13). CPQ (104.7 mg, 0.24 mmol), p-methylstyrene (56.6 mg, 0.48 mmol), AIBN (3.5 mg), and chloroform (2 mL) were placed in an ampule, which was degassed completely by the freeze-thaw method (repeated 3 times), filled with nitrogen gas, and sealed. The mixture was heated at 60 °C for 69 h. The copolymer was precipitated in excess hexane. The copolymer was dissolved in a small amount of 1,2-dichloroethane and reprecipitated with excess hexane. This procedure was repeated 6 times to remove unreacted CPQ. The dried polymer (27.6 mg, 17% yield) was obtained as a pale-yellow powder. The molecular weight determined by GPC was 4500 ($\bar{M}_n$). Anal. Calcd for $(C_{31}H_{24}N_2)_n$: C, 87.70; H, 5.71; N, 6.59. Found: C, 87.55; H, 5.82; N, 6.53. ^{13}C NMR spectral data are shown in Table VI.

Polymerization Procedure. In the case of ionic homopolymerization with butyllithium and boron trifluoride etherate, a given amount of **1** and dry solvent, such as toluene or 1,2-dichloroethane, were placed in a flame-dried test tube with a stirring bar; the test tube was then sealed with a septum and flushed with argon. The tube was set in a thermostated bath at 25 °C. A given amount of catalyst was added to the solution by syringe, and the mixture was allowed to stir for a given time before it was quenched with a small amount of methanol. An aliquot was then removed for immediate GPC analysis. For the polymerization with butyllithium, the reaction mixture was poured into excess hexane to precipitate the polymeric product; this was dissolved again in a small amount of 1,2-dichloroethane and reprecipitated.

Table I
First Reduction Potentials[a]

compound	E_1, V[b]
TCNQ	+0.21
1	−0.11
CPQ	−0.65

[a] Solvent, acetonitrile containing $Bu_4N^+ClO_4^-$ (0.1 mol/L); reference electrode, Ag/AgCl; scanning rate, 100 mV/min. [b] Relative error: ±0.01 V.

Table II
Homopolymerization of 1 with Various Catalysts

initiator	solvent (mL)	time, h	conversion, %	$\bar{M}_n$
AIBN[a]	$CHCl_3$ (0.5)	26	0	
BuLi[b]	toluene (5)	24	12.7	640
$BF_3{\cdot}Et_2O$[b]	$ClCH_2CH_2Cl$ (5)	24	0	

[a] Initiator, 5 mol %; temperature, 60 °C. [b] Initiator, 10 mol %; temperature, 25 °C.

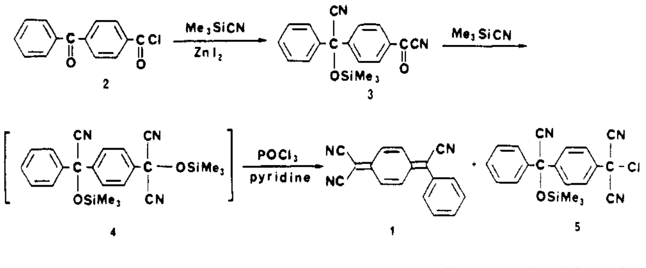
In the case of free radical homopolymerization with AIBN, a given amount of **1**, AIBN, and chloroform was placed in an ampule, which was degassed by the freeze-thaw method (repeated 3 times), filled with nitrogen, and sealed. After 26 h at 60 °C, an aliquot was removed for GPC analysis.

For copolymerization, given amounts of **1** (or TCNQ) and a comonomer (MeSt, IBVE, CEVE, NVCz, and t-BuSt), solvent (1,2-dichloromethane or toluene), with or without AIBN, were placed in an ampule, which was degassed completely by the freeze-thaw method (repeated 3 times), filled with nitrogen, and sealed. The ampule was set in a bath at 60 °C for the polymerization. When the MeSt and t-BuSt were used as comonomer, the reaction mixture was poured into excess methanol to precipitate the polymer. When the IBVE, CEVE, or NVCz were used as a comonomer, hexane was used as a precipitant. For purification, the polymer was reprecipitated and dried under reduced pressure.

Polymer Characterization. The polymer composition was established by elemental analysis. The number-average molecular weight ($\bar{M}_n$) of the polymers was determined without correction by gel permeation chromatography (GPC) using polystyrene standards.

Results

Synthesis of 7-Phenyl-7,8,8-tricyanoquinodimethane (1). The title compound **1** was successfully prepared by the two different synthesis routes. Route 1 was patterned after the synthesis of TCNQ reported by Yamaguchi and Hanafusa.[9]



In route 1, the reaction of 4-benzoylbenzoyl chloride (**2**) with trimethylsilyl chloride in the presence of zinc iodide in refluxing benzene gave **3** in 86% yield, which was converted to **4** with trimethylsilyl cyanide in the presence of small amount of pyridine at 120 °C. The latter reaction was followed by infrared spectrophotometry: the formation of **4** was confirmed by the disappearance of the 2220- and 1680-cm^{-1} peaks. The dicyanosiloxymethyl group of **4** decomposed on silica gel and alumina. Therefore, **4** was used in the next reaction without purification. **4** was allowed to react with phosphorus oxychloride in the presence of pyridine[8] at room tempera-

Table III
Spontaneous Copolymerizations of 1 with MeSt in Chloroform and of TCNQ with *t*-BuSt in Acetonitrile at 60 °C

run[a]	1, mg	MeSt, mg	1, mol %	solv, mL	time, day	polymer, mg	yield, %	anal. found % H	% C	% N	copolymer comp, 1 mol %	$\bar{M}_n$[b]
1	101.0	55.5	45.7	5	1	16.4	10.5	4.88	83.74	11.38	51.0	3900
2	100.4	57.0	44.9	5	3	22.5	22.5					4200
3	100.6	56.5	45.1	5	6	39.5	25.1					4000
4	101.0	50.9	47.9	5	13	57.2	37.7					4100
5	100.4	49.0	48.6	2	7	86.7	58.0	4.83	83.59	11.57	51.6	6300
	TCNQ	*t*-BuSt		CH_3CN							TCNQ	
6	75.0	69.3	45.3	10	16 (h)	36.7	25.4	5.58	79.84	14.59	53.2	10200

[a] Run nos. 1–4: [1] + [MeSt] = 0.17 mol/L. Run no. 5: [1] + [MeSt] = 0.4 mol/L. [b] Determined by GPC, chloroform eluent, polystyrene standard.

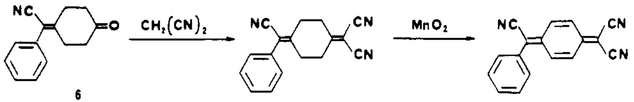
Table IV
Copolymerizations of 1 with Various Electron-Rich Olefins at 60 °C

run	1, mg	donor, mg	1, mol %	AIBN, mg	solvent (mL)	time, h	yield, mg (%)	copolymer comp,[a] 1 mol %	$\bar{M}_n$[b]
1	1.0	CEVE, 252.2	0.17	0	$(CH_2Cl)_2$ (1)	48	trace		
2	105.4	CEVE, 54.7	44.6	0	$(CH_2Cl)_2$ (5)	118	9.0 (5.6)	51.6	1800
3	105.5	CEVE, 58.7	42.8	1.4	$(CH_2Cl)_2$ (5)	184	18.3 (11.1)	48.7	1600
4	1.2	IBVE, 210.0	0.17	0	$(CH_2Cl)_2$ (1.5)	48	trace		
5	101.3	IBVE, 43.4	47.0	0	$(CH_2Cl)_2$ (5)	123	14.7 (10.2)	48.8	2200
6	100.5	IBVE, 42.6	47.4	1.2	$(CH_2Cl)_2$ (5)	66	19.1 (13.3)	47.8	1600
7	1.5	NVCz, 106.8	1.1	0	toluene (2)	24	trace		
8	61.0	NVCz, 47.4	49.4	0	toluene (5)	117	37.8 (34.9)	50.1	2500
9	62.0	NVCz, 51.5	47.6	1.0	toluene (5)	72	34.4 (30.3)	54.4	1700

[a] Determined from the elemental analysis. [b] Determined by GPC, chloroform eluent, polystyrene standard.

ture for 24 h to yield 1 and 5 in 21% and 28% yield, respectively. The treatment of 5 with more phosphorus oxychloride–pyridine at room temperature also afforded 1 in 20% yield, strongly suggesting that 5 is an intermediate. 1 was obtained as purple needles, and the total yield in four steps was 15%.

In route 2, the Knoevenagel reaction of 4-(cyanophenylmethylene)cyclohexanone 6[6] with malononitrile in the presence of tetrabutylammonium acetate and acetic acid in refluxing benzene gave 7 in 83% yield as a white-needled crystal. The oxidation of 7 with activated manganese dioxide in 1,2-dichloroethane afforded 1 in 28% yield. The total yield in four steps was 16%.



Electron-Accepting Character. The first reduction potential, E_1, of 1 was measured by cyclic voltammetry. The result is shown in Table I, along with the data for 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 7,8-dicyano-7,8-diphenylquinodimethane (CPQ).[7] It is obvious that 1 is of intermediate electron-accepting character between TCNQ and CPQ, as expected from their chemical structures. The electron-accepting character of 1 can be explained in terms of Hammett's substituent constant, σ_p, of cyano ($\sigma_p = +0.66$)[10] and phenyl ($\sigma_p = -0.01$)[10] and the number of substituents.

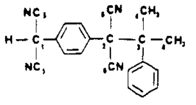
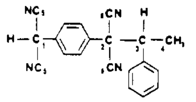
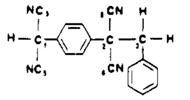
Homopolymerization. Homopolymerization of 1 was attempted with conventional radical, anionic, and cationic catalysts such as AIBN, butyllithium, and boron trifluoride etherate (Table I). It was found that 1 homopolymerized with butyllithium (low yield) but not with AIBN and boron trifluoride etherate. TCNQ does not homopolymerize with these initiators in the same conditions. The behavior of 1 is similar to that of other sterically crowded quinodimethanes, such as CPQ[7] and 7,8-diphenyl-7,8-dimethoxycarbonylquinodimethane,[11] which also react slowly to give low molecular weight homopolymers.

Copolymerization. The results for the spontaneous copolymerization of 1 with *p*-methylstyrene (MeSt) in chloroform at 60 °C are shown in Table III, together with data for the TCNQ–*t*-BuSt system in acetonitrile at 60 °C for comparison. As the copolymer of MeSt with TCNQ is insoluble in chloroform, *t*-BuSt was chosen as a comonomer for TCNQ. All copolymerizations described in Table III proceeded without precipitation. Spontaneous copolymerization did occur in both systems, and copolymers are obtained as white powders with approximately a 1:1 composition. The molecular weight of the copolymers of the 1–MeSt and TCNQ–*t*-BuSt systems is about 4000 and 10 200, respectively, corresponding to a degree of polymerization (DP) of 10 and 28 based on an alternating structure. The difference in DP can be attributed to the steric effect of the substituents on the exocyclic position. Taft's parameter, E_s, which is the usual parameter describing steric effects of substituents, is reported to be −0.51[12] and −3.82,[12] respectively, for cyano and phenyl groups.

For the copolymerization of the 1–MeSt systems, the molecular weight of the obtained copolymer and the conversion as a function of time are shown in Figure 1. The molecular weight of the copolymer is almost constant regardless of time and conversion. This is similar to conventional radical copolymerizations. This suggests that the propagation mode is not diradical coupling but chain addition.

The results for the copolymerization of 1 with CEVE, IBVE, and NVCz, which are more electron-donating than MeSt, are summarized in Table IV. When a small amount of 1 was used as a catalyst, the 1–CEVE, 1–IBVE, and 1–NVCz systems gave only a trace amount of reaction products. When about 100 mg of 1 was used with and without radical catalyst, the reaction product could be obtained in these sufficient amounts to be characterized. Reaction products obtained in three systems (run nos. 2, 3, 5, 6, 8, 9) were pale-brown powders which were soluble in chloroform, 1,2-dichloroethane, ethyl acetate, and benzene and insoluble in hexane. The molecular

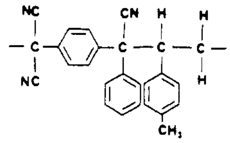
Table V
^{13}C NMR Chemical Shifts (ppm) of Model Compounds in Chloroform-*d*

compound	carbon						
					CN		
	1	2	3	4	5	6	Ar
 10	27.6	47.4	53.4	24.9	111.2	114.5	127.0, 127.9 128.1, 128.2 128.8, 129.8 132.1, 138.1
 9	27.6	48.9	51.1	17.0	111.1	113.6 114.3	126.1, 128.1 128.2, 128.4 128.7, 129.1 133.9, 135.8
 8	27.7	48.7	43.6		111.0	114.0	128.0, 128.4 128.5, 128.9 129.2, 130.4 130.7, 134.5

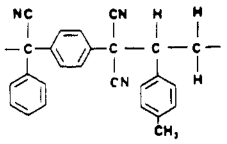
weights of the products were measured by GPC to be 1500~2500. Their elemental analyses show that the products are composed of equimolar amounts of 1 and the donor monomers, consistent with alternating copolymers.

Orientation Determination in the Copolymer of 1 with MeSt by ^{1}H and ^{13}C NMR Spectra. The ^{1}H NMR spectrum of the copolymer of 1 with MeSt is shown in Figure 2; the absorption peaks can be assigned to the respective protons of the chemical structure shown. The methine and methylene protons of the MeSt unit of the copolymer in the δ 3–4 ppm region are more deshielded than the corresponding protons of the homopolymer of MeSt, which generally appear at δ 1–2 ppm.[13] Presumably, the deshielding arises from the electron withdrawal by the neighboring dicyanomethylene and cyanophenylmethylene groups, showing that the MeSt unit is linked directly to 1 on both sides. Therefore, the copolymer of 1 with MeSt is really alternating.

There are two possible structures for an alternating copolymer of 1 with MeSt (**14a** and **14b**)



14a



14b

The ^{1}H NMR spectra of **14a** and **14b** are expected to be nearly identical, so the ^{13}C NMR spectra were used to determine which one is formed.

In order to determine the orientation, we prepared three model compounds and three reference alternating copolymers, whose ^{13}C NMR spectral data are summarized in Tables V and VI, respectively. The ^{13}C NMR spectral data for the alternating copolymer of 1 with MeSt are also shown in Table VI. The chemical shift for each carbon in the reference alternating copolymers was assigned on the basis of the NMR spectra of the three model compounds (Table V) and by using the APT (attached proton test) method.

The aromatic peaks in the spectra of 1–MeSt copolymer and model copolymers do not give us any information about the orientation of the alternating units because of serious overlapping of the peaks.

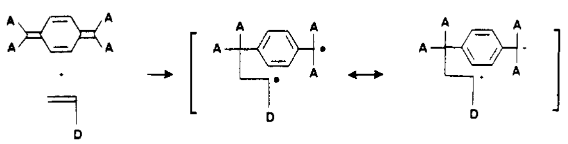
From the backbone carbons, the methylene carbon is the easiest to recognize because it absorbs at higher field. However, the spectra of the reference copolymers show that no distinction can be made between a CH$_2$ unit next to a dicyanocarbon unit or next to a phenylcyanocarbon unit. Therefore, no information about the structure of 14 can be obtained from the 39.7 ppm peak.

From the reference copolymer spectra, we can conclude that the exocyclic carbon of the quinodimethane unit next to the CH$_2$ always occurs at a slightly lower field than the exocyclic carbon next to the methine carbon. The 49.3 ppm peak in the 1–MeSt copolymer spectrum is therefore assigned to the quinodimethane carbon next to the CH$_2$ unit. Comparing the shifts of this carbon in the reference copolymers, we can see that they are independent of the substituents: C1 with two cyano substituents, or with one phenyl and one cyano, absorbs at roughly the same field.

The peak at the lowest field is due to the methine carbon. The shift of this carbon (C3) is almost the same for copolymers **11** and **12** (53.0 and 53.4 ppm), while in **13** the peak appears at 48.7 ppm. We can thus determine that C3 next to a dicyanocarbon unit has a shift at lower field than C3 next to a phenylcyanocarbon unit. This peak in the 1–MeSt copolymer appears at 53.5 ppm, indicating that this copolymer has structure **14b**. This is corroborated by the slight shift difference (~1 ppm) for C2.

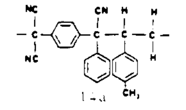
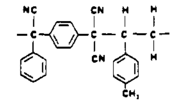
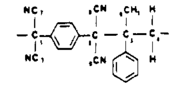
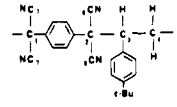
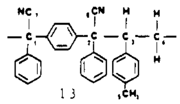
Discussion

In analogy to the reactions of electron-rich olefins with electrophilic olefins, we proposed that the initiating species in the spontaneous polymerizations observed in the electron-rich olefin/electrophilic quinodimethane systems was a *p*-phenylenetetramethylene.[4] Also in analogy to the olefin systems, we proposed that this *p*-phenylenetetramethylene could be either predominantly a zwitterion or a diradical, depending on the substituents



where A represents electron-accepting substituents such as cyano or ester groups and D represents electron-donating substituents such as alkoxy or carbazyl groups. In contrast to the olefin systems, these quinodimethane systems do not lead to any cycloadducts, due to the structure of the reactants. Also, the *p*-phenylenetetrameth-

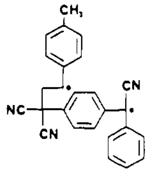
Table VI
^{13}C NMR Chemical Shifts (ppm) of Alternating Copolymers of 1 with MeSt, of TCNQ with α-MeSt and *t*-BuSt, and of CPQ with MeSt in Chloroform-*d*

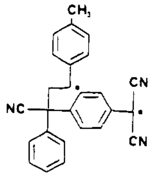
copolymer	1	2	3	4	5	6	$-C^b(C^aH_3)_3$	7	8	Ar
 14a	49.3	48.1 48.2	53.5	39.7	21.1			113.3 114.1 118.5 119.3		125.5–131.4 137.5–141.7
 14b										
 11	50.5	48.0	53.0	38.0		19.8		111.7	113.4 114.6	125.8–135.9
 12	49.7	47.8	53.4	40.2			a: 31.1 b: 34.8	112.6	113.5 114.2	126.3–128.8 129.8–133.5
 13	49.5	49.2	48.7	40.2	21.7			118.8 (br)		125.7–129.7 135.9–139.5

ylene intermediates lean much more toward the diradical side, because of the incorporated phenyl group.

The influence of the substituents is evident from the comparison of the behavior of the title compound 1 with TCNQ.[14,15] The less electrophilic 1 copolymerizes spontaneously with all three donor monomers, CEVE, IBVE, and NVCz. The more electrophilic TCNQ with CEVE also leads to a copolymer, but with the more electron-rich olefins, IBVE and NVCz, the cationic homopolymerization of the latter is observed. Therefore, we propose that 1 forms a diradical *p*-phenylenetetramethylene intermediate with all three donor monomers, which initiates the radical copolymerization. With the more electrophilic TCNQ, the character of the initiating *p*-phenylenetetramethylene intermediate is predominantly zwitterionic, thus initiating the cationic homopolymerization. This is in accordance with the "bond-forming initiation theory."[1]

The fact that the 1–MeSt system led to an alternating copolymer suggests that, if *p*-phenylenetetramethylene is the initiator, it is indeed diradical. From our study of the olefin/olefin reactions, the orientation of the donor olefin in the diradical initiator is known. Thus, two different *p*-phenylenetetramethylene diradical intermediates (**15a** and **15b**) are possible, depending on the acceptor moiety:


15a


15b

We postulate that the formation of **15a** is favored over **15b** in the initiation reaction, because a phenyl group stabilizes a radical much better than a cyano, but we have no direct evidence on this point.

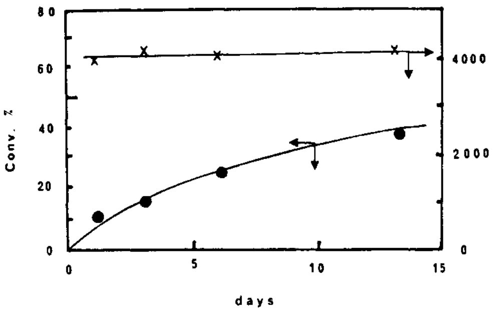


Figure 1. Relationship of conversion and of molecular weight of the copolymer with time for the copolymerization of the 1–MeSt system.

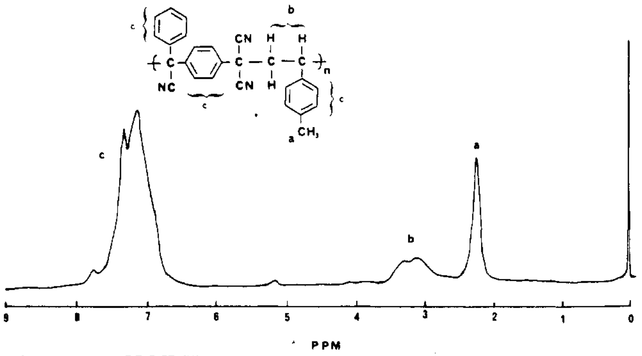
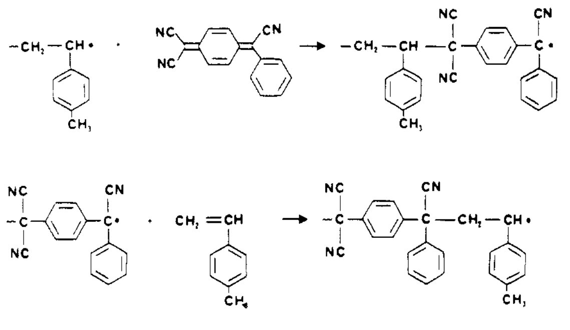


Figure 2. ^{1}H NMR spectrum of the copolymer of 1 with MeSt (run no. 5) in chloroform-*d*.

If diradical intermediates are formed, then there are two possible propagation mechanisms: either the diradicals couple (polycondensation) or a diradical acts as initiator (chain addition). If the propagation takes place via diradical coupling reaction, intermediates **15a** and **15b** would lead to the alternating copolymers with structures of **14a** and **14b**, respectively. Diradical **15a** is the preferred structure; therefore, radical coupling would lead to copolymer with structure **14a**. This structure is not in agreement with the polymer structure **14b** as determined on the basis of ^{13}C NMR spectral data, ruling out the radical coupling mechanism. On the other hand, if the propagation takes place via chain addition reaction, copolymerization should be governed by both formation of the most stable radical and the least steric hindrance. This would result in the alternating copolymer with the structure of **14b**, according to the mechanism



The structure of the polymer obtained via a chain addition reaction is in agreement with the ^{13}C NMR spectral data. This is also consistent with the result obtained from the relationship of molecular weight with time and conversion.

In summary, 7-phenyl-7,8,8-tricyanoquinodimethane (1) as a new unsymmetrical electrophilic quinodimethane was synthesized successfully. 1 can homopolymerize with an anionic catalyst but not with radical and cationic ones. Title compound 1 copolymerized spontaneously in an alternating fashion with MeSt, IBVE, CEVE, and NVCz at 60 °C. The propagation mode of the copolymerization for the 1-MeSt system was determined to be chain addition like a conventional radical copolymerization on the basis of both the relationship of molecular weight of the 1-MeSt copolymer with time (conversion) and the results of the ^{13}C NMR spectral examination. Validity of "bond-forming initiation mechanism" was supported from the comparison of the polymerization behavior of the title compound 1 with TCNQ.

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