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Synthesis and Polymerization of 7-Alkoxycarbonyl-7,8,8-tricyanoquinodimethanes and 7,7-Bis(alkoxycarbonyl)-8,8-dicyanoquinodimethanes

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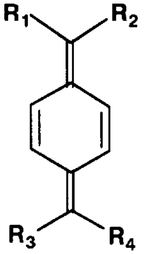
Abstract: Attempts were made to prepare novel 7-alkoxycarbonyl-7,8,8-tricyanoquinodimethanes (ethoxy(**5a**), isopropoxy(**5b**), and *tert*-butoxy(**5c**)), 7,7-bis(alkoxycarbonyl)-8,8-dicyanoquinodimethanes (ethoxy(**6a**), isopropoxy(**6b**), and *tert*-butoxy(**6c**)), and 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene(**6d**). **5c** and **6d** were obtained as yellow and orange needles, respectively, but **5a**, **5b** and **6a-c** could not be isolated as crystals. Homopolymerizations of **5c** and **6d** and their copolymerizations with styrene were studied. © 1997 Elsevier Science Ltd.

INTRODUCTION

Unsubstituted quinodimethane (QM) is so reactive that it polymerizes spontaneously even at -78 °C.[1,2] The QM is stable only in the gas phase or in a very dilute solution at very low temperature.[2] However, when the hydrogen atoms on the exocyclic carbons of the QM were substituted with cyano and/or ester groups, the substituted QM became stable (less reactive) and isolable as crystals at room temperature, e.g., 7,7,8,8-tetracyanoquinodimethane (**1**),[3] 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes (**2a** and **2b**),[3-5] 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes (**3a**, **3b**, and **3c**),[6-9] and 7,7,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes (**4a**, **4b**, and **4c**).[10] We have studied a series of these isolable electron-accepting cyano- and/or ester-substituted quinodimethanes in their polymerization behaviors. **1** carrying four cyano groups and **2b** carrying four ethoxy groups are not homopolymerizable with any initiators,[4] but **2a** carrying four methoxy groups is homopolymerizable with anionic initiator,[5] and also **1**, **2a**, and **2b** are copolymerizable as acceptor monomers with donor monomers such as styrene and some vinyl ethers in perfectly alternating fashions.[4,11,12] While, **3a-c** carrying two cyano and two ester groups, and **4a** and **4b** carrying one cyano and three ester groups except for bulky *tert*-butoxy group (**4c**) are homopolymerizable with radical and anionic initiators and weak bases, and also copolymerizable with styrene in random fashions.[6-10] These isolable electron-accepting cyano- and/or ester-substituted quinodimethanes change their polymerization behaviors depending primarily on the number of the cyano and ester groups and secondly on the kinds of alkoxy groups. As the difference in substitution mode on the electron-accepting substituted quinodimethanes significantly affects their polymerization behavior, it is expected that synthesis of a new type of cyano- and ester-subustituted quinodimethanes different from above-mentioned ones and study of their polymerization behaviors would make the relationship of their polymerizabilities with a substitution mode more clear.

In this work were described the synthesis and polymerizations of 7-ethoxycarbonyl-, 7-isopropoxycarbonyl-, and 7-*tert*-butoxycarbonyl-7,8,8-tricyanoquinodimethanes (**5a**, **5b**, and **5c**) and 7,7-bis(ethoxycarbonyl)-, 7,7-bis(isopropoxycarbonyl)-, and 7,7-bis(*tert*-butoxycarbonyl)-8,8-dicyanoquinodimethanes (**6a**, **6b**, and **6c**) and 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (**6d**).



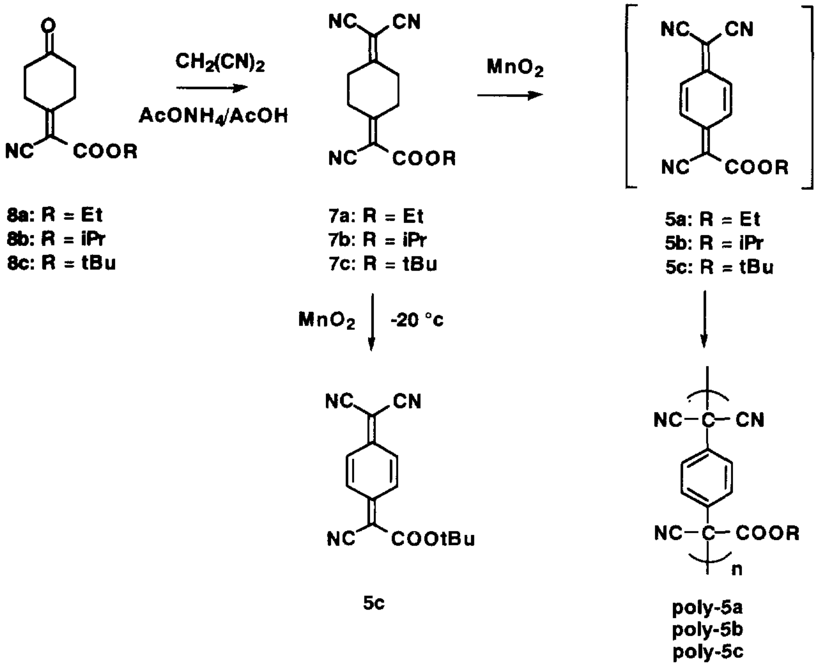
1: $R_1=R_2=R_3=R_4=CN$
2: $R_1=R_2=R_3=R_4=COOR$ (R=Me(a), Et(b))
3: $R_1=R_4=CN$, $R_2=R_3=COOR$ (R=Me(a), Et(b), Bu(c))
4: $R_1=CN$, $R_2=R_3=R_4=COOR$ (R=Et(a), iPr(b), tBu(c))
5: $R_1=R_2=R_3=CN$, $R_4=COOR$ (R=Et(a), iPr(b), tBu(c))
6: $R_1=R_2=CN$, $R_3=R_4=COOR$ (R=Et(a), iPr(b), tBu(c), =CMe_2(d))

RESULTS AND DISCUSSION

Monomer Synthesis and Electron-accepting Property

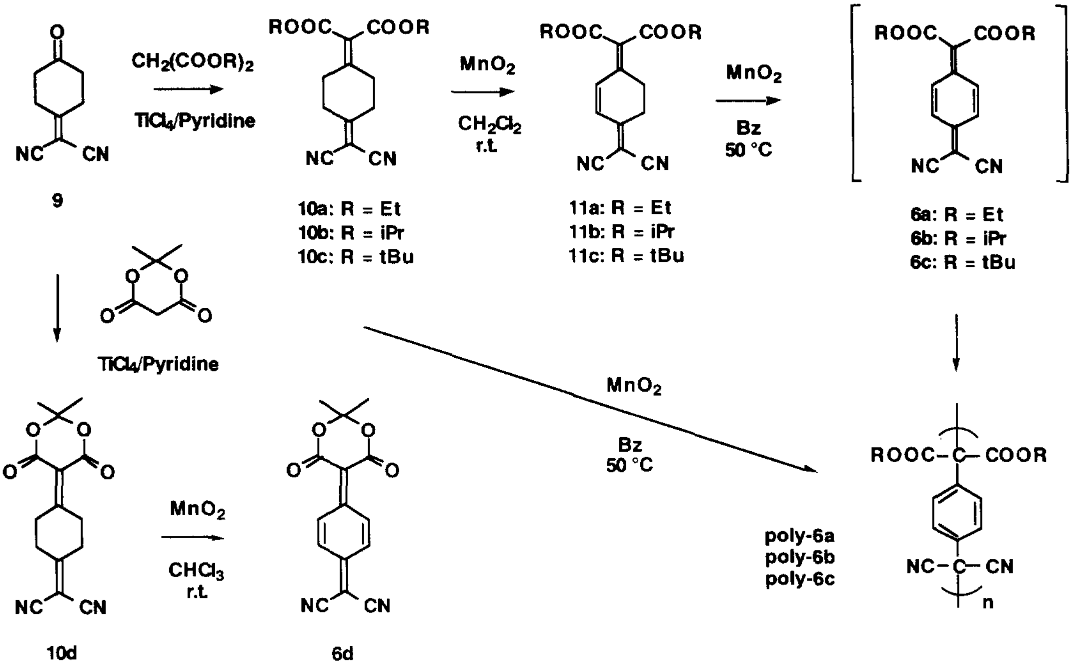
Attempts were made to prepare 7-alkoxycarbonyl-7,8,8-tricyanoquinodimethanes (**5a-c**) and 7,7-bis(alkoxycarbonyl)-8,8-dicyanoquinodimethnes (**6a-c**) with three kinds of alkoxy groups such as ethoxy, isopropoxy, and *tert*-butoxy, and 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (**6d**) via the reaction routes shown in Schemes 1 and 2, respectively. The Knoevenagel condensation of 4-[(alkoxycarbonyl)cyanomethylene]cyclohexanones (**8a-c**)[13,14] with alkyl cyanoacetates afforded 1-[(alkoxycarbonyl)cyanomethylene]-4-(dicyanomethylene)cyclohexanes (**7a-c**) in 47-75% yields. Oxidation reactions of **7a-c** with an activated manganese dioxide in benzene at room temperature gave yellow solutions, which exhibited the absorption maxima at 405 nm for **7a**, 406 nm for **7b**, and 406 nm for **7c**, corresponding to the absorptions characteristic of substituted quinodimethanes because the **3a-c**[6,7] and **4a-c**[10] solutions in benzene are reported to show absorption maxima at 397-404 and 383-384 nm, respectively. However, the yellow color of the resulting solutions faded away on removal of benzene, and pale yellow film-like products were obtained as residue, which were insoluble in benzene, chloroform, dichloromethane, tetrahydrofuran (THF), ethyl acetate, acetone, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexane, and methanol. The elemental analysis values of the film-like products were in good agreement with the calculated ones of monomeric **5a-c**. It is considered, therefore, that the film-like products are homopolymers of **5a-c** (**poly-(5a-c)**). Unfortunately, their molecular weights could not be measured because of their insolubility toward common solvents. In order to isolate monomeric **5a-c**, the reaction

Scheme 1



solutions were concentrated to the volume of about 30 mL and into them was added excess of hexane and then the resulting solutions were cooled to -20 °C. Yellow needles were obtained without fading from the reaction solution of **7c**, but a mixture of white and yellow solids was obtained from the reaction solutions of **7a** and **7b**, respectively. All attempets to isolate only yellow solids from the reaction solutions of **7a** and **7b** failed because their polymerizations took place easily at room temperature. The IR, ^{1}H NMR, and UV-Vis spectra and elemental analysis values of the yellow needles obtained from the reaction solution of **7c** strongly supported the chemical structure of monomeric **5c**. However, its melting point could not be determined exactly because of concurrent polymerization. Previously, we pointed out that reactivities of 7,8-diacyl-7,8-dicyanoquinodimethanes[15] and 11,12-dialkylthio-11,12-dicyano-2,6-naphthoquinodimethanes[16] significantly depend on the steric hindrance effect of acyl or alkylthio substituents, that is, substituted quinodimethanes with bulky substituents are less reactive. The fact that **7c** with bulky *tert*-butoxy substituent could be isolated as crystals in a monomeric state at room temperature and **7a** and **7b** with less bulky ethoxy and isopropoxy ones could not, supports our previous findings.[15,16]

1-[Bis(alkoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexanes (**10a-c**) and 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)cyclohexane (**10d**) were prepared in 24-44% yields by the Knoevenagel condensation of 4-(dicyanomethylene)cyclohexanone (**9**)[14] with alkyl malonates and with isopropylidene malonate (Meldrum's acid)[17], respectively, using titanium tetrachloride and pyridine as the dehydrating system.[18] Oxidation reactions of **10a-c** with an activated manganese dioxide in benzene at 50 °C afforded yellow solutions like as the cases of **7a-c** in their oxidation reactions and these yellow-colored solutions exhibited the characteristic UV-vis spectra for substituted quinodimethanes such as **3a-c**,[6,7] **4a-c**,[10] Scheme 2



and **5a-c**. However, the yellow color of all solutions faded away on removal of benzene to give white solids as residue in 27-35% yields. The white solids were not soluble in benzene and were partially soluble in chloroform, acetone, DMF, DMSO, and acetonitrile, and insoluble in hexane and methanol. Their elemental analysis values were in good agreement with the calculated ones of monomeric **6a-c**. The white solids were separated into two parts, chloroform-soluble and chloroform-insoluble parts. The molecular weights of the chloroform-soluble parts were measured by GPC to be 1200-1900. For the chloroform-insoluble parts, their IR spectra were almost same to those of the chloroform-soluble parts, indicating that the chloroform-insoluble parts are composed of higher molecular weight than 1900. It is concluded, therefore, that the white solids are homopolymers of **6a-c** (**poly-(6a-c)**). Low yields (27-35%) of the residue are probably due to loss of polymers with high molecular weights produced in preparation of **6a-c** by a filtration treatment because their polymers are almost insoluble in benzene. However, oxidation reactions of **10a-c** in dichloromethane at room temperature for 30 min gave 1-[bis(alkoxycarbonyl)methylene]-4-dicyanomethylene-2-cyclohexenes (**11a-c**) in 44-58% yields. Further oxidation reactions of **11a-c** with an activated manganese dioxide in benzene at 50 °C also produced **poly-(6a-c)**, indicating that **11a-c** are isolable intermediates in the course of preparation of **6a-c**. Contrary to the cases of **5a-c**, even **6c** bearing more bulky *tert*-butoxy group as well as **6a** and **6b** bearing less bulky ethoxy and isopropoxy groups were too reactive to be isolated as pure crystalline materials, though **6a-c** exist as monomeric state in a dilute solution as shown by UV-vis spectral measurement. Fortunately, oxidation reaction of **10d** with an activated manganese dioxide in chloroform at room temperature gave **6d** as orange needles in 80% yield. Its IR, ^{1}H NMR, and UV-vis spectra and elemental analysis values strongly supported the chemical structure of monomeric **6d**. However, its melting point could not be determined exactly because of concurrent polymerization, as well as **5c**. Introduction of more bulky and cyclic substituent such as isopropylidene malonate on the quinonoid structure made 7,7-bis(alkoxycarbonyl)-8,8-dicyanoquinodimethane less reactive and easily obtainable as pure crystals at room temperature.

Electron-accepting properties of **5c** and **6d** isolated as crystals were estimated as the values of the first reduction potential, E_1, by cyclic voltammetry using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as solvent and Ag/AgCl as reference electrode. The value for **5c** and **6d** were measured to be -0.19 V and +0.13 V, respectively, and also for comparison those of **1**, **3b**, **4a**, and **2b** were measured to be +0.16 V, -0.22 V, -0.66 V, and -0.86 V, respectively. **5c** is an intermediate in electron-accepting property between **1** and **3b** as expected from the difference in the electron-accepting character between the cyano (σ_p= 0.45)[19] and ester (σ_p= 0.66)[19] groups and in the number of them. However, **6d** has the stronger electron-accepting property than both **3b** and **5c**, and the same one as **1**. This is just like the unexpectedly high acidity of Meldrum's acid because of its cyclic structure.

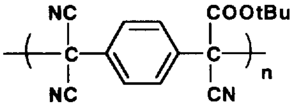
Polymerization

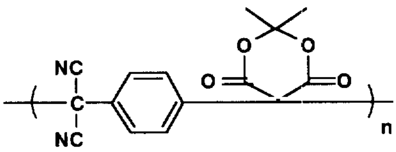
Polymerizations of only **5c** and **6d** except for **5a**, **5b**, and **6a-c**, which could not be obtained as crystals in pure state, were studied. Homopolymerizations of **5c** and **6d** were attempted with the radical initiator 2,2'-azobis(isobutyronitrile) (AIBN), the anionic initiator butyllithium, the weak bases triethylamine and pyrrolidine, and cationic initiator boron trifluoride etherate in order to investigate their polymerizability. The results of the polymerizations are summarized in Table 1. The polymerization systems became heterogeneous with the time because of deposition of polymer. All polymers were obtained as white solids, which were insoluble in benzene, chloroform, dichloromethane, THF, acetone, ethyl acetate, DMF, DMSO, hexane, and methanol. The elemental analysis values of the products obtained were in good agreement with the calculated ones for the homopolymers of **5c** and **6d**. IR spectrum of a homopolymer of **5c** exhibited absorption bands at 2230 cm^{-1} due to the nitrile group, 1717 and 1242 cm^{-1} due to the ester group, 1480, 1434, and 1396 cm^{-1} due to the

Table 1. Homopolymerizations of **5c** and **6d** with Various Initiators.

Run no.	**5c** or **6d** mg	Initiator (**I**)	[**5c** or **6d**] /[**I**]	Solv. mL	Temp. °C	Time h	Conv. %
			5c				
1	21.5	AIBN	12	Benzene, 20	50	1	75
2	21.9	BuLi	20	Toluene, 30	0	1	100
3	21.8	Et_3N	17	Toluene, 30	0	1	89
4	22.2	pyrrolidine	16	Benzene, 20	rt	1	100
5	21.5	$BF_3 \cdot Et_2O$	20	CH_2Cl_2, 30	0	1	0
			6d				
6	31.0	AIBN	38	$CHCl_3$, 4.5	60	20	57
7	53.1	BuLi	59	Toluene, 20	0	2	73
8	50.9	Et_3N	50	Toluene, 17	0	2	90
9	54.5	pyrrolidine	54	Toluene, 20	0	2	89
10	54.7	$BF_3 \cdot Et_2O$	50	CH_2Cl_2, 20	0	2	0

carbon-carbon double bonds of the aromatic ring, and 823 cm^{-1} due to out-of-plane deformation of *para*-disubstituted benzene, characteristic of a two-adjacent-hydrogen system, respectively. IR spectrum of a homopolymer of **6d** exhibited absorption bands at 2220 cm^{-1} due to the nitrile group, 1745, 1710 and 1287 cm^{-1} due to the ester group, 1523, 1478, 1394, and 1374 cm^{-1} due to the carbon-carbon double bonds of the aromatic ring, and 786 cm^{-1} due to out-of-plane deformation of *para*-disubstituted benzene, characteristic of a two-adjacent-hydrogen system, respectively. Moreover, absorption peaks at 1519 cm^{-1} observed in **5c** and **6d** due to conjugated carbon-carbon double bonds disappear in both polymers. Further characterizations except for IR spectra and elemental analysis were not performed because of their insolubility. It can be pointed out from the Table 1 that **5c** and **6d** are homopolymerizable with radical and anionic initiators, and weak bases. Polymerizations of quinodimethanes are known to occur through the exocyclic methylene groups or the disubstituted methylene ones with reversion of the ring to the stable aromatic structure.[1,2,4-12] It is considered therefore that the polymers obtained with AIBN, butyllithium, and weak bases have the following structures:





5a and **6d** were not polymerizable with boron trifluoride etherate under the experimental conditions shown in Table 1, as well as **3a-c** and **4a-c** reported previously.[6,7,10] These polymerization behaviors of **5c** and **6d** are similar to those of homopolymerizable substituted quinodimethanes such as **3a-c** and **4a-c**.[6-8,10]

The copolymerizations of **5c** with styrene in the presence of AIBN in benzene at 50 °C and of **6d** with styrene in the absence and presence of AIBN in chloroform at 60 °C were carried out. The results of the copolymerizations are summarized in Table 2. All polymers were obtained as white powders. Polymers obtained by the copolymerization of **5c** with styrene are insoluble in methanol, benzene, toluene, chloroform, dichloromethane, acetone, ethyl acetate, THF, DMF, DMSO, hexane and methanol. The IR spectra and elemental analysis values of polymers obtained were in good agreement with those of the homopolymer of **5c**. Unfortunately, further characterizations except for IR spectrum and elemental analysis were not performed because of their insolubility. All polymers obtained are composed of only **5c** unit regardless of monomer feed ratios, indicating that **5c** is more highly reactive monomer than styrene. On the other hand, polymers obtained by the copolymerization of **6d** with styrene are soluble in chloroform, dichloromethane, THF, acetone, DMF, and DMSO, but insoluble in hexane, methanol, and diethyl ether. The copolymers of **6d** with styrene were alwalys composed of about 50 mol% of the **6d** unit regardless of the monomer feed ratios. The ^{1}H NMR spectrum in chloroform-*d* of the copolymer of Run no. 5 is shown in Figure 1, where each peaks is assingnable to the respective protons of the chemical structure illustrated therein. The methine and methylene protons of the styrene monomer unit in the copolymer appears at the regions of 2.0-5.3 ppm, indicating that they are much more subject to deshielding than the corresponding ones of polystyrene, genarally appearing at the region of 1-2 ppm.[20] Presumably, the deshielding arises from an electron withdrawal by the neighboring dicyanomethylene and isopropylidene malonate group when the styrene unit is sandwiched between **6d** units in the copolymer. It is ,therefore, concluded that **6d** copolymerizes as an acceptor monomer with styrene in a perfectly alternating fashion and it reacts at the exocyclic methylene sites. The methine and methylene protons in the ^{1}H NMR spectrum are observed as broad peaks, indicative of coexistence of four kinds of monomer units placements in

Table 2. Copolymerizations of **5c** and of **6d** with Styrene

Run	Monomer Feed			AIBN	Time	Conv.	Copolym. Compn.				M_n[c]
no.	**5c** or **6d**	Styrene	**5c** or **6d**	mg	min	%	Anal.			**5c** or **6d**	/10^4
	mg	mg	mol%				%H	%C	%N	mol%	
			copolymerization[a] of **5c** with styrene at 50 °C								
1	29.2	1132.1	0.9	0.1	20	2.1	5.66	68.81	15.04	100	-
2	29.6	48.9	18.4	0.1	20	33.3	5.49	68.85	15.13	100	-
3	29.6	12.4	47.1	0.1	20	80.7	5.81	68.75	15.20	100	-
			copolymerization[b] of **6d** with styrene at 60 °C								
4	35.0	87.0	12.5	-	30	32.9	3.78	71.76	7.16	48.8	2.4
5	96.1	80.9	30.6	-	90	40.4	3.43	71.16	7.35	51.3	5.4
6	153.2	95.1	37.2	0.6	20	3.7	2.93	71.92	7.11	48.2	5.2
7	150.2	53.9	50.4	-	45	25.9	3.90	71.59	7.21	49.5	1.7
8	159.6	44.1	57.6	-	90	24.3	4.27	71.34	7.31	50.8	4.2
9	124.6	22.2	67.7	-	90	12.3	3.68	71.23	7.36	51.3	9.6

a Solvent: benzene, 30 mL.

b Solvent: chloroform, 3 mL for Run no. 4; 9 mL for Run nos. 7 and 9; 10 mL for Run nos. 5, 6, and 8.

c Determined by GPC using THF as an eluent and standard polystyrenes as reference.

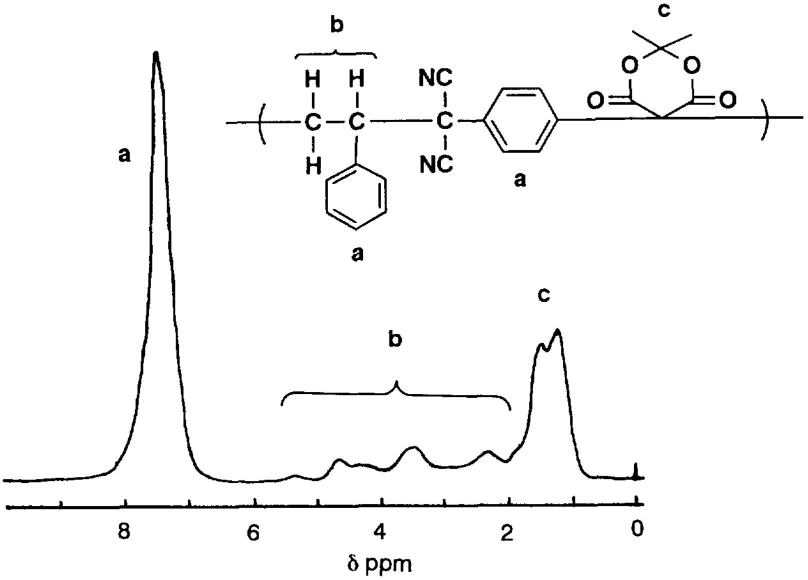
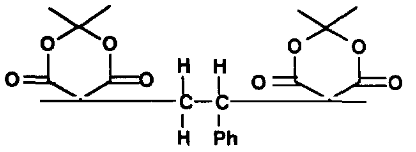
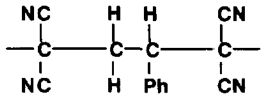
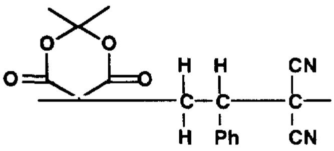


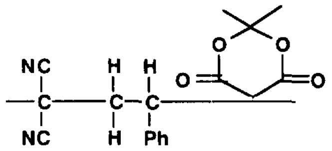
Figure 1. ^{1}H NMR spectrum for the copolymer (Run no. 5 in Table 2) of **6d** with styrene in chloroform-*d*.

the copolymer as shown in the following:









It is suggested, therefore, that the propagation mode of the alternating copolymerization of **6d** with styrene is chain addition like a conventional radical copolymerization. Copolymerization behavior of **6d** with styrene is very different from that of **5c** with styrene. Previously, we pointed out that polymerization fashion depends significantly upon homopolymerizability of substituted quinodimethanes, that is, homopolymerizable substituted quinodimethanes such as **3a-c** and **4a-b** copolymerizes with styrene in the random fashion,[7,10] while nonhomopolymerizable and poorly homopolymerizable ones such as **1**, **2a-b** and **4c** copolymerizes with styrene in the alternating fashion,[4,10-12] and that the very stable and unreactive polymer radical with the terminal unit of the more conjugative monomer undergoes a cross propagation under the favor of a strong charge-transfer interaction with the comonomer such as styrene.[21,22] As **5c** is highly homopolymerizable, but has weak electron-accepting property, it is considered that random copolymerization (exclusively homopolymerization of **5c**) took place. On the other hand, as **6d** (E_1 = + 0.13 V) is almost as strongly electron-accepting as **1**(E = +0.16 V), it is considered that alternating copolymerization of **6d** with styrene took place by the favor of extremely greater polar interaction between **6d** and styrene even though **6d** is homopolymerizable. It is pointed out therefore that polar interaction plays a dominant role in determining the alternating fashion of copolymerization.

In summary, **5c** and **6d** were successfully prepared as yellow and orange needles, respectively, in pure state. **6d** is as strongly electron-accepting as **1**. **5c** and **6d** were homopolymerizable with radical and anionic initiartors, and weak bases such as triethylamine and pyrrolidine, but not with cationic initiator. The copolymerizations of **5c** with styrene afforded exclusively homopolymer of **5c** regardless of monomer feed ratios, but copolymerization of **6d** with styrene gave their alternating copolymers even though **6d** is homopolymerizable, probably due to great polar interaction between **6d** and styrene. It was pointed out that polar interaction is an important factor for the alternating copolymerization.

EXPERIMENTAL

Copolymer compositions were established by elemental analysis. The number-average molecular weights, M_n, of the homopolymers (chloroform-soluble parts) and copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as a reference and THF as an eluent without correction. ^{1}H NMR measurement was carried out in chloroform-*d* with tetramethylsilane as an internal standard. The first reduction potentials of **5c** and **6d** were determined by the voltammetric measurement at room temperature at a scanning rate of 100 mV/s using a dichloromethane as the solvent containing tetrabutylammonium perchlorate (0.1 mol/L) as the supporting electrolyte, and Ag/AgCl, glassy carbon, and platinum wire were used as reference, working, and counter electrodes, respectively. A Yanaco micro melting point apparatus was used for the melting point measurement, a JEOL JNM-EX270 FT NMR spectrometer for ^{1}H NMR spectroscopy, JASCO IR-700 and JASCO UVIDEC-430B spectrometers for infrared and UV-Vis spectroscopy, respectively, a Yanaco CHN Corder MT-3 for elemental analysis, GPC Tosoh HLC-803D with a series of four columns (Tosoh G2000H, G2500H, G3000H, and G4000H) for measuring number average molecular weights, and a Yanaco New Cyclic Voltammetric Analyzer VMA-010 for measuring first reduction potentials, respectively.

1-[(Alkoxycarbonyl)cyanomethylene]-4-(dicyanomethylene)cyclohexanones (7a-c)

4-[(Alkoxycarbonyl)cyanomethylene]cyclohexanones (**8a-c**) (7.1 mmol) and malononitrile (7.7 mmol) were refluxed in the presence of 0.24 g of ammonium acetate and 0.6 g of acetic acid in 50 ml of benzene using a Dean-Stark water separator to isolate water formed for 26 h. The reaction mixture was washed with 30 mL of saturated sodium chloride aqueous solution and 30 mL of saturated sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove solvent to give **7a-c**, which were recrystallized from isopropyl ether to afford white needles.

1-[Cyano(ethoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexanone (**7a**). Compound **7a** was prepared in a 75% yield from 4-[cyano(ethoxycarbonyl)methylene]cyclohexanone (**8a**)[13,14]: mp 127.0-128.0 °C; IR (KBr) ν_{CH} 2948, ν_{CN} 2210, $\nu_{\mathrm{C=O}}$ 1687, $\nu_{\mathrm{C=C}}$ 1570, $\nu_{\mathrm{C\text{-}O}}$ 1255, 1089 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.31 (q, *J* = 7.26 Hz, 2H), 3.32 (t, *J* = 6.93 Hz, 2H), 3.03 (s, 4H), 2.92 (t, *J* = 6.93 Hz, 2H), 1.36 (t, *J* = 7.26 Hz, 3H). Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87%; H, 5.14%; N, 16.45%; O, 12.54%. Found: C, 65.61%; H, 5.16%; N, 16.52%.

1-[Cyano(isopropoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexanone (**7b**). Compound **7b** was prepared in a 47% yield from 4-[cyano(isopropoxycarbonyl)methylene]cyclohexanone (**8b**)[13]: mp 116.0-117.0 °C; IR (KBr) ν_{CH} 2876, ν_{CN} 2208, $\nu_{\mathrm{C=O}}$ 1690, $\nu_{\mathrm{C=C}}$ 1574, $\nu_{\mathrm{C\text{-}O}}$ 1256, 1084 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.12 (m, *J* = 6.27 Hz, 1H), 3.31 (t, *J* = 6.93 Hz, 2H), 2.98 (s, 4H), 2.92 (t, *J* = 6.93 Hz, 2H), 1.34 (t, *J* = 6.27 Hz, 6H). Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90%; H, 5.62%; N, 15.60%; O, 11.88%. Found: C, 66.95%; H, 5.53%; N, 15.62%.

1-[Cyano(*tert*-butoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexanone (**7c**). Compound **7c** was prepared in a 74% yield from 4-[cyano(*tert*-butoxycarbonyl)methylene]cyclohexanone (**8c**)[10]: mp 134.0-135.0 °C; IR (KBr) ν_{CH} 2944, ν_{CN} 2196, $\nu_{\mathrm{C=O}}$ 1686, $\nu_{\mathrm{C=C}}$ 1519, $\nu_{\mathrm{C\text{-}O}}$ 1239, 1127 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.28 (t, *J* = 6.93 Hz, 2H), 2.96 (s, 4H), 2.91 (t, *J* = 6.93 Hz, 2H), 1.54 (s, 9H). Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82%; H, 6.06%; N, 14.82%; O, 11.30%. Found: C, 68.10%; H, 6.21%; N, 14.71%.

7-Alkoxycarbonyl-7,8,8-tricyanoquinodimethanes (5a-c)

Compounds **7a-c** (100 mg) were dissolved in 50 mL of benzene, and then into the resulting solution was added 0.83 g of an activated manganese dioxide (available from Aldrich Co.) and 0.50 g of molecular sieves 3A and stirred for 1 hr at room temperature. The reaction mixture was filtered to remove insoluble solids to give a yellow solution, the color of which gradually faded with evaporation of benzene and, upon complete evaporation of solvent, to give pale yellow films. The residue films were triturated with excess of diethyl ether and then collected by the centrifugation method and dried under reduced pressure until a constant weight was reached. All products were obtained as pale yellow films, which were insoluble in benzene, chloroform, methanol, ethyl acetate, acetone, THF, methanol, and hexane. The molecular weights of the films could not be measured because of their insolubility.

7-Ethoxycarbonyl-7,8,8-tricyanoquinodimethane (**5a**): yield 27%: IR (KBr) ν_{CH} 3062, 2948, ν_{CN} 2232, $\nu_{C=O}$ 1726, $\nu_{C\text{-}O}$ 1231 cm^{-1}. Calcd for $(C_{14}H_9N_3O_2)_n$: C, 66.93%; H, 3.62%; N, 16.72%; O, 12.78%. Found: C, 66.81%; H, 3.78%;N, 16.61%.

7-Isopropoxycarbonyl-7,8,8-tricyanoquinodimethane (**5b**): yield 17%: IR (KBr) ν_{CH} 3066, 2948, ν_{CN} 2232, $\nu_{C=O}$ 1717, $\nu_{C\text{-}O}$ 1239 cm^{-1}. Calcd for $(C_{15}H_{11}N_3O_2)_n$: C, 67.91%; H, 4.19%; N, 15.84%; O, 12.06%. Found: C, 67.86%; H, 4.22%; N, 15.78%.

7-*tert*-Butoxycarbonyl-7,8,8-tricyanoquinodimethane (**5c**): yield 22%: IR (KBr) ν_{CH} 3062, 2946, ν_{CN} 2230, $\nu_{C=O}$ 1717, $\nu_{C\text{-}O}$ 1242 cm^{-1}. Calcd for $(C_{16}H_{13}N_3O_2)_n$: C, 68.80%; H, 4.70%; N, 15.04%; O, 11.46%. Found: C, 68.85%; H, 4.66%; N, 15.11%.

Compounds **7a-c** (100 mg) were dissolved in 100 mL of benzene, and then heated at 50 °C. Into the resulting solution was added 0.83 g of an activated manganese dioxide and stirred for 5 min. After filtration a yellow filtrate was placed under reduced pressure to evaporate the solvent until its volume amounted to about 30 mL. Into the resulting solution was added 150 mL of hexane and chilled to -20 °C for overnight. The mixture of white and yellow solids for 7-ethoxycarbonyl- and 7-isopropoxycarbonyl-7,8,8-tricyanoquinodimethanes (**5a** and **5b**) and the yellow needles for 7-*tert*-butoxycarbonyl-7,8,8-tricyanoquinodimethane (**5c**) were filtered while cold, recovering them in 20-30 % yields. The white products were insoluble in common organic solvents as well as above-mentioned case.

7-Ethoxycarbonyl-7,8,8-tricyanoquinodimethane (**5a**): yield 24%: IR (KBr) ν_{CH} 3062, 2948, ν_{CN} 2232, $\nu_{C=O}$ 1726, $\nu_{C\text{-}O}$ 1231 cm^{-1}. Calcd for $(C_{14}H_9N_3O_2)_n$: C, 66.93%; H, 3.62%; N, 16.72%; O, 12.78%. Found: C, 66.82%; H, 3.50%; N, 16.56%.

7-Isopropoxycarbonyl-7,8,8-tricyanoquinodimethane (**5b**): yield 14%: IR (KBr) ν_{CH} 3066, 2948, ν_{CN} 2232, $\nu_{C=O}$ 1717, $\nu_{C\text{-}O}$ 1239 cm^{-1}. Calcd for $(C_{15}H_{11}N_3O_2)_n$: C, 67.91%; H, 4.19%; N, 15.84%; O, 12.06%. Found: C, 67.85%; H, 4.16%; N, 15.80%.

7-*tert*-Butoxycarbonyl-7,8,8-tricyanoquinodimethane (**5c**): yield 26%, mp could not be determined because of concurrent polymerization: IR (KBr) ν_{CH} 2944, ν_{CN} 2196, $\nu_{C=O}$ 1686, $\nu_{C=C}$ 1519, $\nu_{C\text{-}O}$ 1239 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.55 (d, J = 9.5 Hz, 1H), 7.59 (d, J = 4.6 Hz, 1H), 7.45 (d, J = 9.9 Hz, 1H), 7.41 (d, J = 2.3 Hz, 1H), 1.60 (s, 9H); UV(benzene): 406 (ε = 3.80 x 10^4) nm. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80%; H, 4.70%; N, 15.04%; O, 11.46%. Found: C, 68.10%; H, 4.82%; N, 15.11%.

1-[Bis(alkoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexanes (10a-c)

Titanium tetrachloride (16 mL, 146 mmol) in 31 mL of carbon tetrachloride was added dropwise under nitrogen to 190 mL of dry tetrahydrofuran (THF) with stirring and cooling at ice bath. This gives a bright yellow precipitate after an exothermic reaction. Then, into the yellow mixture were added 4-(dicyanomethylene)cyclohexanone (**9**)[14] (62 mmol) and alkyl malonate or isopropylidene malonate[17] (62 mmol). To the resulting brown suspension was added dropwise 24 mL (300 mmol) of pyridine in 26 mL of THF over 30 min, and the reaction mixture was stirred at room temperature for 3 days, then quenched with 300 mL of water and 200 mL of dichloromethane. The layers were separated. The aqueous layer was extracted three times with 200 mL of chloroform and the combined organic fractions were successibly washed with 100 mL of saturated sodium chloride aqueous solution, 100 mL of saturated sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent to give a yellow viscous oil. For the **10a-c**, the yellow oil was dissolved in a small amount of dichloromethane and the resulting solution was passed through a silica gel column using dichloromethne as an eluent. The first elution band was collected and placed under reduced pressure to remove solvent to give **10a-c** as white solids, which were recrystallized from hexane for **10a-c** to give white needles. For the **10d**, the yellow oil was recrystallized from acetone to give white needles.

1-[Bis(ethoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexane (**10a**). Compound **10a** was prepared in a 38% yield from **9** and diethyl malonate: mp 102.5-103.5 °C; IR (KBr) ν_{CH} 2946, ν_{CN} 2210, $\nu_{C=O}$ 1671, $\nu_{C=C}$ 1602, 1561, ν_{C-O} 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.31 (q, J = 7.26 Hz, 4H), 2.93 (m, 8H), 1.33 (t, J = 7.26 Hz, 4H). Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56%; H, 6.01%; N, 9.26%; O, 21.17%. Found. C, 63.65%; H, 5.95%; N, 9.18%.

1-[Bis(isoproxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexane (**10b**). Compound **10b** was prepared in a 30% yield from **9** and diisopropyl malonate[23]: mp 110.0-111.0 °C; IR (KBr) ν_{CH} 2940, ν_{CN} 2210, $\nu_{C=O}$ 1676, $\nu_{C=C}$ 1613, 1570, ν_{C-O} 1207 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.13 (m, J = 6.26 Hz, 2H), 2.86 (m, 8H), 1.29 (t, J = 6.26 Hz, 12H). Calcd for $C_{18}H_{22}N_2O_4$: C, 65.43%; H, 6.73%; N, 8.47%; O, 19.37%. Found. C, 65.64%; H, 6.80%; N, 8.52%.

1-[Bis(*tert*-butoxycarbonyl)methylene]-4-(dicyanomethylene)cyclohexane (**10c**). Compound **10c** was prepared in a 24% yield from **9** and di(*tert*-butyl) malonate[23]: mp 130.5-133.5 °C; IR (KBr) ν_{CH} 2940, ν_{CN} 2212, $\nu_{C=O}$ 1671, $\nu_{C=C}$ 1615, 1567, ν_{C-O} 1271 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85 (m, 4H), 2.83 (m, 4H), 1.51 (s, 18H). Calcd for $C_{20}H_{26}N_2O_4$: C, 67.01%; H, 7.33%; N, 7.81%; O, 17.85%. Found. C, 67.06%; H, 7.30%; N, 7.78%.

1-(2,2-Dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)cyclohexane (**10d**). Compound **10d** was prepared in a 44% yield from **9** and isopropylidene malonate[17]: mp 119.0-120.0 °C; IR (KBr) ν_{CH} 2904, ν_{CN} 2214 and 2170, $\nu_{C=O}$ 1687, $\nu_{C=C}$ 1571, ν_{C-O} 1281 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.36 (t, J = 6.60 Hz, 4H), 2.98 (t, J = 6.60 Hz, 4H), 1.75 (s, 6H). Calcd for $C_{15}H_{14}N_2O_4$: C, 62.92%; H, 4.94%; N, 9,79%; O, %. Found. C, 62.94%; H, 4.39%; N, 9.98%.

7,7-Bis(alkoxycarbonyl)-8,8-dicyanoquinodimethanes (6a-c)

Compounds **10a-c** (200 mg) were dissolved in 100 mL of dichloromethane, and then into the resulting solutions was added 1.0 g of an activated manganese dioxide. The resulting mixture was stirred at room temperature for 20 min. The filtrate was placed under reduced pressure to remove solvent to obtain a pale yellow viscous oil, which was dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column using dichloromethane as an eluent. The pale yellow elution band was collected and placed under reduced pressure to remove solvent to give pale yellow solids, which were identified to be 1-[bis(alkoxycarbonyl)methylene]-4-dicyanomethylene-2-cyclohexenes (**11a-c**). Recrystallization of all **11a-c** from a mixture solution of benzene and hexane gave pale yellow needles.

1-[Bis(ethoxycarbonyl)methylene]-4-dicyanomethylene-2-cyclohexene (**11a**): yield 44%; mp 129.7-131.0 °C; IR (KBr) ν_{CH} 2944, ν_{CN} 2206, $\nu_{C=O}$ 1693, $\nu_{C=C}$ 1674, ν_{C-O} 1205 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.56 (d, *J* = 9.9 Hz, 1H), 7.03 (d, *J* = 9.9 Hz, 1H), 4.31 (q, *J* = 7.26 H, 4H), 2.93 (m, 4H), 1.33 (t, *J* = 7.26 H, 6H): UV(CHCl$_3$) 334 (ε = 3.1 x 10^4) nm. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99%; H, 5.38%; N, 9.32%; O, 21.31%. Found: C, 63.52%; H, 5.40%; N, 9.12%.

1-[Bis(isopropoxycarbonyl)methylene]-4-dicyanomethylene-2-cyclohexene (**11b**): yield 53%; mp 130.0-131.5 °C; IR (KBr) ν_{CH} 2944, ν_{CN} 2204, $\nu_{C=O}$ 1677, $\nu_{C=C}$ 1544, ν_{C-O} 1245, 1203, 1092 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.56 (d, *J* = 9.9 Hz, 1H), 6.99 (d, *J* = 9.9 Hz, 1H), 5.17 (m, 2H), 1.31 (d, *J* = 6.27 H, 6H), 1.30 (d, *J* = 6.27 Hz, 6H): UV (CHCl$_3$) 336 (ε = 2.8 x 10^4) nm. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.83%; H, 6.15%; N, 8.53%; O, 19.49%. Found: C, 65.71%; H, 6.10%; N, 8.41%.

1-[Bis(*tert*-butoxycarbonyl)methylene]-4-dicyanomethylene-2-cyclohexene (**11c**): yield 58%; mp 116.0-118.0 °C; IR (KBr) ν_{CH} 2942, ν_{CN} 2206, $\nu_{C=O}$ 1673, $\nu_{C=C}$ 1549, ν_{C-O} 1142, 1255 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.57 (d, *J* = 9.9 Hz, 1H), 6.98 (d, *J* = 9.9 Hz, 1H), 2.91 (m, 4H), 1.53 (s, 18H): UV(CHCl$_3$) 337 (ε = 2.58 x 10^4) nm. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.39%; H, 6.80%; N, 7.86%; O, 17.95%. Found: C, 67.75%; H, 7.09%; N, 7.68%.

Compounds **10a-c** (100 mg) were dissolved in 100 mL of benzene, and then into the resulting solutions was added 1.0 g of an activated manganese dioxide. The mixture was stirred under nitrogen at 50 °C for 5 min, and then the reaction mixture was filtered to remove insoluble solids to give a yellow solution, the color of which gradually faded with evaporation of benzene and, upon complete evaporation of solvent, to give the white solid. The residue solid was triturated with excess of hexane and then collected by the centrifugation method and dried under reduced pressure until a constant weight was reached. All products were obtained as white powders. The products obtained were characterized as follows.

7,7-Bis(ethoxycarbonyl)-8,8-dicyanoquinodimethane (**6a**): yield 27.2%; IR (KBr) ν_{CH} 2944, ν_{CN} 2192, $\nu_{C=O}$1707, ν_{C-O} 1243, 1019 cm^{-1}. Calcd for $(C_{16}H_{14}N_2O_4)_n$: C, 64.42%; H, 4.74%; N, 9.39%; O, 21.45%. Found: C, 64.40%; H, 4.66%; N, 9.45%. M_n (chloroform-soluble part) = 1200. ^{1}H NMR (CDCl$_3$) (chloroform-soluble part) δ 7.8-6.9 (broad 4H), 4.6-4.2 (br 4H), 1.5-1.2 (br 6H).

7,7-Bis(isoproxycarbonyl)-8,8-dicyanoquinodimethane (**6b**): yield 35.4%; IR (KBr) ν_{CH} 2944, ν_{CN} 2192, $\nu_{C=O}$ 1703, $\nu_{C\text{-}O}$ 1252, 1087 cm^{-1}. Calcd for $(C_{18}H_{18}N_2O_4)_n$: C, 66.24%; H, 5.57%; N, 8.58%; O, 19.61%. Found: C, 66.11%; H, 5.49%; N, 8.55%. M_n (chloroform-soluble part) = 1900. ^{1}H NMR ($CDCl_3$) (chloroform-soluble part) δ 7.5-7.0 (broad 4H), 5.5-5.0 (br 2H), 1.7-1.2 (br 12H).

7,7-Bis(*tert*-butoxycarbonyl)-8,8-dicyanoquinodimethane (**6c**): yield 32.7%; IR (KBr) ν_{CH} 2942, ν_{CN} 2192, $\nu_{C=O}$ 1705, $\nu_{C\text{-}O}$ 1269, 1141 cm^{-1}. Calcd for $(C_{20}H_{22}N_2O_4)_n$: C, 67.77%; H, 6.27%; N, 7.90%; O, 18.06%. Found: C, 67.81%; H, 6.80%; N, 7.93%. M_n (chloroform-soluble part) = 1550. ^{1}H NMR ($CDCl_3$) (chloroform-soluble part) δ 7.3-7.0 (broad 4H), 1.7-1.4 (br 18H).

1-(2,2-Dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (6d)

Compound **10d** (532 mg) was dissolved in 1000 mL of chloroform, and then into the resulting solution was added 2.52 g of activated manganese dioxide and 5.68 g of molecular sieves 3A. The mixture was stirred under nitrogen at room temperature for 4 hr, and then the reaction mixture was filtered to remove insoluble solids to give a yellow solution. It was placed under reduced pressure to evaporate the solvent until its volume amounted to about 300 mL. The resulting solution was passed through a silica gel column using chloroform as an eluent. The yellow elution band was collected and placed under reduced pressure to remove solvent until its volume amounted to about 150 mL and then into the resulting solution was added 200 mL of hexane and chilled to -20 °C for overnight. **6d** (426 mg, 80.5% yield) was obtained as orange needles: mp could not be determined because of concurrent polymerization; IR (KBr) ν_{CH} 2954, ν_{CN} 2200, $\nu_{C=O}$ 1678, $\nu_{C=C}$ 1520, $\nu_{C\text{-}O}$ 1259 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.40 (d, J = 10.2 Hz, 2H), 7.49 (d. J = 10.2 Hz, 2H), 1.80 (s, 6H); UV($CHCl_3$) 410 ($\varepsilon = 4.89 \times 10^4$) nm. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83%; H, 3.58%; N, 9.92%; O, 22.67%. Found: C, 63.66%; H, 3.47%; N, 9.86%.

Other Materials

AIBN was recrystallized from methanol. Commercial butyllithium (1.6 *M* in hexane) and activated manganese dioxide (Aldrich Co.) were used without further purification. Styrene was washed with 2 % sodium hydroxide aqueous solution and water and dried over anhydrous magnesium sulfate for 1 day. Its supernatant was dried again over calcium hydride with stirring at room temperature for 12 h and distilled under reduced pressure. Benzene (bp 80 °C) and toluene (bp 110 °C) were washed in sequence with concentrated sulfuric acid, water, a 5% aqueous sodium hydroxide solution, and again water, dried over anhydrous calcium chloride, refluxed over metal sodium for 12 h, and then distilled. Dichloromethane (bp 40 °C), chloroform (bp 61 °C), and carbon tetrachloride (bp 75 °C) were refluxed over calcium hydride for 12 h and then distilled. Tetrahydrofuran (THF; bp 65 °C) was refluxed over lithium aluminum hydride for 12 h and distilled, and then the distillate was distilled again over benzophenone-sodium. Pyridine (bp 116 °C), pyrrolidine (bp 87 °C), and triethylamine (bp 89 °C) were distilled over potassium hydroxide. Titanium tetrachloride (bp 136 °C) was distilled over copper powder under nitrogen. Tetrabutylammonium perchlorate (Aldrich Co.) was dried under reduced pressure at 150 °C for 12 h.

Diethyl malonate, ethyl cyanoacetate, and isopropyl cyanoacetate (these three: Tokyo Kasei Co.) were used without further purification. Di(*tert*-butyl) malonate and di(isopropyl) malonate were prepared from the reactions of malonyl dichloride with *tert*-butyl alcohol and with isopropyl alcohol, respectively.[23] Isopropylidene malonate was prepared according to the method reported by Davidson and Bernhard.[17]

Polymerization Procedure

Radical Polymerization: Given amounts of **5c** or **6d**, styrene as a comonomer if necessary, benzene or chloroform as a solvent, and 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator were placed in a glass ampule, which was degassed by the freeze-thaw method (repeatedly three times) and sealed. It was placed in a bath thermostated at 50 °C or 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess of hexane to precipitate the product which was purified in three or more cycles of a redissolution-reprecipitation method. Dichloromethane and hexane were used as a solvent and a precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

Ionic Polymerization: The polymerization was carried out with the apparatus reported previously.[7] A given amount of **5c** or **6d** as a monomer was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of solvent such as benzene, toluene, or dichloromethane by a syringe. After the resulting solution was degassed by the freeze-thaw method (repeated twice), the apparatus was filled with nitrogen and sealed. Then, it was set in a bath thermostated at 0 °C or room temperature and a fixed amount of butyllithium, boron trofluoride etherate, triethylamine, or pyrrolidine was injected into it by a syringe. After a given time of the reaction, the reaction mixture was poured into excess hexane to deposit a polymeric product. The precipitated polymeric product was dissolved again in a small amount of dichloromethane and the resulting solution was poured into hexane for purification. When no polymeric product was deposited in this process, the hexane solution was placed under reduced pressure to remove volatile materials. An aliquot of the residue was dissolved in a small amount of benzene and the resulting benzene solution was subjected to GPC to determine the molecular weight of the reaction product.

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