7-Chloro-7-phenyl-8,8-dicyanoquinodimethane. A Novel Initiator for Cationic Polymerizations

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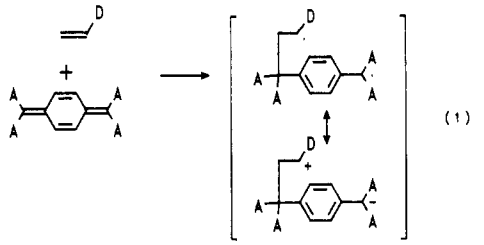
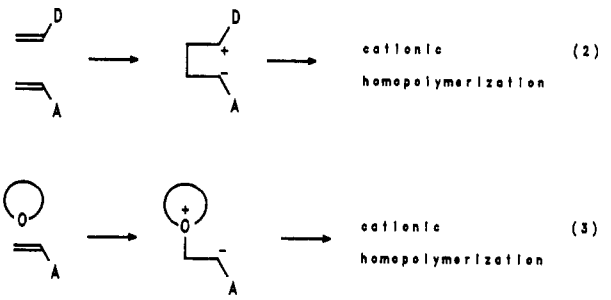
Introduction

In the bond-forming initiation theory, we have proposed that the spontaneous polymerizations observed when electron-rich and electron-poor olefins are mixed are initiated by tetramethylene intermediates.[1] These tetramethylenes can be either zwitterionic or diradical and can thus initiate either ionic homopolymerizations or free-radical copolymerization.[2] More recently, we have extended this theory to the reactions of electron-rich olefins with electrophilic quinodimethanes.[3] In this case, the intermediate resulting from bond formation between the reacting portions is a *p*-phenylenetetramethylene, either zwitterionic or diradical, depending on the terminal substituents as in the olefin–olefin case (eq 1; D = donor substituent, A = acceptor substituent).

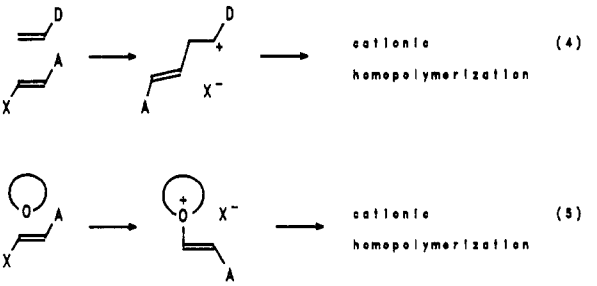


(1)

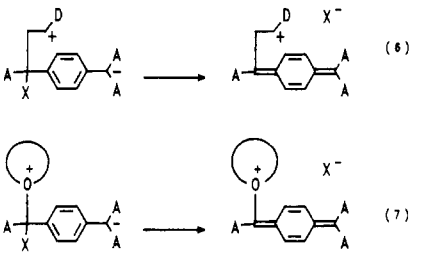
The cationic homopolymerization of vinyl monomers can thus be initiated by electrophilic multisubstituted olefins, via a zwitterionic tetramethylene[4] (eq 2). But these same electrophilic ethylenes can also initiate the ring-opening polymerization of oxacyclic monomers by a similar mechanism, as has been shown by Stille and by our group[5,6] (eq 3; D = electron-donating substitutents such as alkoxy and carbazolyl groups, A = electron-accepting substituents such as cyano or carbomethoxy group). However, all these zwitterionic intermediates have the disadvantage that the counterion in the propagation reaction is a carbanion.



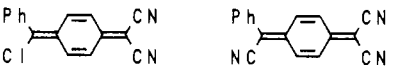
The efficiency of such zwitterionic initiators was greatly increased by using electrophilic multisubstituted olefins with a good leaving group in the β-position.[7-9] Its expulsion leaves a carbenium–gegenion pair, which initiates and propagates more effectively (eqs 4 and 5; X = leaving group such as chloride, iodide, or sulfonate).



By analogy in the quinodimethane cases, we propose that a *p*-phenylenetetramethylene zwitterion intermediate could become a more effective cationic initiator for the cationic polymerization of donor vinyl monomers and oxacyclic monomers if the electrophilic *p*-quinodimethane has a good leaving group (eqs 6 and 7). In this work,



7-chloro-7-phenyl-8,8-dicyanoquinodimethane (**1**) was synthesized as a new electrophilic quinodimethane with the leaving group Cl, and its effectiveness as a cationic initiator was compared with 7-phenyl-7,8,8-tricyanoquinodimethane (PTCQ, **2**) reported previously[10] and with Stille's results for tetracyanoquinodimethane (TCNQ).[11]



1 PTCQ 2

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 with a Thomas-Hoover capillary melting point apparatus and were uncorrected. Number-average molecular weights 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.

Monomer Synthesis. 4-(Bromomethyl)benzophenone (4): 4-Methylbenzophenone (**3**; 20 g, 0.1 mol) and 2,2′-azobis(isobutyronitrile) (AIBN; 150 mg) were dissolved in 230 mL of carbon tetrachloride, and *N*-bromosuccinimide (NBS; 18 g, 0.1 mol) was added to the solution. The mixture was refluxed with stirring for 24 h and then filtered to remove succinimide. The solvent was evaporated to obtain a yellow solid, which was recrystallized from a mixture of hexane and benzene (1:3 by volume) to give 17.3 g (63% yield) of **4** as white needles: mp 103–105 °C; IR (KBr) 3056, 3023 (ν_{CH}), 1648 (ν_{CO}), 1279 (ν_{CBr}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (m, 4 H), 7.60 (m, 1 H), 7.5 (m, 4 H), 4.53 (s, 2 H).

4-(Cyanomethyl)benzophenone (5): Sodium cyanide (5 g, 0.1 mol) was dissolved in a mixture of water (12.5 mL), ethanol (12.5 mL), and *p*-dioxane (15 mL). Compound **4** (13.8 g, 0.05 mol) was added, and the mixture was stirred at room temperature for 48 h. The reaction mixture was poured into 1 L of ice water, extracted with ether (100 mL × 2), and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove ether, resulting in a pale brown residue, which

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was dissolved in 2 mL of ethyl acetate. The resulting solution was passed through a silica gel column with a mixture of hexane and ethyl acetate (7:3 by volume) as eluent. The second elution band was collected and the solvent evaporated to give 8 g (73% yield) of **5** as white crystals: mp 57–58 °C; IR (KBr) 3061, 2958 (ν_{CH}), 2247 (ν_{CN}), 1649 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, J = 8 Hz, 2 H), 7.79 (d, J = 8 Hz, 2 H), 7.61 (t, J = 8 Hz, 1 H), 7.50 (d, J = 8 Hz, 2 H), 7.47 (d, J = 8 Hz, 2 H), 3.85 (s, 2 H). Anal. Calcd for $C_{15}H_{11}NO$: C, 81.42; H, 5.02; N, 6.33. Found: C, 81.27; H, 4.93; N, 6.08.

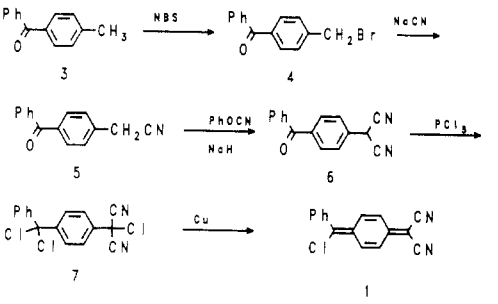
4-(Dicyanomethyl)benzophenone (6): A solution of **5** (5.0 g, 22.6 mmol) and phenyl cyanate[12] (2.38 g, 22.6 mmol) in 20 mL of tetrahydrofuran was added dropwise to the suspension of sodium hydride (1.2 g, 50 mmol) in 40 mL of tetrahydrofuran with stirring under nitrogen. After it was stirred for 24 h at room temperature, the reaction mixture was poured carefully into ice water (200 mL) and acidified with 6 N hydrochloric acid. The suspension was extracted with 1,2-dichloroethane (100 mL × 3). The combined extracts were washed with water (100 mL × 2), dried over anhydrous magnesium sulfate, and placed under reduced pressure to yield a yellow solid, which was dissolved in 100 mL of diethyl ether. The resulting ether solution was extracted with saturated sodium carbonate (100 mL × 2), and the combined extracts were acidified with concentrated hydrochloric acid to give crude **6** as a pale brown solid, which was filtered out, rinsed with water, and then dried under reduced pressure. Crude **6** was recrystallized from a mixture of benzene and hexane to give 3.2 g (57% yield) of **6** as white platelets: mp 140–141 °C; IR (KBr) 2899 (ν_{CH}), 2259 (ν_{CN}), 1649 (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (d, J = 8 Hz, 2 H), 7.80 (d, J = 8 Hz, 2 H), 7.65 (m, 3 H), 7.52 (m, 2 H), 5.19 (s, 1 H). Anal. Calcd for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.10; N, 11.37. Found: C, 78.09; H, 3.94; N, 11.00.

1-(Dichlorophenylmethyl)-4-(dicyanochloromethyl)benzene (7): Compound **6** (1.3 g, 5.3 mmol) was dissolved in 50 mL of 1,2-dichloroethane, and 3.5 g of phosphorus pentachloride was added. The resulting mixture was refluxed for 48 h. The reaction mixture was poured into 200 mL of ice water, extracted with 1,2-dichloroethane (100 mL × 2), and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to give a red viscous material, which was dissolved in 2 mL of benzene. The resulting benzene solution was passed through a silica gel column with benzene as eluent. The first light yellow elution band was collected and the solvent evaporated to give 1.4 g (78% yield) of **7** as a yellow oil, which was used without further purification: IR (NaCl) 2250 (ν_{CN}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (s, 4 H), 7.62 (m, 2 H), 7.42 (m, 3 H).

7-Chloro-7-phenyl-8,8-dicyanoquinodimethane (1): Compound **7** (0.4 g, 1.2 mmol) was dissolved in 30 mL of benzene, and 1 g of copper powder was added. The mixture was refluxed for 2 h and then filtered to remove unreacted copper and copper chloride. The filtrate was concentrated to 2 mL and passed through a silica gel column with benzene as eluent. The dark red elution band was collected and the solvent evaporated to give 0.3 g of purple solid, which was recrystallized from a mixture of benzene and hexane, yielding 0.25 g (80% yield) of **1** as purple needles: mp 159–160 °C; IR (KBr) 2213, (ν_{CN}), 1605, 1585 ($\nu_{C=C}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (dd, J = 10 and 2 Hz, 1 H), 7.54 (m, 5 H), 7.28 (dd, J = 10 and 2 Hz, 1 H), 7.21 (dd, J = 10 and 2 Hz, 1 H), 7.06 (dd, J = 10 and 2 Hz, 1 H); UV ($ClCH_2CH_2Cl$) 444 nm ($\epsilon = 2.7 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $C_{16}H_9N_2Cl$: C, 72.60; H, 3.43; N, 10.58; Cl, 13.39. Found: C, 72.69; H, 3.18; N, 10.54; Cl, 13.10.

Other Materials. *p*-Methoxystyrene (MeOSt) [bp 42 °C (0.5 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 under nitrogen. 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 under nitrogen. *N*-Vinylcarbazole (NVCz) was recrystallized from hexane. 7-Phenyl-7,8,8-tricyanoquinodimethane (PTCQ) was prepared according to the method described previously.[10] 1,3-Dioxepane (DOP) (bp 120 °C) was prepared from 1,4-butanediol and paraformaldehyde according to the method described by Astle et al.[13] and was refluxed over calcium hydride for 48 h, distilled, and stored under nitrogen. 1,3,5-Trioxane (TOX) was recrystallized from diethyl ether under nitrogen (repeated three times). Nitromethane (bp 100 °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. Tetrabutylammonium perchlorate was dried at 160 °C for 10 h under reduced pressure.

Scheme I



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

Polymerization Procedure. Given amounts of 1 (or PTCQ), a monomer (MeOSt, IBVE, CEVE, NVCz, DOP, or TOX), and a solvent (1,2-dichloroethane, toluene, or nitromethane) were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times), filled with argon, and sealed. The ampule was set in a bath at a given temperature (28 or 60 °C) for the polymerization. The reaction mixture was poured into excess hexane to precipitate the polymer; this was dissolved again in a small amount of 1,2-dichloroethane, reprecipitated in hexane, and dried under reduced pressure. When the polymeric product did not precipitate, the hexane solution was placed under reduced pressure to remove the volatile material, and then the residue was dissolved in chloroform. The chloroform solution was analyzed by using gel permeation chromatography.

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 of 7-Chloro-7-phenyl-8,8-dicyanoquinodimethane (1). The title compound 1 was successfully prepared by the synthesis route depicted in Scheme I. The bromination of *p*-methylbenzophenone (**3**) with *N*-bromosuccinimide in the presence of AIBN in refluxing carbon tetrachloride gave the bromomethyl derivative **4** in 63% yield, which was converted to the cyanomethyl derivative **5** in 73% yield by reaction with sodium cyanide. **5** was reacted with phenyl cyanate in the presence of sodium hydride in tetrahydrofuran at room temperature for 24 h to yield *p*-(dicyanomethyl)benzophenone (**6**) in 57% yield. The reaction of **6** with phosphorus pentachloride in refluxing 1,2-dichloroethane afforded **7** in 78% yield, which was dechlorinated with copper in benzene to give title compound **1** in 80% yield. Title compound **1** was recrystallized to form purple needles. The total yield in five steps was 16%.

Electron-Accepting Character. The first reduction potential, E_1, of **1** was measured by cyclic voltammetry to be −0.37 V. This is smaller than −0.11 V of 7-phenyl-7,8,8-tricyanoquinodimethane (**2**, PTCQ), indicating that **1** is less electron-poor than PTCQ. The smaller electron-accepting character of **1** compared with PTCQ can be

Table I
Homopolymerizations of Vinyl and Cyclic Monomers by 1

1, mg	donor[a] (mg)	[donor]/[1]	solvent (mL)	temp, °C	time, h	homopolymer yield, mg (%)	M_n[b]
1.3	MeOSt (60.0)	89	$(CH_2Cl)_2$ (0.5)	60[c]	24	1.0 (1.7)	3260
1.4	MeOSt (68.3)	96	CH_3NO_2 (0.5)	60[c]	27	17.7 (25.9)	6750
1.9	IBVE (110.1)	161	CH_2Cl_2 (0.5)	60	24	0	
1.0	IBVE (80.0)	217	CH_3NO_2 (0.5)	60[c]	75	44.7 (55.9)	3000
2.5	NVCZ (100.3)	58	$C_6H_5CH_3$ (5)	60[c]	24	81.7 (81.5)	10900
2.7	NVCZ (101.0)	52	$(CH_2Cl)_2$ (5)	28	28	73.0 (72.3)	10400
4.1	DOP (525.0)	343	bulk	60	45	14.5 (2.8)	1160
1.6	DOP (262.5)	171	$(CH_2Cl)_2$ (0.25)	60	94	17.5 (6.7)	4300
1.4	DOP (262.5)	171	CH_3NO_2 (0.25)	60	68	136.4 (52)	5100
1.5	TOX (222.2)	433	CH_3NO_2 (0.5)	60	126	0	

[a] Abbreviations: MeOSt = *p*-methoxystyrene, IBVE = isobutyl vinyl ether, NVCZ = *N*-vinylcarbazole, DOP = 1,3-dioxepane, TOX = 1,3,5-trioxane. [b] Determined by GPC. Polystyrene standard. Chloroform eluent. [c] At room temperature no homopolymer obtained in 24 h.

explained in terms of Hammett's substituent constant, σ_p, of cyano (σ_p = +0.66)[14] and chloro (σ_p = +0.23)[14] groups.

Polymerization. Polymerizations were carried out with various electron-rich vinyl and cyclic monomers such as *p*-methoxystyrene, isobutyl vinyl ether, *N*-vinylcarbazole, 1,3-dioxepane, and 1,3,5-trioxane. Because very electron-rich monomers are reacted with the rather electron-poor title compound, cationic homopolymerization of the former is expected.[3] Therefore only a small amount of 1 as "initiator" is mixed with an exceess of the donor monomer. The results of the polymerizations in the presence of 1 are summarized in Table I.

As to the vinyl monomers in the presence of 1, for 24 h in 1,2-dichloroethane at 60 °C, *p*-methoxystyrene gave only a trace of polymer but in the more polar solvent nitromethane gave a 26% yield. Similarly, isobutyl vinyl ether gave no polymer in 1,2-dichloroethane but in nitromethane gave a 56% yield. The more reactive *N*-vinylcarbazole gave an 81% yield of polymer, even in the nonpolar solvent toluene at 60 °C and in 1,2-dichloroethane at 28 °C gave a 72% yield.

As to the oxacyclic monomers, 1,3-dioxepane gave only low yields in bulk or in 1,2-dichloroethane but in nitromethane gave a 52% yield of polymer. The less reactive 1,3,5-trioxane gave no polymer even in nitromethane.

In contrast, the spontaneous polymerizations of vinyl monomers with PTCQ (2) yielded alternating copolymers from IBVE and NVCZ.[10] *p*-Methoxystyrene behaved similarly in giving only alternating copolymer. Accordingly, the ability of chloride to depart as a leaving group and generate a cation completely changes the polymerization mechanism from diradical to cationic. This occurs despite the overall weaker electron-poor character of 1 relative to PTCQ as demonstrated by the cyclic voltammetry results. Our proposed mechanism in eq 2 receives strong support from these results.

Our mechanism is further supported by the results for oxacyclic monomers. Despite its greater electron-poor nature, PTCQ did not polymerize 1,3-dioxepane, even in nitromethane.[10] The ability of 1 to initiate its polymerization must be traceable to the ability of chloride to act as a leaving group (eq 7).

Finally, it is also of interest to compare these results with the earlier results obtained by Stille and his colleagues with TCNQ.[11] TCNQ is much more electrophilic than either 1 or PTCQ. According to these workers, TCNQ polymerized vinyl ethers and cyclic acetals in reasonable to good yields even at room temperatures, so that TCNQ is a more active initiator than 1 or PTCQ, again presumably by way of the corresponding *p*-phenylene zwitterions (eq 1). Its greater activity parallels its more electron-deficient character.

A much more active initiator should result by replacing the Cl in 1 with a better leaving group such as a sulfonate. Experiments along these lines are in progress.

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