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Spontaneous Polymerization Mechanism of Electron-Accepting Substituted Quinodimethane with *p*-Methoxystyrene

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ABSTRACT: Spontaneous reactions of 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM 1) with *p*-methoxystyrene (MeOSt) were investigated in chloroform at room temperature at different monomer feed ratios. Reaction products obtained as hexane-insoluble and hexane-soluble fractions were characterized by elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The hexane-insoluble products were to be copolymers of 7-(4-methoxyphenyl)-8,8-dicyanoquinodimethane (QM 2) with small amounts (3−6 mol %) of the QM 1, and the reaction product in the hexane-soluble fractions was to be the one-to-one adduct (Cycloadduct) of methylene Meldrum's acid (MM) with MeOSt. It was found that in the spontaneous reaction of the QM 1 with MeOSt a side reaction involving a metathesis process took place to form new two products, QM 2 and MM, and the former polymerized and the latter underwent the cycloaddition reaction with MeOSt. The formation of the Cycloadduct was also confirmed by a model reaction using 1-[(6-hydroxy-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-5-yl)-methyl]pyridinium hydroxide as a precursor of the MM and MeOSt. To identify the reactive intermediate, the spontaneous reactions of the QM 1 with MeOSt were carried out in the presence of 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) and methanol. No products trapped by TEMPO were obtained, but in the case of methanol the one-to-one-to-one adduct (Adduct) of the QM 1, MeOSt, and methanol was isolated. It was concluded, therefore, that the spontaneous reaction of the QM 1 with MeOSt might proceed via a zwitterionic tetramethylene intermediate.

Introduction

Spontaneous reactions of electron-accepting olefins and electron-donating olefins give alternating copolymers and/or homopolymers of electron-donating olefins. To explain these spontaneous reactions, Hall and coworkers have proposed the "bond-forming initiation theory",[1,2] where tetramethylene intermediates, which are diradical or zwitterionic depending upon the nature of the substituents on the olefins, are formed between electron-accepting olefins and electron-donating ones, and the diradical intermediate leads to an alternating copolymer and the zwitterionic one leads to a homopolymer. This theory has been extended to the spontaneous reactions of electron-donating dienes such as 1,3-butadienes with electron-accepting olefins such as cyano- and ester-trisubstituted ethylenes,[3,4] where [4 + 2] cycloadducts and/or homopolymers of the diene derivatives were formed, and also to the spontaneous reactions of electron-accepting substituted quinodimethanes such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane, and 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane with electron-donating olefins such as styrenes and vinyl ethers,[5−9] where alternating copolymers with styrenes and homopolymers of vinyl ethers were formed. In the electron-accepting substituted quinodimethanes/electron-donating olefins systems studied, symmetrically substituted quinodimethanes, having the same four substituents on exocyclic carbons of the quinodimethanes, were used as an electron-accepting olefin component, but unsymmetrically substituted quinodimethanes, where two substituents on exocyclic carbons at the 7-position are different from those at the 8-position, have not been investigated yet. The use of unsymmetrically substituted quinodimethanes would allow one to know the primary reaction site by means of product analysis and also provide further information about a reactive intermediate in the spontaneous reactions of the electron-accepting substituted quinodimethanes/electron-donating olefins systems. Recently, we have synthesized successfully an electron-accepting unsymmetrically substituted quinodimethane, 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM 1), and the QM 1 (first reduction potential (E_1) = +0.13 V) was found to be as strongly electron-accepting as TCNQ (E_1 = +0.16 V).[10]

In this work, spontaneous reactions of the QM 1 with an electron-donating olefin, *p*-methoxystyrene (MeOSt), were investigated in order to elucidate the initiation mechanism.

Experimental Section

Materials. 1-(2,2-Dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM 1) was prepared according to the method reported previously.[10] 1-[(6-Hydroxy-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-5-yl)methyl]pyridinium hydroxide was prepared according to the method reported by Zia-Ebrahimi et al.[11] Commercial *p*-methoxystyrene (MeOSt) (Aldrich Co., bp 41−42 °C/0.5 mmHg) was distilled under reduced pressure and commercial chloroform (Wako Pure Chem. Industries, Ltd., bp 61.1 °C) was distilled over calcium hydride. 2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO) (Aldrich Co.) was used without further purification.

Spontaneous Reaction of QM 1 with MeOSt. QM 1 (212 mg, 0.751 mmol) and 10 mL of chloroform were placed in a 50 mL volume glass ampule, and into the resulting solution was added a solution containing a given amount of MeOSt in 10 mL of chloroform, and a TEMPO if necessary, with a syringe

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Table 1. Spontaneous Reactions of the QM 1 with MeOSt in Chloroform[a] at Room Temperature for 1 h

entry	QM 1/mg	MeOSt/mg	QM 1/mol %	polymer yield[b]/mg	copolymer composition[c] QM 1/mol %:QM 2/mol %	M_n [d]/10^5
1	212	101	50	101	4:96	2.6
2	212	202	33	173	6:94	1.7
3	212	505	17	188	3:97	1.8
4[e]	212	101	50	52	25:75	0.16

[a] $CHCl_3$, 20 mL. [b] Hexane-insoluble fraction. [c] Determined by ^1H NMR. [d] Determined by GPC (THF eluent, polystyrene standards). [e] TEMPO (5.9 mg, 0.05 mol %) was added.

under nitrogen. After stirring at room temperature for 1 h, the reaction mixture was poured into a large amount of hexane to deposit a polymeric product as a hexane-insoluble fraction. The polymeric product was purified by dissolution−reprecipitation method using chloroform as a solvent and hexane as a precipitant, respectively, and dried under reduced pressure until the constant weight was attained. The supernatant was placed under reduced pressure to remove a solvent and give a residue as a hexane-soluble fraction, which was dried under reduced pressure until the constant weight was attained. The polymeric and residue products were characterized.

Model Reaction of Methylene Meldrum's Acid (MM) with MeOSt: Formation of Cycloadduct. MeOSt (143 mg, 1.07 mmol) and 1-[(6-hydroxy-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-5-yl)methyl]pyridinium hydroxide (250 mg, 1.06 mmol) as a precursor of the MM were dissolved in 5 mL of chloroform, and into the resulting yellow solution was added dropwise 0.29 g of 20% hydrochloric acid, which was stirred vigorously for a few minutes until the solution becomes colorless. The reaction mixture was washed well with water, dried over anhydrous magnesium sulfate, and then removed solvent to give 280 mg (90% yield) of 1-(4-methoxyphenyl)-7,7-dimethyl-6,8-dioxaspiro-[3,5]nonane-5,9-dione (Cycloadduct) as white crystals; mp 94.0−96.0 °C. IR (KBr): ν_{C-H} 2890, $\nu_{C=O}$ 1674, $\nu_{C=C}$ 1599, ν_{C-O-C} 1286 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29 (d, J = 8.58 Hz, 2H), 6.92 (d, J = 8.58 Hz, 2H), 5.15 (dd, J = 2.31, 10.2 Hz, 1H), 3.82 (s, 3H), 2.44−2.50 (m, 2H), 2.07−2.21 (m, 2H), 1.75 (s, 3H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 164.6 (C=O), 163.3 (C=O), 159.9 (Ar), 130.3 (Ar), 127.4 (Ar), 114.0 (Ar), 105.8 ($C(CH_3)_2$), 81.7 (⟩C⟨), 77.9 (⟩CH−), 55.3 (OCH_3), 29.1 ($-CH_2-$), 26.1 (CH_3), 24.6 (CH_3), 17.9 ($-CH_2-$). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25; O, 27.56. Found: C, 65.37; H, 6.22; O, 28.41.

Spontaneous Reaction of QM 1 with MeOSt in the Presence of Methanol: Formation of Adduct. QM 1 (100 mg, 0.354 mmol) and 5 mL of chloroform as solvent were placed in a glass ampule under nitrogen. Into the resulting solution was added a solution of MeOSt (47.5 mg, 0.354 mmol) in 10 mL of chloroform containing 1 mL of methanol with a syringe, and the mixture was stirred at room temperature for 1 h. The reaction mixture was placed under reduced pressure to remove solvent and give a residue, which was dissolved in a small amount of benzene. The resulting solution was passed through a silica gel column by using benzene as an eluent. The first elution band was collected, combined, and placed under reduced pressure to remove solvent and give a pale yellow viscous oil, which was recrystallized from a mixture solution of dichloromethane and hexane to give 19 mg (12% yield) of the one-to-one-to-one adduct (Adduct) of the QM 1, MeOSt, and methanol as white powders; mp 71.5−73.0 °C. IR (KBr): ν_{C-H} 2944, 2900, ν_{CN} 2264, $\nu_{C=O}$ 1738, $\nu_{C=C}$ 1513, ν_{C-O-C} 1286 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.73 (d, J = 8.58 Hz, 2H), 7.52 (d, J = 8.57 Hz, 2H), 7.27 (d, J = 8.91 Hz, 2H), 6.87 (d, J = 8.91 Hz, 2H), 5.05 (s, 1H), 4.30 (dd, J = 5.61, 10.2 Hz, 1H), 3.79 (s, 3H), 3.10 (s, 3H), 3.06 (dd, J = 10.2, 14.2 Hz, 1H), 2.51 (dd, J = 5.61, 14.2 Hz, 1H), 1.79 (s, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 167.0 (C=O), 160.0 (C=O), 159.6 (Ar), 138.2 (Ar), 132.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 126.7 (Ar), 114.0 (Ar), 111.2 (CN), 105.3 ($C(CH_3)_2$) , 79.4 ($C(CN)_2$), 77.2 (⟩CH−), 56.4 (OCH_3), 56.3 (⟩C⟨), 55.3 (OCH_3), 49.9 ($-CH_2-$), 28.9 (CH_3), 27.6 (CH_3). Anal. Calcd for $C_{25}H_{24}N_2O_6$: C, 66.95; H, 5.39; N, 6.25; O, 21.41. Found: C, 67.28; H, 5.46; N, 6.01; O, 21.25.

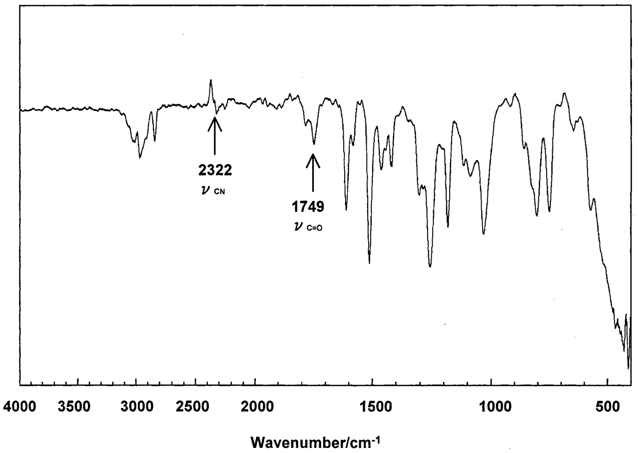


Figure 1. IR spectrum (film) of the product obtained as the hexane-insoluble fraction (entry 1).

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer using tetramethylsilane as an internal standard in chloroform-*d*. IR spectrum was recorded on a Jasco IR-700 spectrometer. Number-average molecular weights (M_n) of the polymers were estimated by gel permeation chromatography on a TOSOH CCPE system equipped with TOSOH UV-8011 ultraviolet (254 nm) detector and two TSK-gel Multipore H_{XL}-M columns (bead size with 5 μm, molecular weight range 5.0×10^2−2.0×10^6) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min and polystyrene standards for calibration at room temperature. A Yanaco micro melting point apparatus and a Yanaco CHN Corder MT-5 were used for melting point measurement and elemental analysis, respectively.

Results and Discussion

Spontaneous Reaction of QM 1 with MeOSt. Spontaneous reactions of the QM 1 with MeOSt at various monomer feed ratios were carried out in chloroform at room temperature for 1 h, and the results are summarized in Table 1.

When the orange QM 1 was mixed with MeOSt in chloroform, a deep red color developed, due to the charge-transfer complex formation. After 1 h, the deep red solutions changed to an orange color (entry 1 in Table 1) and to colorless (entries 2 and 3 in Table 1) depending upon the monomer feed ratios. Reaction products were divided into two parts, hexane-insoluble and hexane-soluble fractions, by pouring the reaction mixture into an excess hexane. The reaction of the QM 1 and MeOSt at an equimolar ratio in monomer feed (entry 1) gave white powder with M_n of 2.6×10^5 as a hexane-insoluble fraction, which was soluble in benzene, chloroform, dichloromethane, THF, and acetone but insoluble in hexane, isopropyl ether, and methanol. IR, ^1H NMR, and ^{13}C NMR spectra of the white powder are shown in Figures 1, 2, and 3, respectively.

The IR spectrum showed absorption peaks at 2322 cm^{-1} due to a carbon−nitrogen stretching vibration of a cyano group and at 1749 cm^{-1} due to a carbon−oxygen

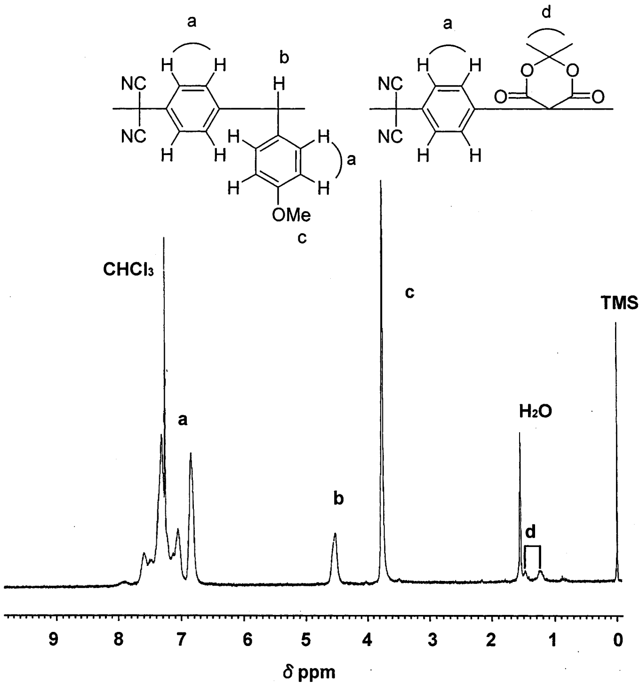


Figure 2. ^{1}H NMR spectrum of the product obtained as the hexane-insoluble fraction (entry 1) in chloroform-*d*.

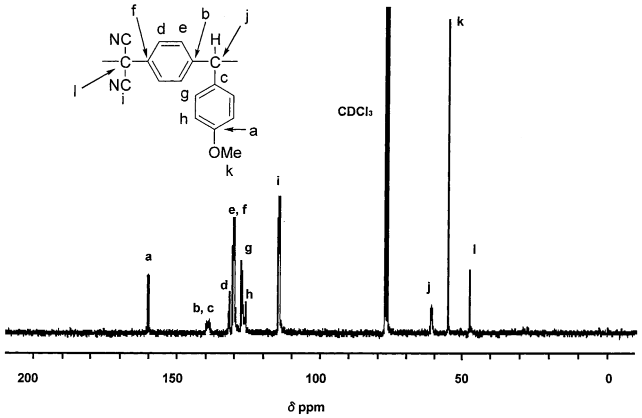


Figure 3. ^{13}C NMR spectrum of the product obtained as the hexane-insoluble fraction (entry 1) in chloroform-*d*.

double-bond stretching vibration of a carbonyl group, respectively, indicating that the QM 1 unit might be incorporated as a component in the polymer, but its content should be a small amount because of the weak intensity. The ^{1}H NMR spectrum showed peaks at 8.0−6.8, 4.5, 3.8, 1.5, and 1.3 ppm. Each peak at 8.0−6.8, 4.5, and 3.8 ppm could be assigned well to each proton of the polymer of a trisubstituted quinodimethane, 7-(4-methoxyphenyl)-8,8-dicyanoquinodimethane (QM 2), of the chemical structure shown in Figure 2. The peaks at 1.5 and 1.3 ppm were significantly smaller and might be assigned to methyl protons of the Meldrum's acid moiety of the QM 1 unit, though the peak due to aromatic protons of the QM 1 unit overlaps with the peak at 8.0−6.8 ppm. It was concluded, therefore, that the white powder obtained as the hexane-insoluble fraction was a copolymer of the QM 1 with the QM 2, which was composed of 4 mol % of the QM 1 unit and 96 mol % of the QM 2 unit, determined by the peak area ratio of methyl protons at 1.5 and 1.3 ppm for the QM 1 unit to a methine proton at 4.5 ppm for the QM 2 unit. The ^{13}C NMR spectrum showed mainly peaks at 159, 140−125, 114, 61, 55, and 47 ppm, which could be assigned well to each carbon of the polymer of the QM 2 shown in Figure 3. The carbon peaks due to the QM 1 unit were merely observed in the figure because of very low content of the QM 1 unit as proved in ^{1}H NMR measurement. To obtain a direct evidence for the formation of the QM 2, we carried out the spontaneous reaction of the QM 1 (0.354 mol/L) and MeOSt (0.354 mol/L) in chloroform-*d* by using an NMR tube at room temperature, and the reaction was followed by NMR spectroscopy. Unfortunately, no peaks due to the QM 2 could be observed during the measurement, and instead only the same peaks due to its polymer as shown in Figure 2 were observed, indicating that the QM 2 is too reactive to exist in a monomer state in this condition. The hexane-soluble fraction gave orange solids as a residue after removing volatile materials. Figure 4 shows the ^{1}H NMR spectrum of the residue, where peaks at 8.4, 7.5, and 1.8 ppm were assigned to each proton of the unreacted QM 1, and peaks at 7.3, 6.9, 5.2, 3.8, 2.44−2.5, 2.07−2.20, 1.75, and 1.73 ppm could be assigned to the each proton of the one-to-one adduct (Cycloadduct) of methylene Meldrum's acid (MM) with MeOSt as illustrated in the figure.

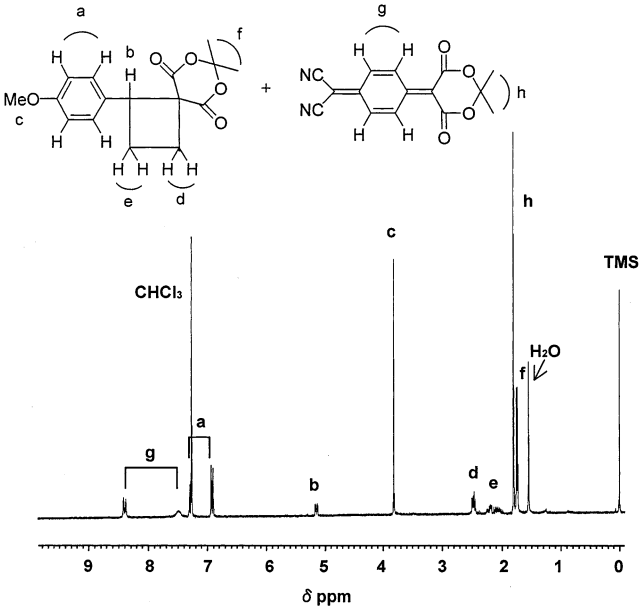
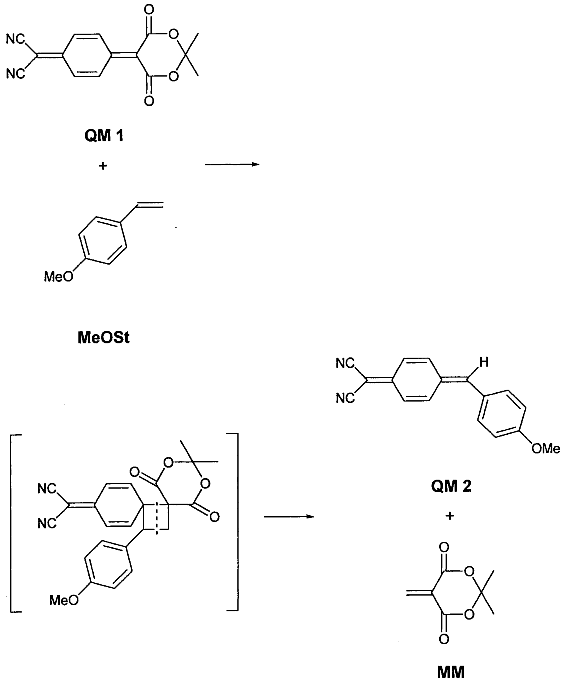


Figure 4. ^{1}H NMR spectrum of the product obtained as the hexane-soluble fraction (entry 1) in chloroform-*d*.

Also, the composition of the unreacted QM 1 and the Cycloadduct in the residue was nearly one to one, determined by the peak area ratio of aromatic protons at 8.4 ppm for the QM 1 to those at 6.9 ppm for the Cycloadduct. No other peaks than the unreacted QM 1 and the Cycloadduct were observed, indicating that only the Cycloadduct might be formed during the spontaneous reaction of the QM 1 with MeOSt. Here, the formation of the Cycloadduct is considered to be due to the cycloaddition reaction of the MM with MeOSt. To confirm the formation of the Cycloadduct by the reaction of the MM with MeOSt, a reaction of 1-[(6-hydroxy-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-5-yl)methyl]pyridinium hydroxide as a precursor of the MM with MeOSt in the presence of acid was carried out at room temperature, and the Cycloadduct was obtained in 90% yield. This supports strongly a selective formation of the Cycloadduct by the reaction of the MM with MeOSt and also the formation of the MM in situ in the spontaneous reaction of the QM 1 with MeOSt. These findings

Scheme 1



indicate that the spontaneous reaction of the QM 1 and MeOSt might form both the QM 2 and the MM. Previously, it was reported that the spontaneous reaction of *N*,*N*-dimethylvinylamine with tricyanoethylene might proceed via a metathesis reaction accompanied by formation of an unstable cyclobutane to generate acrylonitrile and 1,1-dicyano-2-*N*,*N*-dimethylaminoethylene.[12] It is considered, therefore, that in the spontaneous reactions of the QM 1 with MeOSt a similar reaction involving a metathesis process as shown in Scheme 1, a formation of cyclobutane ring, followed by its cleavage to the generation of the QM 2 and MM, might take place.

Here, it is important to understand a possibility about a cleavage of the cyclobutane formed as an intermediate as shown in Scheme 1. Therefore, each bond length of the cyclobutane was estimated by the MM2 method, and the following values were obtained: C5−C8 = 1.567 Å, C8−C14 = 1.561 Å, C14−C17 = 1.550 Å, C17−C5 = 1.565 Å (Figure 5).

The bond length of C5−C8 was the longest one among them though the degree was small, suggestive of the possible cleavage at this bond to form the QM 2 and the MM. As the MeOSt could react with not only the QM 1, but also with the MM formed by the cleavage of the cyclobutane derived from QM 1 and MeOSt, the spontaneous reactions of the QM 1 with MeOSt were carried out at a large amount of MeOSt. When the spontaneous reaction of the QM 1 with MeOSt was carried out at the QM 1/MeOSt ratio of 33 mol %/67 mol % in monomer feed (entry 2 in Table 1), the QM 1 was consumed completely, and the copolymers of the QM 1 with the QM 2 and only the Cycloadduct were obtained. In the same reaction at the QM 1/MeOSt ratio of 17 mol %/83 mol % in monomer feed (entry 3 in Table 1), the QM **1** was consumed completely, and the copolymers of the QM 1 with QM 2 and the Cycloadduct and the unreacted MeOSt were obtained. The yields of the hexane-insoluble parts and also the copolymer compositions (QM 1 unit /QM 2 unit of 6 mol %/94 mol % for the entry 2 and of 3 mol %/97 mol % for the entry 3) were almost same for both cases, regardless of the amount of MeOSt. These findings, especially no observation of the unreacted QM 1 in the case of entry 2, support strongly that the spontaneous reaction of the QM 1 with MeOSt should take place according to Scheme 1.

To obtain some information about the reactive intermediate formed in the system, the spontaneous reaction of the QM 1 with MeOSt was carried out in the presence of TEMPO as a radical inhibitor under the same condition as entry 1 (entry 4 in Table 1). The white powder obtained as a hexane-insoluble fraction was a copolymer of the QM 1 with the QM 2, which was composed of 25 mol % of the QM 1 unit and 75 mol % of the QM 2 unit. The content of the QM 1 unit in the copolymer was higher compared to that in the copolymers obtained in entries 1 and 2, but the polymer yield and the molecular weight (1.6×10^4) were lower compared with the corresponding ones obtained without TEMPO. The TEMPO in the system suppressed the polymer yield and the molecular weight but not completely inhibited the polymerization of the QM 2. It is well-known that an unsubstituted quinodimethane is too reactive to isolate it in a pure monomer state at room temperature, but an introduction of electron-donating or electron-accepting substituents on the exocyclic carbons of the quinodimethane structure makes them less reactive, sometimes nonhomopolymerizable, and isolable as crystals at room temperature.[13−17] However, as the quinodimethane, QM 2, formed in this spontaneous reaction is trisubstituted one, it is considered to be still highly reactive and polymerizable in this reaction condition. The facts that the TEMPO suppressed polymer yield and lowered the molecular weight of the polymer indicate that the copolymer obtained as the hexane-insoluble fraction was formed by radical mech-

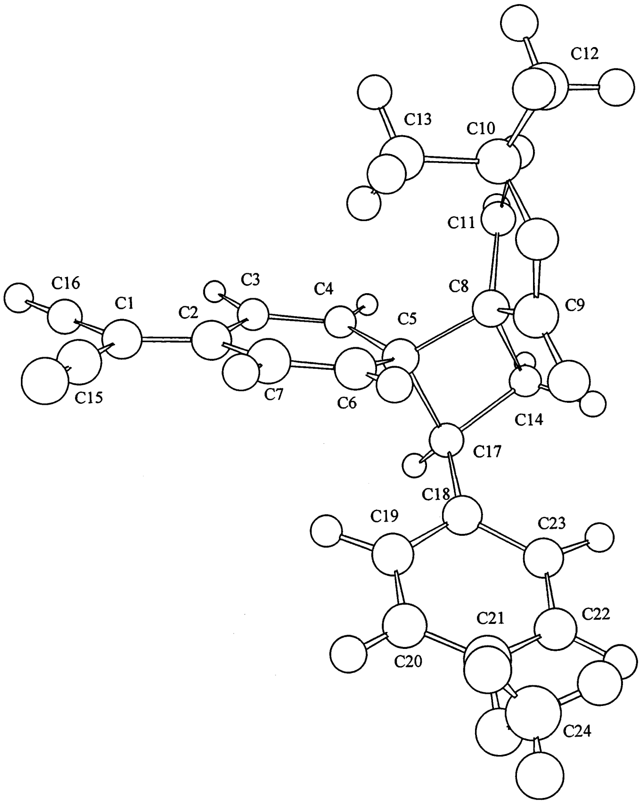


Figure 5. Structure model of cyclobutane intermediate optimized by the MM2 method.

anism. In the hexane-soluble fraction, the unreacted QM 1 and the Cycloadduct were observed, and no adducts trapped by TEMPO were found unlike the spontaneous reaction of MeOSt with dimethyl cyanofumarate in the presence of TEPMO, where the one-to-one-to-one adduct of the MeOSt, dimethyl cyanofumarate, and TEMPO was formed.[18] It is, therefore, suggested that a zwitterionic intermediate rather than a diradical one might be formed as a reactive intermediate to form the cyclobutane in the reaction of the QM 1 with MeOSt.

Reaction of QM 1 with MeOSt in the Presence of Methanol. When the TEMPO was added to trap a diradical intermediate as the reactive intermediate, no trapped products were obtained as already mentioned. It is expected, therefore, that possible another intermediate might be a zwitterionic intermediate. It was reported that the zwitterionic intermediate in the spontaneous reaction of cyanoallene with methoxyallene could be trapped by methanol.[19] Therefore, we tried to trap the zwitterionic intermediate by methanol. The ^{1}H NMR spectrum of a product isolated from a hexane-soluble fraction of the reaction mixture is shown in Figure 6, where each signal could be assigned well to the corresponding protons of the chemical structure shown in the figure.

The IR and ^{13}C NMR spectra also supported the formation of the one-to-one-to-one adduct (Adduct) of the QM 1, the MeOSt, and methanol. This strongly indicates that a zwitterionic phenylene−tetramethylene intermediate is formed in the spontaneous reaction of the QM 1 with MeOSt. Therefore, the Adduct is considered to be formed according to the following route: formation of the zwitterionic tetramethylene intermediate by the reaction of the QM 1 and MeOSt, followed by a transformation to the zwitterionic phenylene−tetramethylene one by aromatization, and then the reaction with methanol. Probably, the reaction system is more polar because of the presence of a large amount of methanol in the reaction mixture, and the formed anion is considered to be transferred rapidly to more stable dicyanobenzyl anion by the aromatization before the cyclobutane formation. On the basis of the above-mentioned results, the mechanism for the spontaneous reaction of the QM 1 with MeOSt was proposed as shown in Scheme 2, where the cyclobutane ring is formed via a zwitterionic tetramethylene intermediate, and then it cleaves via a metathesis process to generate the QM 2 and the MM, the former of which copolymerizes with the QM 1 to give a copolymer and the latter of which reacts with MeOSt to form the Cycloadduct.

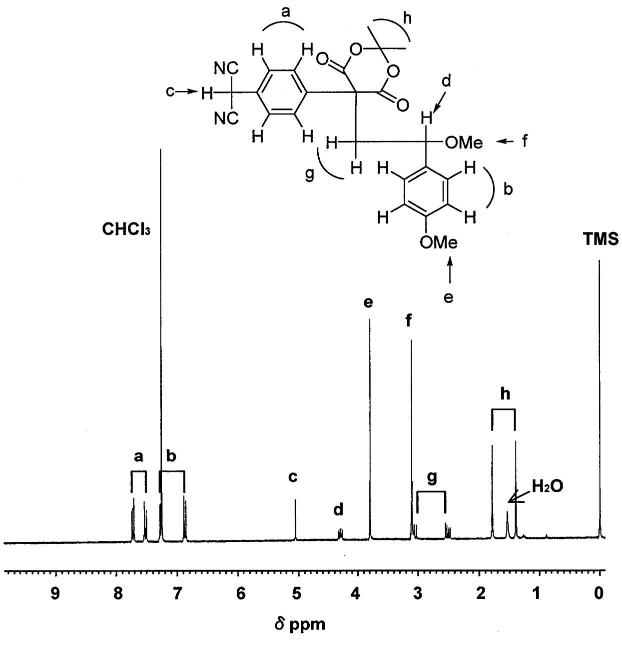
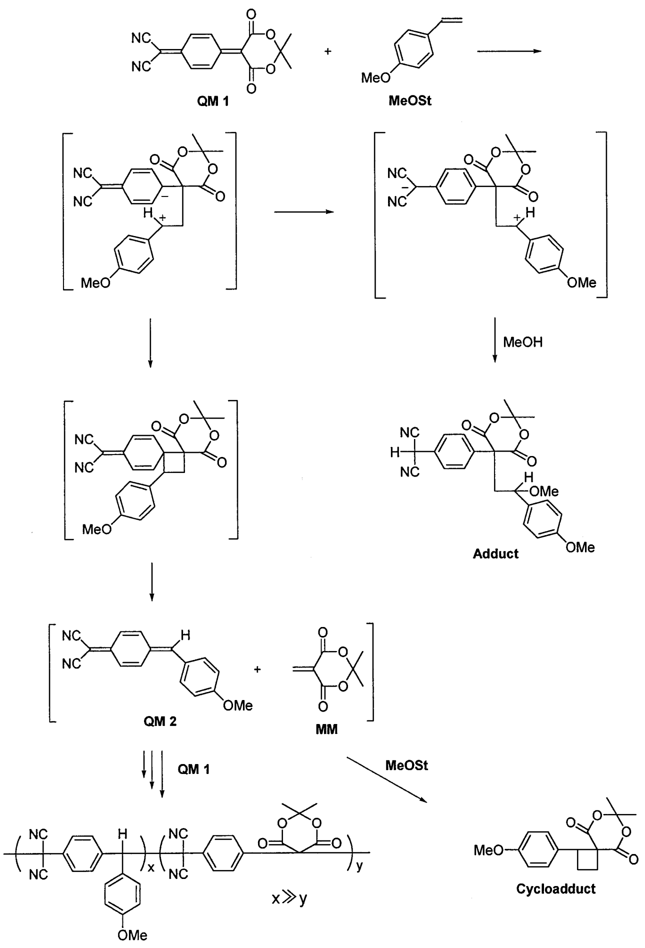


Figure 6. ^{1}H NMR spectrum of the Adduct obtained by the spontaneous reaction of the QM 1 with MeOSt in the presence of methanol in chloroform-*d*.

Scheme 2



The spontaneous reactions of quinodimethanes with electron-donating olefins can be explained well by the bond-forming initiation theory via a tetramethylene intermediate proposed for the spontaneous reactions of electron-accepting olefins with electron-donating olefins.

Conclusions

Spontaneous reactions of the QM 1 with MeOSt were investigated; the reaction products were characterized, and also a trap reaction of the intermediate by methanol was conducted. It was found that the spontaneous reaction of the QM 1 with MeOSt might proceed via a formation of zwitterionic tetramethylene intermediate like the reactions of electron-accepting olefins and electron-donating olefins and that the zwitterionic tetramethylene intermediate formed an unstable cyclobutane to give the QM 2 and the MM, respectively, the former of which copolymerized with the QM 1 to give a copolymer containing a small amount of the QM 1 unit and the latter of which reacted with MeOSt to form the Cycloadduct.

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