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Preparation and Polymerization of a New Type of Stable Quinodimethanes with Captodative Substituents: 7,8-Bis(ethylthio)-, 7,8-Bis(phenylthio)-, and 7,8-Bis(*tert*-butylthio)-7,8-dicyanoquinodimethanes

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ABSTRACT: 7,8-Bis(ethylthio)-7,8-dicyanoquinodimethane (**3a**), 7,8-bis(phenylthio)-7,8-dicyanoquinodimethane (**3b**), and 7,8-bis(*tert*-butylthio)-7,8-dicyanoquinodimethane (**3c**) as quinodimethanes with captodative substituents were successfully prepared as stable crystals at room temperature. The first reduction potential values of **3a**, **3b**, and **3c** were measured in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) by cyclic voltammetry to be −0.76, −0.61, and −0.70 V, respectively. **3a** is homopolymerizable with 2,2′-azobis(isobutyronitrile) (AIBN), butyllithium, triethylamine, and boron trifluoride etherate initiators. **3b** is, even though in low level, homopolymerizable with AIBN and butyllithium but is not homopolymerizable with triethylamine and boron trifluoride etherate. **3c** is not homopolymerizable with any of these initiators.

Previously it was reported that 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes (**1**)[1,2] and 7,8-diacyl-7,8-dicyanoquinodimethanes (**2**),[3] carrying two kinds of electron-accepting substituents at each 7 and 8 position, are obtainable as stable crystals at room temperature, are homopolymerizable with free radical and anionic initiators, the latter of which gives high polymers of **1** with a molecular weight above two million, and are copolymerizable with styrene in a random fashion. In addition, kinetic study[4] of their radical polymerizations revealed that values of entropy of polymerization for **1** and **2** are nearly constant and one-third as large as those for vinyl monomers, suggesting that those quinodimethane compounds polymerize as a new class of monomers different from vinyl and related compounds.

Recently, Viehe et al.[5] pointed out a strong resonance stabilization effect on a carbon radical carrying both electron-accepting (cyano, alkoxycarbonyl groups, etc.) and electron-donating groups (alkylthio, alkoxy groups, etc.) and called it a captodative substituent effect. Quinodimethanes carrying both captive and dative substituents at each 7 and 8 position were expected interestingly to exhibit homopolymerizability similar to **1** and **2** because of carrying different substituents at each 7 and 8 position. In addition, when a pair of captive and dative substituents are selected properly, they should change in their polar character from electron accepting to electron donating and there is the probability of obtaining a quinodimethane compound of polarity close to neutral. Furthermore they might polymerize in a peculiar manner due to the strong resonance stabilization effect, the so-called captodative substituent effect. However, those compounds have not been prepared yet.

This work describes the preparation of 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane (**3a**), 7,8-bis(phenylthio)-7,8-dicyanoquinodimethane (**3b**), and 7,8-bis(*tert*-butylthio)-7,8-dicyanoquinodimethane (**3c**) as captodative substitutional quinodimethanes and their homopolymerizations.

Experimental Section

7,7,8,8-Tetrakis(ethylthio)-*p*-xylene (5a). Terephthaldehyde (**4**) (22.64 g (168.8 mmol)) and ethyl mercaptan (41.95 g (675.1 mmol)) were dissolved in 250 mL of chloroform at room temperature. Boron trifluoride etherate (10.6 mL) was added dropwise to it with stirring. After the reaction mixture was kept at room temperature for 24 h, it was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove volatile material and to obtain 43.0 g of pale yellow viscous ma-

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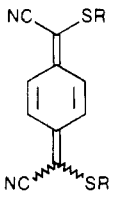


3a, R = Et
b, R = Ph
c, R = *t*-Bu

terial as a residue which was recrystallized from pentane to give 40.35 g (69% yield) of **5a** as a white crystalline solid: mp 42–43 °C; IR (KBr) ν_{CH} 2970–2880, $\nu_{C=C}$ 1460, 1420 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.41 (s, 4 H), 4.91 (s, 2 H), 2.50 (q, J = 7.2 Hz, 8 H), 1.21 (t, J = 7.2 Hz, 12 H). Anal. Calcd for $C_{16}H_{26}S_4$: C, 55.47; H, 7.58; S, 36.95. Found: C, 55.60; H, 7.17; S, 37.28.

7,7,8,8-Tetrakis(phenylthio)-*p*-xylene (5b). The compound **5b** was prepared in 87.7% yield from **4** and thiophenol in a process similar to that for **5a**: mp (benzene–hexane) 123–125 °C; IR (KBr) ν_{CH} 3050, $\nu_{C=C}$ 1500, 1475, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 24 H), 5.36 (s, 2 H). Anal. Calcd for $C_{32}H_{26}S_4$: C, 71.36; H, 4.88; S, 23.77. Found: C, 71.38; H, 4.58; S, 24.04.

7,7,8,8-Tetrakis(*tert*-butylthio)-*p*-xylene (5c). The compound **5c** was prepared in 47.4% yield from **4** and *tert*-butylmercaptan in a process similar to that for **5a**: mp (pentane) 135–136 °C; IR (KBr) ν_{CH} 2950–2860, $\nu_{C=C}$ 1470, 1420 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 4 H), 5.00 (s, 2 H), 1.26 (s, 36 H). Anal. Calcd for $C_{24}H_{42}S_4$: C, 62.4; H, 9.25; S, 27.91. Found: C, 62.95; H, 9.40; S, 27.65.

7,8-Bis(ethylthio)-7,8-dicyano-*p*-xylene (6a). **5a** (4.0 g (11.5 mmol) and mercuric cyanide (5.83 g (23.1 mmol)) were dissolved in 20 mL of acetonitrile and the solution was warmed at 60 °C. Iodine (5.86 g (23.1 mmol)) was added in one portion to the warm solution with stirring. Then, red solid material was immediately deposited. The reaction mixture was kept at room temperature with stirring for 20 min and 70 mL of carbon tetrachloride was added. The red, solid material was filtered and washed with small amount of carbon tetrachloride. The filtrate and the washing were combined, washed twice with aqueous saturated sodium sulfate solution (50 mL × 2), dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove acetonitrile and carbon tetrachloride and to obtain 3.1 g of pale yellow viscous material as residue which was dissolved in 5 mL of benzene and, then, the resulting solution was passed through a column (1.5 cm diameter × 30 cm high) packed with silica gel with benzene as eluent. The first elution band portion was evaporated to dryness to give 2.47 g (77.4 % yield) of **6a** as pale yellow viscous oil which hardly crystallized: IR (neat) ν_{CN} 2250, $\nu_{C=C}$ 1610, 1510, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.52 (s, 4 H), 4.80 (s, 2 H), 2.78 (q, J = 7.2 Hz, 2 H), 2.72 (q, J = 7.2 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 6 H). Anal. Calcd for $C_{14}H_{16}N_2S_2$: C, 60.85; H, 5.85; N, 10.13; S, 23.16. Found: C, 60.78; H, 5.98; N, 10.10; S, 23.14.

7,8-Bis(phenylthio)-7,8-dicyano-*p*-xylene (6b). The compound **6b** was prepared in 51.5% yield from **5b**, mercuric cyanide, and iodine in a process similar to that for **6a**: mp (dichloromethane–hexane) 155–156 °C; IR (KBr) ν_{CN} 2050, $\nu_{C=C}$ 1580, 1510, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40 (s, 10 H), 7.30 (s, 4 H), 4.94 (s, 2 H). Anal. Calcd for $C_{22}H_{16}N_2S_2$; C, 70.95; H, 4.34; N, 7.52; S, 17.19. Found: C, 71.19; H, 4.06; N, 6.97; S, 17.80.

7,8-Bis(*tert*-butylthio)-7,8-dicyano-*p*-xylene (6c). The compound **6c** was prepared in 23.0% yield from **5c**, mercuric cyanide, and iodine in a process similar to that for **6a**: mp (hexane) 98–99 °C; IR (KBr) ν_{CN} 2250, $\nu_{C=C}$ 1510, 1460, 1420 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50 (s, 4 H), 4.71 (s, 2 H), 1.49 (s, 18 H). Anal. Calcd for $C_{18}H_{24}N_2S_2$: C, 65.03; H, 7.29; N, 8.42; S, 19.25. Found: C, 64.61; H, 7.83; N, 8.03; S, 19.53.

7,8-Bis(ethylthio)-7,8-dicyanoquinodimethane (3a). **6a** (0.5 g (1.85 mmol)) was dissolved in 10 mL of chloroform and the solution cooled at 0 °C under nitrogen. *N*-Chlorosuccinimide (NCS) (0.48 g (3.62 mmol)) was added to it with stirring. After the mixture was kept for 5 min, 0.25 mL (1.81 mmol) of triethylamine was added. The color of it changed from pale yellow to red. The reaction mixture was washed twice with ice water (50 mL × 2), dried over anhydrous magnesium sulfate, and placed under reduced pressure to evaporate the solvent until its volume became 2 mL. The resulting concentrate was passed through a column (1.5 cm diameter × 30 cm high) packed with silica gel with chloroform as eluent. The red elution band was collected and placed under reduced pressure to remove solvent and to obtain 280 mg of red solid, which was recrystallized from hexane to give 243 mg (49% yield) of **3a** as red-needle crystals: mp 115–116 °C; IR (KBr) ν_{CN} 2200, $\nu_{C=C}$ 1520, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20 (d, J = 1.8 Hz, 2 H), 7.17 (d, J = 1.8 Hz, 2 H), 3.13 (q, J = 7.2 Hz, 4 H), 1.39 (t, J = 7.2 Hz, H); UV (benzene) 470 (ϵ = 5.76 × 10^4) nm. Anal. Calcd for $C_{14}H_{14}N_2S_2$: C, 61.30; H, 5.16; N, 10.21; S, 23.33. Found: C, 61.12; H, 5.13; N, 10.35; S, 23.40.

7,8-Bis(phenylthio)-7,8-dicyanoquinodimethane (3b). The compound **3b** was prepared by using **6b** in 61.1% yield according to a process similar to that for **3a**: mp(hexane) 154–155 °C; IR (KBr) ν_{CN} 2200, $\nu_{C=C}$ 1580, 1480, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 14 H); UV (benzene) 470 (ϵ = 4.6 × 10^4) nm. Anal. Calcd for $C_{22}H_{14}N_2S_2$: C, 71.31; H, 3.82; N, 7.56; S, 17.31. Found: C, 70.95; H, 3.90; N, 7.48; S, 17.67.

7,8-Bis(*tert*-butylthio)-7,8-dicyanoquinodimethane (3c). The compound **3c** was prepared by using **6c** in 65.8% yield according to a process similar to that for **3a**. Recrystallization of **3c** from hexane gave two kinds of crystals, i.e., red needles in 29.0% yield and purple needles in 36.8% yield. Red needles: mp 123–124 °C; IR (KBr) ν_{CN} 2200, $\nu_{C=C}$ 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (dd, J = 10.8, 1.8 Hz, 2 H), 7.30 (dd, J = 10.8, 1.8 Hz, 2 H), 1.52 (s, 18 H); UV (benzene) 458 (ϵ = 4.26 × 10^4) nm. Anal. Calcd for $C_{18}H_{22}N_2S_2$: C, 65.40; H, 6.72; N, 8.48; S, 19.40. Found: C, 65.35; H, 6.67; N, 8.45; S, 19.53. Purple needles: mp 123–124 °C; IR (KBr) ν_{CN} 2200, $\nu_{C=C}$ 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59 (d, J = 1.8 Hz, 2 H), 7.33 (d, J = 1.8 Hz, 2 H), 1.52 (s, 18 H); UV (benzene) 458 (ϵ = 4.33 × 10^4) nm. Anal. Calcd for $C_{18}H_{22}N_2S_2$: C, 65.40; H, 6.72; N, 8.48; S, 19.40. Found: C, 65.38; H, 6.70; N, 8.42; S, 19.50.

Other Materials. Commercial benzene and toluene were washed with concentrated sulfuric acid and water, dried over calcium chloride, refluxed over metal sodium, and distilled at 80 and 109 °C, respectively. Moreover, toluene was distilled over benzophenone–metal sodium. Dichloromethane was refluxed over calcium hydride and distilled at 39.5 °C. Triethylamine was refluxed over metal sodium and distilled at 88.5 °C. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Boron trifluoride etherate was distilled under nitrogen at reduced pressure. Butyllithium (Aldrich Co.) was used without further purification. Tetrabutylammonium perchlorate was heated at 160 °C under reduced pressure for 20 h prior to use.

Cyclic Voltammetry. Voltammetric measurement was carried out in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) at room temperature. A Ag/AgCl, a glassy carbon, and a platinum wire were used as reference, working, and third electrodes, respectively.

Procedure of Polymerization. In the cases of ionic polymerization with butyllithium, boron trifluoride etherate, and triethylamine initiators, the polymerization was carried out under argon and dry conditions by using the apparatus reported previously.[2] After the time of polymerization, the reaction mixture was poured into excess hexane to deposit the polymeric product, which was dissolved again in a small amount of dichloromethane, and the resulting solution was poured into excess hexane for purification. The polymeric product obtained was dried under reduced pressure. When the polymeric product was not deposited, the hexane solution was placed under reduced pressure to remove the volatile material, and then the residue was dissolved in tetrahydrofuran (THF). The THF solution was subjected to gel permeation chromatography (GPC).

In the case of free radical polymerization with AIBN, a given amount of monomer, AIBN, and benzene was placed in an ampule, which was degassed by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization. The following procedure was carried out similarly to the above-mentioned ionic polymerization.

Instruments for Measurement. Instruments for UV–vis, ^{1}H NMR, and IR spectral determination were JASCO UVIDEC-403B, Hitachi R-600, and JASCO A-100, respectively. Elemental analysis, GPC, and voltammetric measurement were performed on a Yanagimoto CHN CORDER MT-2; a Toyo Soda

Table I
First Reduction Potentials[a]

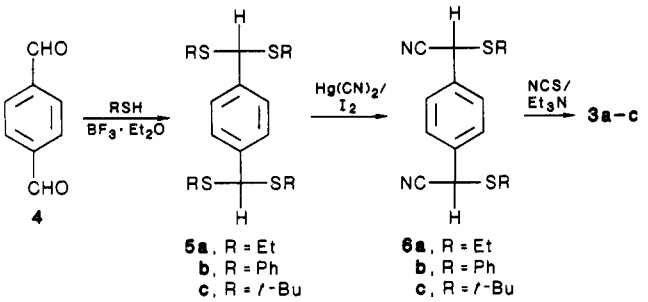
compd	E_1, V[b]	compd	E_1, V[b]
TCNQ	+0.19	**3c** (purple crystal)	−0.70
3b	−0.61	**3a**	−0.76
3c (red crystal)	−0.69	ETQ	−1.16

[a] Solvent, dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); reference electrode, Ag/AgCl. [b] Relative error, ±0.01 V.

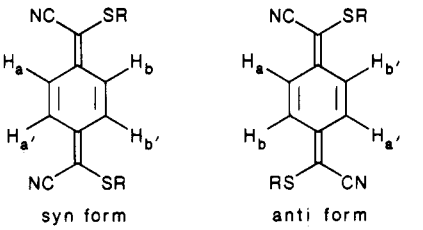
HLC-803D with a series of two columns, Toyo Soda G3000H and G2500H; and a Yanagimoto New Cyclic Voltammetric Analyzer VMA-010, respectively.

Results and Discussion

Preparation of 7,8-Bis(ethylthio)- (3a), 7,8-Bis(phenylthio)- (3b), and 7,8-Bis(*tert*-butylthio)-7,8-dicyanoquinodimethane (3c). **3a-c** are successfully prepared according to the following scheme:



The reaction of terephthalaldehyde (4) with thiol compounds such as ethyl mercaptan, thiophenol, or *tert*-butyl mercaptan in the presence of boron trifluoride etherate in chloroform at room temperature gave respective thioacetals (5), which were converted into 7,8-bis(alkylthio)- and 7,8-bis(arylthio)-7,8-dicyano-*p*-xylenes (6) by reacting 5 with mercuric cyanide and iodine in acetonitrile at 60 °C according to the method of Pochat.[6] When this reaction was carried out for a time loner than 5–10 min, the yield of 6 decreased rather than increased, probably due to an undesired reaction taking place on 6. The oxidation of 6 with NCS and triethylamine in chloroform at 0 °C gave 3 in 50–65% yield. The oxidation of **6a** with activated manganese dioxide[7] in benzene at room temperature gave **3a** only in very low yield not above 4% and large amounts of the polymer of **3a** in yield above 50% ($\bar{M}_n$ = 300–4000, by GPC) as a byproduct. When **3a**, **3b**, and **3c** were recrystallized from hexane, the former two compounds gave only red-needle crystals and the last gave two kinds of crystals, i.e., red and purple needles. The ^{1}H NMR spectrum of **3a** revealed two doublet peaks at δ 7.20 and 7.17, each of which is split with the coupling constant of 1.8 Hz. The values of α-, β-, and γ-coupling constants between hydrogen atoms on the benzene nucleus were reported to be 6–10, 1–3, and 0–1 Hz,[8] respectively. It can be seen from values of the coupling constants that these two doublet peaks are split through the β-coupling of the two kinds of hydrogen atoms, H_a and H_b, on the nucleus of the syn form of **3a**. Although the spliting through γ-coupling of the two kinds of hydrogen atoms, H_a and $H_{b'}$, on the nucleus should exist, this γ-coupling constant is too small, 0–1 Hz, to be observed by our 60-MHz ^{1}H NMR instrument. It was concluded therefore that **3a** obtained



configuration of **3**

is a syn form. Unfortunately, the ^{1}H NMR spectrum of **3b** showed a serious overlapping of the protons on the quinodimethane nucleus with phenyl protons on the phenylthio group to prevent determination of any coupling constants due to its configuration. Two kinds of crystals, i.e., red and purple needles, of **3c** exhibited the same UV–vis spectra in benzene. The ^{1}H NMR spectrum of red-needle crystals of **3c** revealed two double doublet peaks at δ 7.62 and 7.30, each of which was split through the two coupling constants of 10.8 and 1.8 Hz. It was considered that these two double doublet peaks are split through both the α-coupling (6–10 Hz) of H_a with H_b and the β-coupling (1–3 Hz) of H_a with $H_{b'}$ on the nucleus of the anti form of **3c**. It was concluded therefore that the red-needle crystals of **3c** are an anti-form isomer. The ^{1}H NMR spectrum of the purple-needle crystals of **3c** revealed two doublet peaks at δ 7.59 and 7.33, each of which is split through the coupling constant of 1.8 Hz, as is also the case for **3a**. It was concluded, on the same reasoning as for the **3a** configuration, that the purple-needle crystals of **3c** are a syn-form isomer.

Electron-Accepting Character. Electron-accepting character of **3a**, **3b**, and **3c** was estimated as a value of first reduction potential, E_1, by cyclic voltammetry in which dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) and Ag/AgCl were used as solvent and reference electrode, respectively. The experimental values of **3a**, **3b**, and **3c** are listed in Table I, together with those of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 7,7,8,8-tetrakis(ethylthio)quinodimethane (ETQ) for comparison. E_1 values of red and purple crystals of **3c** are −0.69 ± 0.01 and −0.70 ± 0.01 V, respectively, indicating that both crystals exhibit the same electron-accepting character. It is obvious that **3a**, **3b**, and **3c** are just intermediate in

Table II
Homopolymerizations[a] of 3a, 3b, and 3c with Various Initiators

run	monomer feed, mg	initiator [I]	[monomer]/[I]	solvent, mL	temp, °C	time, h	conv, %	$\bar{M}_n$[b] × 10^{-4}
				3a				
1	40.20	AIBN	24.2	benzene, 10	60	4	25.6	5.0
2	29.96	Et_3N	9.7	toluene, 10	0	18	11.7	1.1
3	30.93	BuLi	9.7	toluene, 10	0	15.5	15.1	1.3
4	30.85	BF_3·Et_2O	11.0	CH_2Cl_2, 10	0	5	4.7	0.8
				3b				
5	39.73	AIBN	22.9	benzene, 8	60	5	11.2	0.66
6	30.09	Et_3N	9.9	toluene, 20	0	18	0	
7	30.82	BuLi	10.0	toluene, 20	0	23	6.3	0.43
8	29.79	BF_3·Et_2O	9.6	CH_2Cl_2, 10	0	12	0	

[a] **3c** (red crystals and purple crystals) gave no polymers under the similar experimental conditions. [b] Determined by GPC; THF eluent.

electron-accepting character between TCNQ and ETQ as expected from their chemical structures. In addition, electron-accepting character of **3a**, **3b**, and **3c** can be explained well in terms of Hammett's substituent constant values, σ_p, of ethylthio (+0.03),[9] phenylthio (+0.29),[10] and *tert*-butylthio groups as dative group, when the σ_p value for *tert*-butylthio group is regarded to be the same as that for the isopropylthio group (+0.07)[9] because *tert*-butyl and isopropyl groups exhibit the same σ_p values of −0.197.[11]

Polymerization. Polymerizations of **3a**, **3b**, and **3c** were attempted with AIBN, butyllithium, triethylamine, or boron trifluoride etherate initiators (Table II). It was found that **3a** is homopolymerizable with all initiators; **3b** is, even though in low level, homopolymerizable with AIBN and butyllithium initiators but not homopolymerizable with boron trifluoride etherate and triethylamine; and **3c** (both red and purple crystals) is not homopolymerizable with any of those initiators. It is noteworthy that **3a** is homopolymerizable with even a weak base like triethylamine, probably attributable not only to the very strong conjugative stabilization of cyano group but also to the sulfur stabilization as pointed out in the chemistry of 1,3-dithianes,[12] and also it is homopolymerizable with a strong Lewis acid like boron trifluoride etherate, assumedly due to the stabilization of cyano and alkylthio groups.[13] This behavior of **3a** in polymerizability toward all types of initiators corresponds to that of styrene and butadiene, both of which are highly conjugated hydrocarbon monomers and are homopolymerizable similarly with all types of initiators such as free radical, anionic (strong base such as alkyl alkali metal and alkali metal), and cationic initiators. It is emphasized that styrene and butadiene are homopolymerizable only with very strong base, whereas **3a** is susceptible even with a weak base such as triethylamine. It is remarkable that **3a** is the monomer most susceptible to a very wide range of initiators such as AIBN (free radical), boron trifluoride etherate (cationic), butyllithium (anionic), and triethylamine (a weak anionic). Since **3b** has a higher first reduction potential (more acidic) than **3a**, it is reasonable that **3b** is less susceptible to acidic initiators such as boron trifluoride etherate, whereas it is unreasonable that **3b** is hardly homopolymerizable with a weak basic initiator such as triethylamine. Moreover, **3c** is intermediate in E_1 value between those of **3a** and **3b**, and **3c** is not homopolymerizable with any of those initiators, suggesting that their polymerizability should be associated with other factors like steric hindrance in addition to their polar character. Taft's steric substituent constants, E_s, of ethyl, phenyl, and *tert*-butyl groups as alkyl group on alkylthio groups of compounds **3** are reported to be −0.07,[14] −0.9,[14] and −1.54,[14] respectively. Among **3a**, **3b**, and **3c**, it can be seen that their polymerizability increases with E_s values of the alkyl groups. **3a** with the ethyl group of the largest E_s value exhibits the highest polymerizability, **3b** with the phenyl group of the intermediate value a moderate polymerizability, and **3c** with the *tert*-butyl group of the least value entirely no polymerizability. Probably it is obvious that polymerizability of compounds **3a**, **3b**, and **3c** suffers seriously from steric hindrance effect of bulkiness of the dative substituent at the 7 and 8 positions. It is conceivable that this high steric hindrance effect is characteristic of the polymerization of the substitutional quinodimethanes.

Registry No. **3a**, 112347-78-1; **3a** (homopolymer), 112347-82-7; **3b**, 112347-79-2; **3b** (homopolymer), 112347-83-8; *syn*-**3c**, 112347-80-5; *anti*-**3c**, 112347-81-6; **4**, 623-27-8; **5a**, 67115-19-9; **5b**, 70227-35-9; **5c**, 112347-75-8; **6a**, 112347-76-9; **6b**, 112347-77-0; **6c**, 112372-86-8; EtSH, 75-08-1; PhSH, 108-98-5; *t*-BuSH, 75-66-1; $Hg(CN)_2$, 592-04-1; *anti*-**3c**, 112347-81-6.

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