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Synthesis of 7-Phenyl-8-(ethoxycarbonyl)-7,8-dicyanoquinodimethane and Its Polymerization

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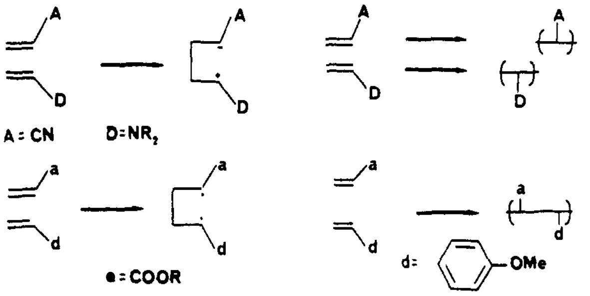
ABSTRACT: 7-Phenyl-8-(ethoxycarbonyl)-7,8-dicyanoquinodimethane (1), a new unsymmetrical electrophilic quinodimethane, was synthesized. The first reduction potential of 1 is −0.33 V by cyclic voltammetry. Compound 1 can be homopolymerized with an anionic catalyst. It spontaneously copolymerized free radically with *p*-methoxystyrene, *p*-methylstyrene, and styrene at 60 °C, and alternating copolymers with high molecular weight were obtained. The propagation mode of the copolymerization for the 1-MeOSt system is discussed. *N*-Vinylcarbazole (NVCz) with 1 under the same conditions formed only NVCz homopolymer by spontaneous polymerization.

Introduction

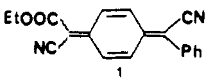
We proposed the "bond-forming initiation theory"[1] to explain the spontaneous polymerizations of electron-rich olefins with electrophilic olefins. The initiating species is a tetramethylene zwitterion or diradical:



If the tetramethylene is a zwitterion, it may initiate cationic or anionic homopolymerization. If it is a diradical, it may initiate free radical copolymerization.

We have extended our theory to reactions of electron-rich olefins with electrophilic *p*-quinodimethane.[2] The spontaneous copolymerization of 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane with *p*-methoxystyrene has been reported.[3] Our interest in the mechanism of the spontaneous reactions of electron-rich olefins with electron-poor quinodimethanes led us to synthesize new unsymmetrical quinodimethanes. Previously, the synthesis of 7-phenyl-7,8,8-tricyanoquinodimethane (PTCQ) and its polymerization have been reported.[4] It was found that spontaneous copolymerization of PTCQ with *p*-methylstyrene proceeds via chain addition in the propagation step.

In order to confirm this, we synthesized 7-phenyl-8-(ethoxycarbonyl)-7,8-dicyanoquinodimethane (1) as another unsymmetrical electrophilic quinodimethane and studied the spontaneous copolymerization of 1 with electron-rich olefins.



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Results and Discussion

Synthesis of 7-Phenyl-8-(ethoxycarbonyl)-7,8-dicyanoquinodimethane (1). Compound 1 was successfully prepared by the synthesis route depicted in Scheme I. The reaction of 1,4-cyclohexanedione monoethylene ketal with benzyl cyanide in the presence of aqueous sodium hydroxide and ethanol gave **3** in 70% yield, which was subsequently deprotected with hydrochloric acid (in 90% yield). Knoevenagel reaction of ethyl cyanoacetate with **4** in the presence of a catalytic amount of β-alanine and acetic acid in refluxing benzene gave compound **5** in 62% yield. Six peaks (δ 33.80, 31.95, 31.85, 29.68, 28.97, 28.53), assigned to methylene carbons, were observed in the ^{13}C NMR spectrum of **5**, and two sets of peaks (δ 1.35 and 1.38 and δ 2.67 and 2.69) for the ethyl groups were observed in the ^{1}H NMR spectrum, indicating that **5** is composed of a mixture of two geometric isomers. When

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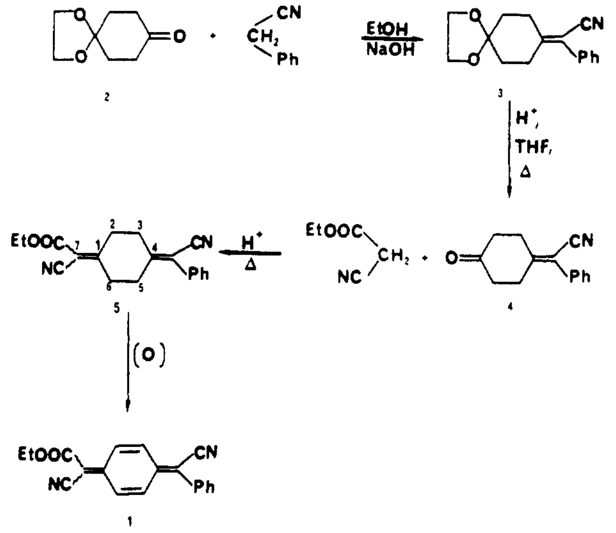
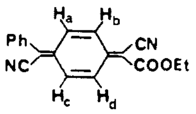
Scheme I

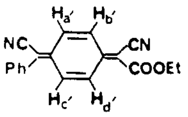


5 was treated with active manganese dioxide in benzene or chloroform, it oxidized completely after 30 min. Analysis of the crude reaction mixture with ^{1}H NMR indicated the presence of 1 along with a polymeric material. However, reducing the reaction time to only 5–10 min led to a reaction mixture that only contained monomer 1. The monomer undergoes rapid spontaneous polymerization ($\bar{M}_n$ = 2000) upon evaporation of the solvent.

Thermal depolymerization of 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane homopolymer under vacuum has been reported previously.[5] Moreover, Iwatsuki et al. noted that the homopolymer of 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane regenerated a small amount of monomer on standing in light.[6] Sublimation of the mixture of 1 with polymeric product at 120–140 °C under reduced pressure gave pure 1 as an orange solid.

Structure of 1. The 500-MHz ^{1}H NMR spectrum of the material, which was sublimed at 120–140 °C and which did not have a sharp point, suggested the presence of two geometric isomers, cis and trans, as evidenced by the pair of peaks at 1.38 and 1.37 ppm for CH_3. However, when the polymeric product was sublimed at a higher temperature, 160–180 °C, a single isomer was obtained as the major product. Four distinct doublets of doublets at 8.36, 7.65, 7.48, and 7.30 ppm, can be observed in the ^{1}H NMR spectrum of the material sublimed at 160–180 °C. Selective double-irradiation NMR experiments showed that the proton at 8.36 ppm is coupled to the proton at 7.30 ppm (J = 10.2 Hz) and to the proton at 7.48 ppm (J = 1.9 Hz). Similarly, when the proton at 7.65 ppm is selectively irradiated, the proton at 7.48 ppm collapsed to a doublet, losing the large coupling of 9.8 Hz. In the ^{1}H NMR spectrum of 7,8-dicarbethoxy-7,8-dicyanoquinodimethane, a large downfield shift of ca. 0.8 ppm is observed for one of the quinonoid protons.[7] This shift is due to the deshielding effect of the ester group. The same downfield shift is observed in the spectrum of 1. The existence of four distinct quinonoid protons is indicative of the different chemical environments of each of these protons. This is best rationalized by a trans structure for 1, with the peak at 8.36 ppm assigned to H_d.





For the cis isomer, one would expect less drastic changes in the chemical environments of the quinonoid protons that lie on the same side as the nitrile groups (H_a' and H_b'). This is clearly manifested by the spectrum of the mixture of the two isomers. The quinonoid proton peaks belonging to the other isomer (cis) are at 8.49, 7.58, and 7.35 ppm. A broad singlet at 7.35 ppm is assigned to the quinonoid protons on the symmetrical side, namely, H_a' and H_b' next to the two CN groups. The peaks at 8.49 and 7.58 ppm, which are coupled to each other with a large coupling constant of 10.1 Hz, are similar to the ones reported for *trans*-1 and are assigned to H_d' and H_c', respectively. With these in mind, we assign the product of sublimation at 160–180 °C as the trans isomer and the product formed alongside trans at 120–140 °C as the cis isomer. The cis-trans isomerization is a consequence of high temperature. No change in the ratio of the two isomers was observed in a solution of 1 in chloroform-*d* left for 4 days at room temperature.

Solubility of 1. Compound 1 is an orange solid that forms a yellow or orange solution, depending on the concentration, and is soluble in toluene, THF, 1,2-dichloroethane, chloroform, benzene, and dichloromethane. The color of these solutions did not change over time. On the other hand, when 1 was dissolved in methanol, the color of the solution faded in a short time. GPC measurement showed a peak with molecular weight of ca. 10^4, indicating that polymerization took place. This behavior is similar to that of 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane,[6] 7,8-diacetyl-7,8-dicyanoquinodimethane,[8] and 7,8-dibenzoyl-7,8-dicyanoquinodimethane[8] reported previously.

Electron-Accepting Character. The first reduction potential, E_1, of 1 was measured by cyclic voltammetry to be −0.33 V, which is smaller than −0.29 V for 7-phenyl-7,8,8-tricyanoquinodimethane (PTCQ). This means that 1 has less electron-accepting character than PTCQ. The reduced electron-accepting character of 1 compared with that of PTCQ can be explained in terms of Hammett's substituent constant, σ_p, of the cyano (σ_p = +0.66)[9] and the alkoxycarbonyl (σ_p = +0.45)[9] groups.

Polymerization. Anionic homopolymerization of 1 in THF using butyllithium or potassium cyanide (5 mol %) as initiator at −78 °C gave light yellow homopolymer of 1 in quantitative yield. When butyllithium was added to the solution 1 in THF, the orange color of the solution faded immediately. On the other hand, in the case of potassium cyanide, it took 2 h to fade. Homopolymer of 1 is soluble in chloroform, dichloromethane, 1,2-dichloroethane, and benzene and insoluble in hexane and methanol.

Spontaneous copolymerization of 1 with styrene derivatives such as styrene (St), *p*-methylstyrene (MeSt), and *p*-methoxystyrene (MeOSt) occurred when the reactants were mixed in 1,2-dichloroethane in equimolar amounts and heated to 60 °C. Quantitative conversion for the copolymerizations of 1 with St, MeSt, and MeOSt was attained in 3 days, 2 days, and 1 day, respectively, indicating that MeOSt is the most reactive among them. This sequence of reactivity of the styrene monomers is consistent with the increase in donor ability. In our bond-forming initiation theory, the stronger donor induces higher push–pull stabilization of the *p*-phenylenetetramethylene intermediate, as reported previously for the olefin–olefin case:[1]

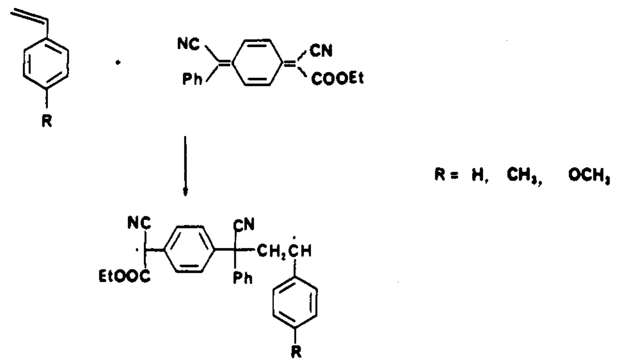
For the copolymerization of the 1–MeOSt system, the molecular weight of the obtained copolymer and the conversion as a function of time are shown in Table I. The molecular weight of the copolymer is almost constant, regardless of time and conversion. Moreover, polymer with

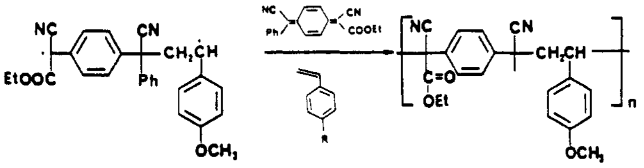
Table I
Spontaneous Copolymerization[a] of 1 with MeOSt at 60 °C

run no.	time, h	polymer mg	polymer yield, %	$\bar{M}_n$[b]
1	2	10	4	9400
2	5	20	27	10000
3	8	35	49	8900
4	12	54	75[c]	9100
5	24	72	100	10800

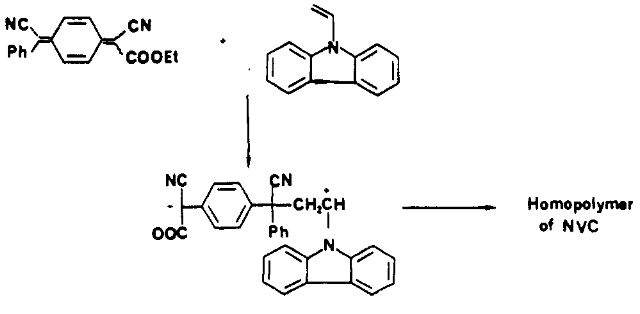
[a] Solvent, 1,2-dichloroethane (5 mL); monomer 1, 50 mg, 0.17 mmol; MeOSt, 22.3 mg, 0.17 mmol. [b] Determined by GPC. Chloroform eluent. [c] Elemental analysis values (C, 77.04; H, 5.45; N, 6.33) are in good agreement with the calculated ones (C, 77.04; H, 5.54; N, 6.42) for the alternating copolymer.

high molecular weight is formed at low conversion. This is the trend expected for chain addition in the propagation step, and not for diradical coupling. This behavior is similar to that for the PTCQ–MeSt system as reported previously.[4]





In the reaction of the stronger donor monomer *N*-vinylcarbazole (NVCz) with 1 under the same conditions (dichloroethane or toluene, 60 °C, and no initiator), homopolymer of NVCz and unreacted 1 were obtained after 10 days. Compound 1 is acting as a "cationic initiator" for homopolymerization of NVCz through formation of a zwitterionic *p*-phenylenetetramethylene intermediate.



Finally, we note that a cyano ester terminus in the quinodimethane is more favorable to homopolymerization than a dicyano terminus.[3] This agrees with the homopolymerizability of 7,8-dicyano-7,8-bis(carbomethoxy)quinodimethane as contrasted with TCNQ.

Experimental Section

Instrumentation. ^{1}H NMR spectra were taken on a Bruker Model WM-250 multinuclear FT spectrometer. 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 point apparatus and were uncorrected. Number-average molecular weights ($\bar{M}_n$) were measured on a Shodex GPC A-804 column calibrated with polystyrene standards with chloroform as eluent and a Spectra Physics UV detector at 254 nm.

Polymer Characterization. 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 standard polystyrene as reference.

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

Monomer Synthesis. 1,1-(Ethylenedioxy)-4-(cyanophenylmethylene)cyclohexane (3). Aqueous sodium hydroxide (4.0 mL, 40%) was added dropwise to a solution of 1,4-cyclohexanedione monoethylene ketal (**2**) (7.8 g, 0.05 mol) and benzyl cyanide (5.85 g, 0.05 mol) in 50 mL of 95% ethanol with stirring within 20 min at room temperature. Stirring was continued for 2 days. A dark brown solution was obtained. Extraction was done with 100 mL of ether. The ethereal solution was washed with water (five times, 30 mL). The yellow ether solution was dried with magnesium sulfate. After evaporation of the ether, a yellow liquid was obtained (11.29 g, 88.5% yield). Distillation under low pressure (0.1 mmHg) gave a light yellow liquid with a boiling point range of 155–160 °C (9 g, 70% yield). This liquid solidified at 5 °C. Recrystallization with hexane gave a white crystalline solid: mp 66.5–67 °C; IR (KBr) ν_{max} 2206 (CN) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.42–7.26 (m, 5 H), 4.00 (m, 4 H), 2.89 (t, 2 H), 2.50 (t, 2 H), 1.89 (t, 2 H), 1.69 (t, 2 H); ^{13}C NMR (CDCl$_3$) δ 158.58 (C$_9$), 133.39 (C$_{10}$), 128.52 (benzene ring), 118.19 (C$_N$), 108.9 (C$_4$), 107.23 (C$_1$), 64.35 (C$_7$, C$_8$), 34.98, 34.86, 31.82, 27.68 (C$_2$, C$_6$, C$_3$, C$_5$). Anal. Calcd for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.41; H, 6.51; N, 5.49.

4-(Cyanophenylmethylene)cyclohexanone (4). A mixture of ketal **3** (12.7 g, 0.05 mol), 100 mL of THF, and 15 mL of 10% aqueous HCl was refluxed 2 days. The mixture was cooled, concentrated to ca. 25 mL, and partitioned between water and ethyl acetate. The organic layer was washed with water (3 times, 30 mL) and dried (MgSO$_4$). Removal of ethyl acetate gave 10.25 g of yellow liquid. Column chromatography (70 g of silica gel, 70–230 mesh, 60 Å) with 20% ethyl acetate/hexane gave 1.8 g of **3** and 7.6 g (73% yield, 90% total yield) of pure crystalline **4**: mp 56–56.5 °C; IR (KBr) ν_{max} 2210 (CN), 1712 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.34–7.43 (m, 5 H), 3.10 (t, 2 H), 2.77 (t, 2 H), 2.63 (t, 2 H), 2.43 (t, 2 H); ^{13}C NMR (CDCl$_3$) δ 208.98 (C=O), 155.4 (C$_7$), 132.82 (C$_8$), 128.69 (benzene), 117.6 (C$_N$), 111.04 (C$_4$), 38.68, 38.60, 31.15, 27.88 (C$_2$, C$_6$, C$_3$, C$_5$). Anal. Calcd for $C_{14}H_{13}ON$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.13; H, 6.16; N, 6.44.

1-(Cyanophenylmethylene)-4-[cyano(ethoxycarbonyl)methylene]cyclohexane (5). A mixture of 4-(cyanophenylmethylene)cyclohexanone (**4**) (2.11 g, 0.01 mol), ethyl cyanoacetate (1.13 g, 0.01 mol), β-alanine (0.1 g), acetic acid (0.1 mL), and benzene (30 mL) was stirred at reflux using a Dean–Stark water separator; 0.18 mL of water was collected. Benzene was removed by rotatory evaporation at 40 °C to yield a light yellow viscous material. Diethyl ether (5 mL) was added to the residue, and then the resulting suspension was scratched to precipitate 1.9 g (62% yield) of **3** as a white solid: mp 134–135.5 °C; IR (KBr) ν_{CN} 2205, 2210, ν_{CO} 1728 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.41–7.29 (m, 5 H), 4.29 (q, 2 H), 3.30 (t, 2 H), 2.95 (t, 2 H), 2.81 (t, 2 H), 2.67 (m, 2 H), 1.35 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 174.88 (C=O), 161.28 (C$_7$), 155.28 (C$_8$), 132.66 (C$_9$), 128.76 (benzene ring), 117.63 (CN), 114.78 (CN), 110.79 (C$_1$), 104.16 (C$_4$), 61.97 (CH$_2$), 33.80, 31.95, 31.85, 29.68, 28.97, 28.53 (belong to C$_2$, C$_3$, C$_5$, and C$_6$, different isomer), 13.96 (CH$_3$). Anal. Calcd for $C_{19}H_{18}O_2N_2$: C, 74.44; H, 5.80; N, 9.11. Found: C, 74.49; H, 5.92; N, 9.15.

7-Phenyl-8-(ethoxycarbonyl)-7,8-dicyanoquinodimethane (1). A mixture of **5** (306 mg, 1.0 mmol), 3A molecular sieves

(1 g), activated manganese oxide (1.2 g), and benzene (10 mL) was stirred at reflux for 5 min, cooled, and filtered on Celite. The orange filtrate was stripped to give crude 1, which was sublimed under reduced pressure at 120–140 °C to afford 137.5 mg (45% yield) of 1 (mixture of trans and cis isomers) as an orange solid. Sublimation of crude product under reduced pressure at 160–180 °C gave mostly the trans isomer of 1 (45% yield). IR (KBr) ν_{CN} 2201, ν_{CO} 1746, 1707 cm^{-1}; ^{1}H NMR ($CDCl_3$) for trans isomer, δ 8.36 (dd, J = 1.9 and 10.2 Hz, H_c), 7.65 (dd, J = 2.1 and 9.8 Hz, H_d), 7.48 (dd, J = 1.9 and 9.8 Hz, H_b), 7.52 (m, phenyl ring, 5 H), 7.30 (dd, J = 2.1 and 10.2 Hz, H_c), 4.34 (q, CH_2), 1.38 (t, CH_3); ^{1}H NMR ($CDCl_3$) for cis isomer, δ 8.49 (dd, J = 0.98 and 10.1 Hz, H_d'), 7.58 (dd, J = 1.15 and 10.1 Hz, H_c'), 7.52 (m, phenyl ring), 7.35 (br s, H_a' and H_b'), 4.28 (q, CH_2), 1.29 (t, CH_3); ^{13}C NMR ($CDCl_3$) for trans isomer, δ 162.13 (C=O), 149.66, 140.10 (C_8), 133.89, 131.12, 131.12, 131.09, 130.44, 130.01, 129.24, 128.52, 128.08, 127.84, 127.69 (C_{1-6}, phenyl ring), 120.80, 117.75 (CN), 62.35 (CH_2), 14.09 (CH_3); MS *m/e* 302 (M^+). Anal. Calcd for $C_{19}H_{14}O_2N_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.27; H, 4.48; N, 9.05.

Other Materials. *p*-Methoxystyrene (MeOSt) (bp 42 °C/0.5 mmHg), *p*-methylstyrene (MeSt) (bp 65 °C/20 mmHg), and styrene (St) (bp 60 °C/40 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 under nitrogen. *N*-Vinylcarbazole (NVCz) was recrystallized from hexane. 1,2-Dichloroethane (bp 83 °C) was 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 for 12 h, and distilled at 109 °C. Tetrabutylammonium perchlorate was dried at 160 °C for 10 h under reduced pressure. Potassium cyanide (Aldrich) and butyllithium (Aldrich; 1.7 M solution in hexane) were used without further purification. Tetrahydrofuran (THF) (bp 67 °C) was distilled over benzophenone–sodium.

Polymerization Procedure. In the case of ionic homopolymerization with butyllithium and potassium cyanide, a given amount of 1 and dry THF 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 −78 °C. A given amount of catalyst (5 mol %) was added to the solution by syringe, and the mixture was allowed to stir for 4 h. The reaction mixture was poured into excess hexane to precipitate the polymeric product; this was dissolved again in a small amount of chloroform and reprecipitated.

For spontaneous copolymerizations, given amounts of 1, a comonomer (MeSt, MeOSt, St, or NVCz), and 1,2-dichloroethane were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated 3 times), filled with argon, and sealed. The ampule was set in a bath at 60 °C for the polymerization. The reaction mixture was poured into excess hexane to precipitate the polymer. For purification, the polymer was reprecipitated (chloroform/hexane) and dried under reduced pressure.

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References and Notes

(1) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(2) Hall, H. K., Jr.; Itoh, T.; Iwatsuki, S.; Padias, A. B.; Mulvaney, J. E. *Macromolecules*, in press.
(3) Brandt, M. W.; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* **1988**, *21*, 1553.
(4) Itoh, T.; Hall, H. K., Jr. *Macromolecules*, in press.
(5) Hall, H. K., Jr.; Bentley, J. H. *Polym. Bull.* **1980**, *3*, 203.
(6) Iwatsuki, S.; Itoh, T.; Iwai, T.; Sawoda, H. *Macromolecules* **1985**, *18*, 2726.
(7) Hall, H. K., Jr.; Cramer, R. J.; Mulvaney, J. E. *Polym. Bull.* **1982**, *7*, 165.
(8) Iwatsuki, S.; Itoh, T.; Sato, T.; Higuchi, T. *Macromolecules* **1987**, *20*, 2651.
(9) Ritchie, C. D.; Sager, W. F. An Examination of Structure–Reactivity Relationship. In *Progress in Physical Organic Chemistry*; Cohen, S. G., Streitwieser, A., Jr., Taft, R. W., Eds.; Interscience: New York, 1964; Vol. 2, pp 323–400.

Registry No. 1, 127666-91-5; 1 (homopolymer), 127666-95-9; (1)(St) (copolymer), 127666-96-0; (1)(MeSt) (copolymer), 127666-97-1; (1)(MeOSt) (copolymer), 127666-98-2; **3**, 127666-92-6; 4, 126724-50-3; **5**, 127666-93-7; MeOSt, 637-69-4; 1,4-cyclohexanedione monoethylene ketal, 4746-97-8; benzyl cyanide, 140-29-4; ethyl cyanoacetate, 105-56-6.

Improved Synthesis of 7,8-Dicyano-7,8-diphenylquinodimethane and Its Spontaneous Copolymerization with Electron-Rich Olefins

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ABSTRACT: 7,8-Dicyano-7,8-diphenylquinodimethane (1) was synthesized in two steps in high yield. Compound 1 copolymerized spontaneously and alternatingly with *p*-methoxystyrene in three solvents, toluene, 1,2-dichloroethane, and nitromethane, at 60 °C. It also copolymerized spontaneously and alternatingly with *N*-vinylcarbazole (NVCz) in toluene and induced homopolymerization of NVCz in 1,2-dichloroethane and nitromethane at 60 °C. The nature of the initiating *p*-phenylenetetramethylene intermediate is discussed on the basis of these solvent effects.

Introduction

Previously, one of us has reported the synthesis, chemical structure, and polymerizability of 7,8-dicyano-7,8-diphenylquinodimethane (1).[1] However, the five-step synthesis gave only an 8% overall yield of 1. Free radical initiated copolymerizations of 1 with styrene, *p*-methoxystyrene, and *p*-aminostyrene were reported. However,

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