(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.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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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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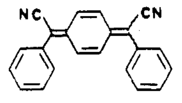


1

spontaneous copolymerization of 1 with electron-rich olefins, except for *p*-aminostyrene, has not been studied yet. Here, we report an improved synthetic method of 1 by a rational route and its spontaneous copolymerization with electron-rich olefins, *p*-methoxystyrene and *N*-vinylcarbazole, in three solvents, toluene, 1,2-dichloroethane, and nitromethane.

Experimental Section

Instrumentation. Infrared and ^{1}H NMR spectra were obtained with a Perkin-Elmer 983 grating infrared spectrophotometer and a Bruker Model WM-250 multinuclear FT spectrometer, respectively. 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 weight (M_n) was 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.

Materials. *p*-Methoxystyrene (MeOSt) (Aldrich) (bp 45 °C/1 mmHg) was 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. *N*-Vinylcarbazole (NVCz) was recrystallized from hexane.

1,2-Dichloroethane (bp 83 °C) and nitromethane (bp 100 °C) were refluxed over calcium hydride for 24 h and then distilled. Toluene (bp 109 °C) was washed with concentrated sulfuric acid and water, dried over calcium chloride, refluxed over sodium metal for 12 h, and distilled.

Monomer Synthesis. 1,4-Bis[cyano(trimethylsiloxy)-phenylmethyl]benzene (3). A mixture of 1,4-dibenzoylbenzene (2) (Alfa) (3 g, 10.5 mmol), trimethylsilyl cyanide (3 g, 30.2 mmol), zinc iodide (150 mg), and benzene (7 mL) was refluxed for 2 days. The reaction mixture was passed through a silica gel column with benzene as eluent. The first elution band yielded crude 3, which was recrystallized from hexane to give 4.38 g (86% yield) of 3 as white needles: mp 112–116 °C; IR (KBr) ν_{CH} (aromatic) 3062, 3031, ν_{CH}(aliphatic) 2958, 2898, ν_{CN} 2232 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.48 (m, 6 H), 7.36 (s, 4 H), 7.33 (m, 4 H), 0.12 (s, 18 H). Anal. Calcd for $C_{28}H_{32}N_2O_2Si_2$: C, 69.37; H, 6.67; N, 5.78. Found: C, 69.16; H, 6.58; N, 5.97.

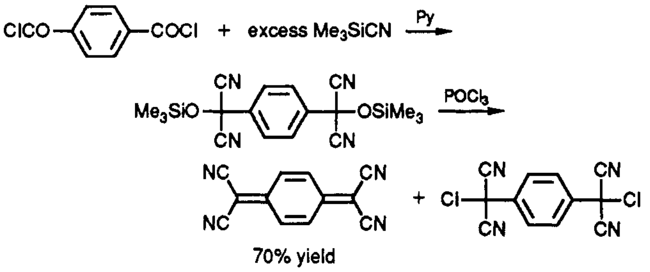
7,8-Dicyano-7,8-diphenylquinodimethane (1). Compound 3 (3.7 g, 7.6 mmol) was dissolved in 37.7 g (275 mmol) of phosphorus trichloride at room temperature. To the resulting solution was added 30.9 g (397 mmol) of pyridine. The solution was heated at 100 °C for 5.5 h. The reaction mixture was poured into a large excess of ice water, extracted with 1,2-dichloroethane (200 mL × 2), and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent, yielding an orange residue, which was dissolved in 5 mL of 1,2-dichloroethane. The resulting 1,2-dichloroethane solution was passed through a silica gel column with 1,2-dichloroethane as eluent. The orange elution band was collected, the solvent evaporated, and the orange solid recrystallized from a mixture of 1,2-dichloroethane and hexane, yielding 1.2 g (51% yield) of 1 as orange platelets: mp 203–204 °C; ^{1}H NMR (CDCl$_3$) δ 7.12 (d, J = 1 Hz, 1 H), 7.25 (dd, J = 10 and 1.5 Hz, 1 H), 7.41 (dd, J = 10 and 1.5 Hz, 1 H), 7.44 (d, J = 1 Hz, 1 H), 7.46–7.53 (m, 10 H); IR (KBr) ν_{CH} 3059, ν_{CN} 2197, $\nu_{C=C}$ 1536 cm^{-1}; UV (ClCH$_2$CH$_2$Cl) 428 nm ($\epsilon = 4.8 \times 10^4$). Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.24; H, 4.62; N, 9.14. Found: C, 86.28; H, 4.63; N, 9.09.

Polymerization Procedure. Given amounts of 1, comonomer (MeOSt or NVCz), and solvent (toluene, 1,2-dichloroethane, or nitromethane) were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times), filled with nitrogen gas, and sealed. The ampule was set in a bath thermostated at 60 °C for the polymerization and opened. The reaction mixture was poured into an excess of hexane to precipitate the polymer. The polymer obtained was dissolved again in a small amount of 1,2-dichloroethane, and the resulting solution was poured into an excess of hexane to precipitate the polymer. This procedure was repeated several times to remove unreacted 1. The polymer obtained was dried under reduced pressure to get constant weight.

Polymer Characterization. Polymer composition was established by elemental analysis. The number-average molecular weight (M_n) of the polymers was determined without correction by gel permeation chromatography (GPC) using standard polystyrene as reference.

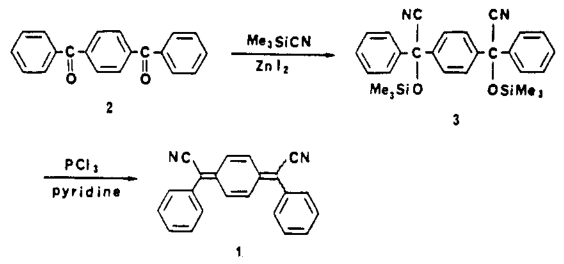
Results and Discussion

Synthesis. Our synthesis was patterned after the work of Yamaguchi and Hanafusa,[2] who used the following route to synthesize TCNQ:



The stoichiometry of this reaction as written is obscure.

When we attempted an analogous synthesis of 7,8-dicyano-7,8-diphenylquinodimethane (1), condensation of *p*-dibenzoylbenzene with excess trimethylsilyl cyanide in the presence of zinc iodide in refluxing benzene gave 3 in 86% yield. In the second step, although we tried to carry out the reaction of 3 with POCl$_3$/pyridine under several different conditions (reagent ratio, reaction time, and reaction temperature), the yield never exceeded 15%. However, when PCl$_3$ was used as a reagent, instead of POCl$_3$, in pyridine at 100 °C, a 51% yield of 1 was obtained. Moreover, this reagent permits us to offer a rational balanced equation:



$$3 + 1PCl_3 \rightarrow 1 + Me_3SiOSiMe_3 + 1POCl_3$$

The total yield of 1 was 44%; thus the yield for our modified procedure for the synthesis of 1 is 6 times greater than the method reported previously. 1 was recrystallized from a mixture of 1,2-dichloroethane and hexane to obtain orange platelets. The ^{1}H NMR spectrum of 1 showed that this orange crystal is composed of a 1:1 mixture of syn- and anti-type isomers, as reported previously.[1]

Spontaneous Copolymerization. The reactions of 1 with *p*-methoxystyrene (MeOSt) and *N*-vinylcarbazole (NVCz) were run in equimolar amounts at 60 °C under a nitrogen atmosphere in three solvents, toluene, 1,2-dichloroethane, and nitromethane. The results are summarized in Table I. These copolymerizations proceeded homogeneously except that polymer precipitated from run no. 6. Reaction products obtained in these

Table I
Spontaneous (Co)polymerization of 7,8-Dicyano-7,8-diphenylquinodimethane (1) with MeOSt and NVCz at 60 °C

run no.	1, mg	donor, mg	1, mol %	solv (mL)	time, h	yield, mg (%)	anal.			copolymer 1, mol %	M_n[a]
							% H	% C	% N		
				MeOSt Donor							
1	77.5	38.7	46	$C_6H_5CH_3$ (5)	96	12.7 (10.9)	4.83	84.50	6.35	50	3170
2	82.2	44.0	45	$(CH_2Cl)_2$ (8)	75	4.0 (3.2)	5.28	83.59	6.38	50	2560
3	80.7	40.0	47	CH_3NO_2 (12)	118	8.2 (6.8)	5.40	84.46	6.35	50	2260
				NVCz Donor							
4	66.2	42.6	50	$C_6H_5CH_3$ (4)	90	9.3 (8.5)	5.06	86.65	8.29	55	12000
5	58.2	38.8	49	$(CH_2Cl)_2$ (2)	72	22.1 (57)	5.60	87.12	7.28	0	5.3×10^5
6	57.5	39.4	48	CH_3NO_2 (12)	5.5	22.7 (57.6)	5.62	87.19	7.19	0	4.7×10^5

[a] Determined by GPC.

systems as white powders were soluble in chloroform, 1,2-dichloroethane, toluene, and acetone and insoluble in hexane.

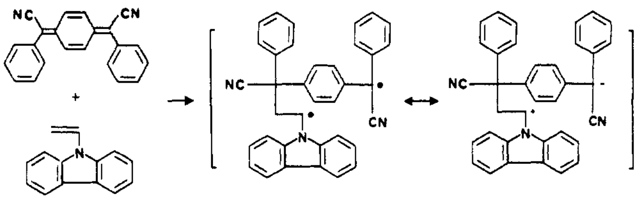
For the 1–MeOSt system, spontaneous copolymerization occurred in the three different solvents, even though copolymer yield was low. Elemental analyses showed that all products (runs 1–3) are composed of equimolar amounts of 1 and MeOSt, indicating alternating copolymers. The molecular weight of these copolymers was measured by GPC to be 2300–3200, corresponding to a degree of polymerization ($\overline{DP}$) of 5–7.

For the 1–NVCz system, spontaneous polymerization also occurred in the three different solvents. The product formed in toluene is composed of equimolar amounts of 1 and NVCz (elemental analysis), suggesting an alternating copolymer. On the other hand, the products formed in 1,2-dichloroethane and nitromethane gave an elemental analysis in good agreement with that of the homopolymer of NVCz. The molecular weight of these polymers was very high, ca. 500 000 ($\overline{DP}$ ~ 2500). 1,2-Dichloroethane (ϵ = 10.52 at 20 °C)[3] and nitromethane (ϵ = 38.57 at 20 °C)[3] are much more polar than toluene (ϵ = 2.38 at 20 °C).[3] In more polar solvents, homopolymerization of NVCz took place instead of copolymerization of 1 with NVCz.

In control experiments, mixtures of NVCz with 1,2-dichloroethane and of NVCz with nitromethane were heated at 60 °C for a similar length of time as the experimental conditions of Table I. Homopolymer of NVCz was not obtained, indicating that 1,2-dichloroethane and nitromethane or a contaminant, if present, cannot initiate the polymerization of NVCz without 1 under these experimental conditions.

We have already reported the solvent effect[4] on the nature of a diradical tetramethylene intermediate, which is proposed as an intermediate[5] for the reaction between electrophilic olefins and electron-rich olefins. It was found that in a borderline case such as the MeOSt–methyl 3,3-dicyanoacrylate system,[4] the medium could shift the nature of the tetramethylene intermediate. For the 1–MeOSt system, no change in polymerization mode with varying solvent polarity was observed. For the 1–NVCz system, however, a change in polymerization mode was observed. The 7,7,8,8-tetracyanoquinodimethane–2-chloroethyl vinyl ether system[5] showed similar behavior.

Recently, we have extended the bond-forming initiation theory,[6] proposed for the olefin–olefin case, to the spontaneous reactions of electrophilic quinodimethane and electron-rich olefins. The *p*-phenylenetetramethylene diradical or zwitterion is proposed as an intermediate.[7] Thus the 1–NVCz system can be represented as follows:



We propose that in the more polar solvents 1,2-dichloroethane and nitromethane, the *p*-phenylenetetramethylene intermediate shifts to more predominantly zwitterionic character compared to its diradical character in the less polar solvent toluene. This is possible because of the through-bond interaction, as has been shown in the olefin–olefin case.[4] The 1-MeOSt system gave alternating copolymer in all three different solvents, and no solvent effect was noted. This suggests that the character of the initiating *p*-phenylenetetramethylene intermediate is predominantly diradical. This is due to the reduced electron-donating character of MeOSt compared to NVCz.

The bond-forming initiation theory, which has been extended to the reaction of electrophilic quinodimethanes with electron-rich olefins, is consistent with the observed solvent effects for the 1–NVCz system.

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Registry No. 1, 121009-20-9; (1)(MeOSt) (alternating copolymer), 122122-92-3; (1)(NVCz) (alternating copolymer), 127666-94-8; 2, 3016-97-5; 3, 127666-90-4; Me_3SiCN, 7677-24-9.