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Spontaneous Polymerization Mechanism of 7,7-Dicyanobenzoquinone Methide with *p*-Methoxystyrene

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ABSTRACT: Spontaneous polymerization of 7,7-dicyanobenzoquinone methide (CQM) with *p*-methoxystyrene (MeOSt) was investigated. An alternating copolymer of CQM with MeOSt was obtained as the hexane-insoluble product, and a small amount of a 1:2 cycloadduct of CQM:MeOSt in addition to large amounts of unreacted CQM and MeOSt was obtained as the hexane-soluble product. To clarify an active intermediate in this reaction, spontaneous polymerizations of CQM with MeOSt were carried out in the presence of additives such as 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) and acetic acid and in three solvents with different polarity. The spontaneous reaction in the presence of the TEMPO did not afford any products trapped by TEMPO. On the other hand, the reaction in the presence of acetic acid gave a 1:1:1 adduct of CQM:MeOSt:acetic acid in a quantitative yield. It was concluded from these results that the spontaneous polymerization of CQM with MeOSt might proceed via a zwitterionic intermediate, which has gauche and trans forms.

Introduction

Spontaneous reactions of electron-accepting olefins and electron-donating olefins give alternating copolymers and/or homopolymers of electron-donating olefins. To explain the product formation by these spontaneous reactions, Hall and co-workers have proposed the “bond-forming initiation theory”,[1−4] where diradical and/or zwitterionic tetramethylene intermediates are formed between electron-accepting olefins and electron-donating ones, the former of which gives alternating copolymers and the latter of which yields homopolymers of electron-donating olefins. This theory has been expanded to spontaneous reactions of electron-donating dienes[3−7] and also of electron-accepting substituted quinodimethanes.[1−4,9−15] For the spontaneous reactions of electron-accepting substituted quinodimethanes with electron-donating olefins, symmetrically substituted electron-accepting quinodimethanes such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane, and so on were used as an electron-accepting monomer. Recently, we found that when unsymmetrically substituted electron-accepting quinodimethane, 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM-1), was used as an electron-accepting monomer in a spontaneous reaction with *p*-methoxystyrene (MeOSt), 7-(4-methoxyphenyl)-8,8-dicyanoquinodimethane (QM-2) and methylene Meldrum’s acid were formed by metathesis reaction via a zwitterionic intermediate, and the former copolymerized with QM-1 via a radical mechanism and the latter reacted with MeOSt to form a 1:1 cycloadduct of methylene Meldrum’s acid:MeOSt.[16] As the case of the QM-1, unsymmetrically substituted quinodimethanes might be interesting monomers to show unexpected polymerization behavior, and also they are expected to provide further information about intermediates in the spontaneous polymerization mechanism because the asymmetry of the compounds allows one to determine the direction of the reaction site. 7,7-Dicyanobenzoquinone methide (CQM) is a member of the quinoid family and is regarded as one of the unsymmetrically substituted quinodimethanes, and also, the electron-accepting property (the first reduction potential: $E_1 = -0.09$ V)[17] of CQM is much weaker than that ($E_1 = +0.13$ V)[18] of QM-1. Therefore, the use of CQM makes it possible to investigate how difference in the electron-accepting property affects a reactive intermediate in the spontaneous polymerization mechanism in addition to the direction of the reaction site. In this work, spontaneous reactions of CQM with MeOSt were investigated in detail, and a reactive intermediate to be formed in this reaction was discussed.

Experimental Section

Materials. 7,7-Dicyanobenzoquinone methide (CQM) was prepared according to the method reported by Hyatt et al.[19] *p*-Methoxystyrene (MeOSt) (Aldrich Co., bp 41−42 °C/0.5 mmHg) was purified by distillation under reduced pressure. Chloroform (Wako Pure Chem. Industries, Ltd., bp 61.1 °C) was distilled over calcium hydride. Benzene (Wako Pure Chem. Industries, Ltd., bp 80.1 °C) and tetrahydrofuran (THF) (Wako Pure Chem. Industries, Ltd., bp 65.4 °C) were purified by distillation over sodium benzophenone. 2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO) (Aldrich Co.) and acetic acid (Nacalai Tesque, Inc.) were used without further purification.

Spontaneous Reaction of CQM with MeOSt. A given amount of CQM was placed in a glass ampule, and into it was added a MeOSt solution in solvent (chloroform, benzene, or THF) and a TEMPO if necessary, which was degassed by the freeze−thaw method (repeated three times) and sealed. After heating at 60 °C for 48 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 the dissolution−reprecipitation method using chloroform as a solvent and hexane as a precipitant 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

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Table 1. Spontaneous Reactions of CQM with MeOSt under Various Conditions at 60 °C for 48 h

	monomer feed					elemental anal.			copolym comp	
entry	CQM/mg	MeOSt/mg	CQM/mol %	solvent[a]	yield[b]/mg	C%	H%	N%	CQM/mol %	M_n[c]/10^3
1	196.0	336.2	33.4	$CHCl_3$	134.2	73.19	4.71	9.82	51.0	8.8
2	293.6	252.3	50.0	$CHCl_3$	187.6	74.65	5.12	9.21	47.6	7.3
3	391.8	168.1	66.8	$CHCl_3$	157.7	72.93	4.71	9.95	51.7	7.2
4	293.5	252.3	50.0	C_6H_6	132.8	75.11	4.89	9.10	46.4	9.5
5	293.5	252.3	50.0	THF	195.2	74.23	5.01	9.13	47.1	8.0
6[d]	293.8	252.2	50.0	$CHCl_3$	306.0	72.55	4.64	10.20	53.1	7.2
7[e]	293.2	252.2	50.0	$CHCl_3$	0					

[a] 10 mL. [b] Hexane-insoluble fraction. [c] Determined by GPC (THF eluent, polystyrene standards). [d] TEMPO (14.1 mg) was added. [e] Acetic acid (1.0 mL) was added.

fraction. Unreacted CQM and MeOSt in the residue were removed first by column chromatography (SiO_2, chloroform), and then the collected third elution band product was purified by column chromatography (SiO_2, diethyl ether/hexane (1/1 v/v)): white solids; 10.8−15.8 mg (2.7−4.0% yield); mp 81.0−83.0 °C. IR (NaCl): ν_{C-H} 2928, $\nu_{C\equiv N}$ 2326, $\nu_{C=O}$ 1671, $\nu_{C-=C}$ 1513, ν_{C-O} 1252, 1250 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (dd, J = 3.30, 10.56 Hz, 1H), 7.24 (d, J = 8.57 Hz, 2H), 7.08 (dd, J = 3.30, 10.22 Hz, 1H), 6.99 (d, J = 8.91 Hz, 2H), 6.93 (d, J = 8.57 Hz, 2H), 6.72 (d, J = 8.91 Hz, 2H), 6.61 (dd, J = 1.97, 10.56 Hz, 1H), 6.35 (dd, J = 1.98, 10.23 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.47 (dd, J = 3.63, 12.87 Hz, 1H), 3.34 (tt, J = 4.61, 12.54 Hz, 1H), 2.70−2.46 (m, 2H), 2.36−2.12 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 183.3 (C═O), 159.3 (Ar), 159.0 (Ar), 147.5 (Ar), 139.5 (Ar), 136.1 (Ar), 133.4 (Ar), 133.3 (Ar), 129.4 (Ar), 129.3 (Ar), 127.6 (Ar), 114.5 (Ar), 113.9, 113.0 (CN) 113.4 (Ar), 55.3, 55.1 (OCH_3), 48.1 (〉C〈), 43.2,37.5 ($-CH_2-$), 39.1,34.7 (CH−), 29.7 ($C(CN)_2$). Anal. Calcd for $C_{27}H_{24}N_2O_3$: C, 76.39; H, 5.70; N, 6.60; O, 11.31. Found: C, 76.92; H, 5.86; N, 6.40; O, 10.82. MS: m/z calcd (M) 424.5, (M + Na^+) 447.5. Found (MALDI−TOF) 447.1.

Reaction of CQM with MeOSt in the Presence of Acetic Acid. CQM (293.2 mg, 1.88 mmol) was placed in a glass ampule, and into it was added a MeOSt (252.2 mg, 1.88 mmol) solution in chloroform (10 mL) and 1.0 mL of acetic acid, which degassed by the freeze−thaw method (repeated three times) and sealed. After heating at 60 °C for 48 h, the reaction product was purified by column chromatography (SiO_2, chloroform): white solids, 636.3 mg (96.6% yield); mp 63.5−65.0 °C. IR (NaCl): ν_{O-H} 3432, $_{C-H}$ 3022, 2946, $\nu_{C\equiv N}$ 2254, $\nu_{C=O}$ 1745, $\nu_{C-=C}$ 1514, $\nu_{C(=O)-O}$ 1248 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.41 (d, J = 8.60 Hz, 2H), 7.22 (d, J = 8.57 Hz, 2H), 6.90 (d, J = 8.91 Hz, 2H), 6.86 (d, J = 9.24 Hz, 2H), 5.86 (dd, J = 2.64, 10.22 Hz, 2H), 2.96 (dd, J = 4.28, 10.39 Hz, 1H), 2.44 (dd, J = 2.47, 14.68 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.6 (C═O), 160.0 (Ar), 157.5 (Ar), 130.0 (Ar), 127.7 (Ar), 127.3 (Ar), 122.7 (Ar), 116.7 (Ar), 115.0, 114.4 (CN), 114.3 (Ar), 71.6 (CH), 55.3 (OCH_3), 47.4 (CH_2), 39.1 ($C(CN)_2$), 21.0 ($-CH_3$). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00; O, 18.26. Found: C, 68.95; H, 5.21; N, 7.89; O, 17.95.

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*. The 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 (GPC) on a Jasco PU-2080 Plus equipped with TOSOH UV-8020 ultraviolet (254 nm) detector and TSK gel G2500H$_8$ (bead size with 10 μm, molecular weight range 1.0 × 10^2−2.0 × 10^4) and TSK gel G3000H$_8$ (bead size with 10 μm, molecular weight range 1.0 × 10^2−6.0 × 10^4) using THF as an eluent at a flow rate of 1.0 mL/min and polystyrene standards for calibration. A Yanaco micro-melting point apparatus and a Yanaco CHN Corder MT-5 were used for melting point measurement and elemental analysis, respectively. Matrix-assisted laser desorption/ionization time-of fight mass (MALDI−TOF MS) measurement was performed on a Shimadzu Kratos Kompact II spectrometer using dithranol and sodium iodide as a matrix and cationization reagent, respectively.

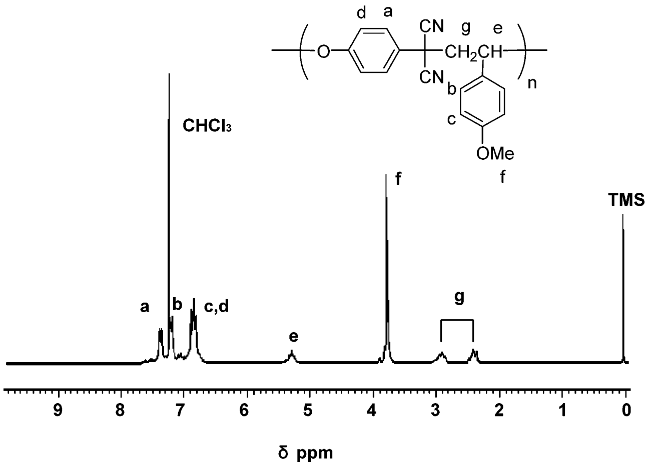
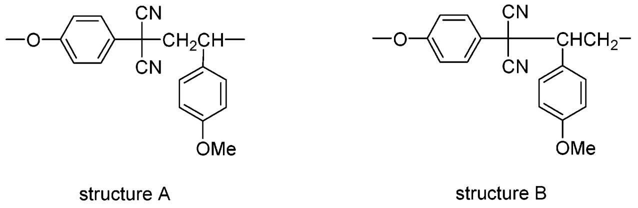


Figure 1. ^1H NMR spectrum of the product obtained as a hexane-insoluble fraction in chloroform-*d*.

Chart 1



structure A

structure B

Results

Spontaneous polymerizations of CQM with MeOSt were carried out at various monomer feed ratios (entries 1−3), in various solvents such as chloroform, benzene, and THF (entries 2, 4, and 5), and in the presence of additives such as TEMPO and acetic acid (entries 6 and 7) at 60 °C, and the results are summarized in Table 1.

When CQM was mixed with MeOSt in chloroform, a deep violet color developed for all reactions due to the formation of charge-transfer complexes. The reaction mixture was divided into hexane-insoluble and hexane-soluble fractions, which were characterized by ^1H NMR, ^{13}C NMR, IR spectra, elemental analysis, and GPC. Spontaneous reactions of CQM with MeOSt at various monomer feed ratios in chloroform (entries 1−3) gave white powders with the M_n of 7200−8800 as the hexane-insoluble fraction, which were composed of 50 mol % of the CQM unit and 50 mol % of the MeOSt unit regardless of monomer feed ratios. The IR spectrum of the white powders showed the absorption peaks at 2050, 1500, and 1250 cm^{-1}, which were assigned to the stretching vibrations due to the carbon−nitrogen bond of cyano group, the carbon−carbon double bond of aromatic ring, and the carbon−oxygen single bond of methoxy group, respectively. The ^1H NMR spectrum of the white powders (entry 2) is shown in Figure 1, where

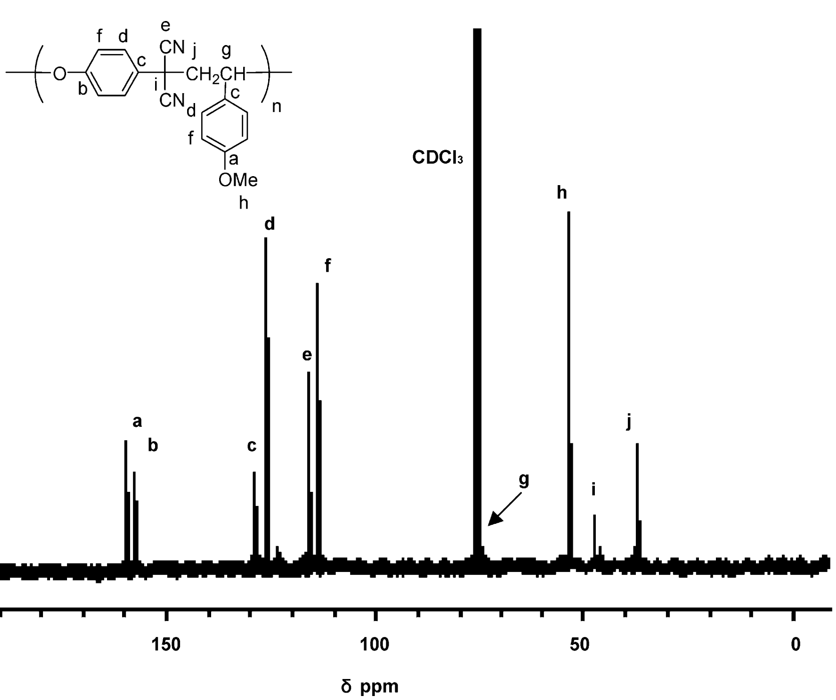


Figure 2. ^{13}C NMR spectrum of the product obtained as a hexane-insoluble fraction in chloroform-*d*.

the peaks at 7.4−6.6, 5.3, 3.7, 2.9, and 2.4 ppm were assigned to aromatic, methine, methoxy, methylene, and methylene protons, respectively.

The methine (5.3 ppm) and methylene (2.9 and 2.4 ppm) protons of the MeOSt unit in the copolymers were observed at lower field than the corresponding ones (1.0−2.0 ppm) of MeOSt homopolymer. This deshielding arises from an electron withdrawal by the neighboring oxygen atom and the dicyanomethylene group, indicating that the MeOSt unit is linked directly to CQM on both. Therefore, the copolymer of the CQM with MeOSt is really alternating. Here, there are two possible structures (structure A and structure B) for the alternating copolymer of CQM with MeOSt (Chart 1).

The chemical shifts and relative intensities of the signals e and g, which have a ratio of 1:2, support strongly that the alternating copolymer of CQM with MeOSt has structure A. Moreover, the peaks at 160, 158, 130, 128, 117, 115, 76, 55, 50, and 39 ppm in the ^{13}C NMR spectrum (entry 2) could be successfully assigned to the respective carbons of the alternating copolymer of CQM with MeOSt illustrated therein (Figure 2). Unfortunately, the terminal structure of the alternating copolymer could not be determined on the basis of their IR, ^{1}H NMR, and ^{13}C NMR spectra because of peak overlapping and weak absorption.

Only alternating copolymers were obtained regardless of monomer feed ratios, and also the maximum of polymer yield was observed at the CQM/MeOSt ratio of 50/50 in mol %. These findings indicate that the alternating copolymerization of CQM with MeOSt takes place. To investigate the solvent effect on the spontaneous polymerization of CQM with MeOSt, the reactions were carried out in different polarity solvents such as benzene (dielectric constant at 20 °C: $\epsilon = 2.28$)[20] as a less polar solvent and THF ($\epsilon = 7.61$)[20] as a more polar one than chloroform ($\epsilon = 4.80$)[20] (entries 2, 4, and 5). Alternating copolymers were obtained as hexane-insoluble products in both solvents as well as in chloroform, and also the polymer yields increased with an increase in the polarity of solvents. The hexane-soluble fractions obtained in the spontaneous reactions of CQM with MeOSt (entries 1−5) were mainly composed of unreacted CQM and MeOSt. However, small amounts of white powders were isolated after removing unreacted monomers by a silica gel column chromatography, and the yields at the CQM/MeOSt ratios of 50/50 in mol % were to be 15.8 mg in benzene (entry 4), 12.2 mg in chloroform (entry 2), and 10.8 mg in THF (entry 5). The ^{1}H NMR spectrum of the white powders obtained in entry 2 is shown in Figure 3, where the peaks were assigned to the respective protons of the chemical structure illustrated therein, a 1:2 cycloadduct of CQM:MeOSt. This chemical structure was also supported by the IR, ^{13}C NMR (Figure 4) spectra, elemental analysis, and MALDI−TOF MS.

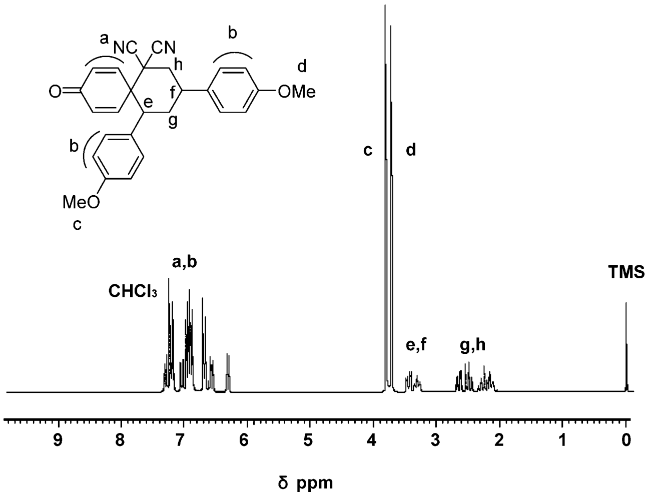


Figure 3. ^{1}H NMR spectrum of the white solids isolated from a hexane-soluble fraction in chloroform-*d*.

To clarify an active intermediate in the spontaneous polymerizations of CQM with MeOSt, the reactions were carried out in the presence of TEMPO as a radical inhibitor and acetic acid as an ionic inhibitor at the CQM/MeOSt ratio of 50/50 in mol % in chloroform at 60 °C for 48 h. For the use of TEMPO (entry 6), the

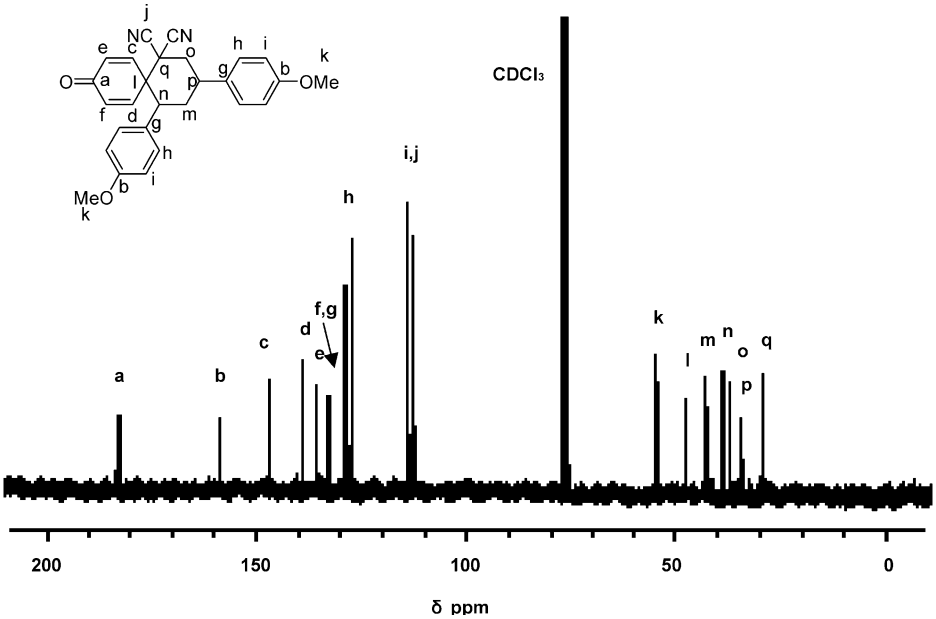


Figure 4. ^{13}C NMR spectrum of the white solids isolated from a hexane-soluble fraction in chloroform-*d*.

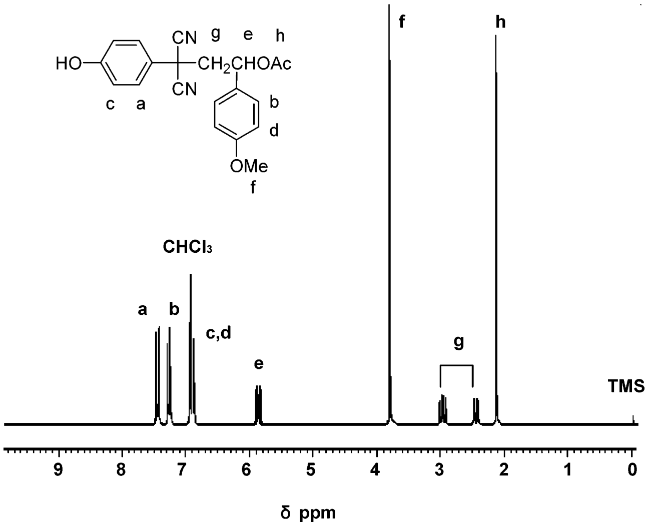


Figure 5. ^{1}H NMR spectrum of the adduct obtained by the spontaneous reaction of the CQM with MeOSt in the presence of acetic acid in chloroform-*d*.

alternating copolymer was obtained as the hexane-insoluble fraction; the molecular weight was almost same as the case without TEMPO (entry 2), and also the hexane-soluble fraction was mainly a mixture of unreacted CQM and MeOSt. On the other hand, the use of acetic acid did not afford alternating copolymers and instead gave white solids, isolated from the reaction mixture by a silica gel column chromatography, in 96.6% yield. ^{1}H NMR and ^{13}C NMR spectra of the white solids are shown in Figures 5 and 6, respectively.

The peaks shown in the figures were assigned to the chemical structure illustrated therein, a 1:1:1 adduct of CQM:MeOSt:acetic acid. The IR spectrum and elemental analysis also supported this chemical structure. However, the 1:2 cycloadduct of CQM:MeOSt and also the 1:2:1 adduct of CQM:MeOSt:acetic acid were not obtained as the reaction products.

Discussion

When CQM was mixed with MeOSt, deep violet color developed in all solvents, indicating the formation of charge-transfer complexes like as the cases of the substituted quinodimethanes/styrene derivatives systems such as the TCNQ/styrene[8] and QM-1/MeOSt[17] systems. Spontaneous reactions of CQM with MeOSt gave alternating copolymers regardless of monomer feed ratios. Addition of TEMPO to the reaction system did not affect the copolymer composition, and also no products trapped by TEMPO were obtained. On the other hand, addition of acetic acid yielded the 1:1:1 adduct of CQM:MeOSt:acetic acid. This indicates that the spontaneous reaction of CQM with MeOSt proceeds via a zwitterionic intermediate, not via a radical one. And also, the chemical structure of the 1:1:1 adduct of CQM:MeOSt:acetic acid is in a good agreement with the repeat unit in the alternating copolymer structure. The maximum of polymer yields was observed at an equimolar feed ratio of CQM and MeOSt, and the polymer yields increased with an increase in solvent polarity. These findings support strongly a polymerization mechanism via a zwitterionic intermediate. Saegusa et al.[21,22] proposed that the spontaneous polymerization of 2-methyl-2-oxazoline with 3-hydroxy-1-propanesulfonic acid sultone takes place to give an alternating copolymer via a ring opening, and this alternating copolymerization proceeds by means of a mechanism via a zwitterionic intermediate. Endo et al.[23] also reported that in the spontaneous polymerization of TCNQ with methoxyallene a zwitterionic intermediate was generated, and an alternating copolymer was obtained by its coupling reaction. It was, therefore, considered that in the spontaneous polymerization of CQM with MeOSt alternating copolymers were formed by the coupling reaction as well as above-mentioned alternating copolymerization systems. Moreover, the 1:2 cycloadduct of CQM:MeOSt was isolated as the reaction product from the hexane-soluble fractions. This product is considered to be formed by addition of another MeOSt molecule to the cationic site of a generated zwitterionic intermediate, followed by cyclization to form the six-membered ring. Therefore, for the spontaneous polymerization of CQM with MeOSt, the mechanism involving a zwitterionic intermediate as shown in Scheme 1 is proposed, where the charge-transfer complex is

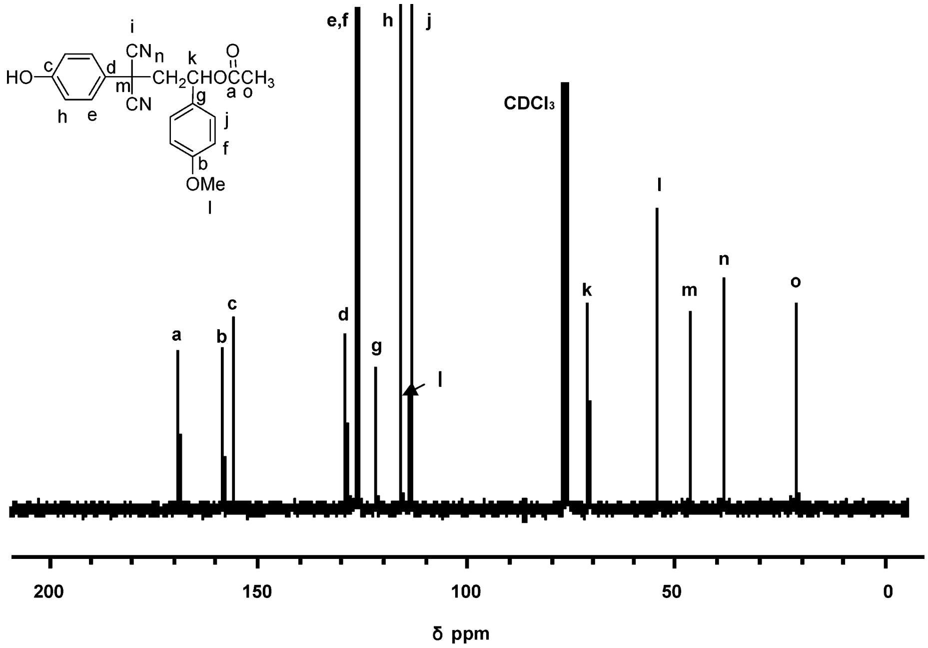
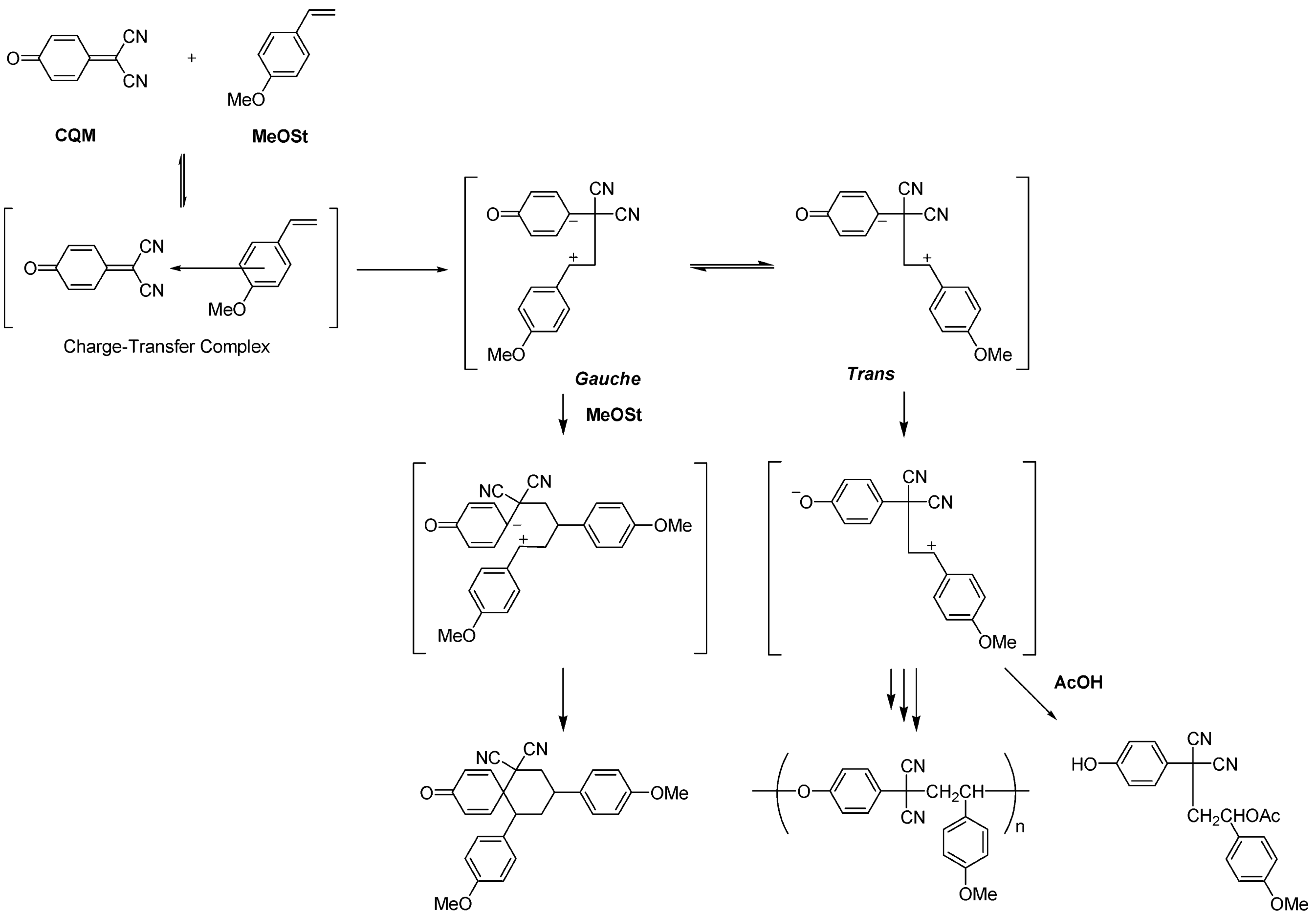


Figure 6. ^{13}C NMR spectrum of the adduct obtained by the spontaneous reaction of the CQM with MeOSt in the presence of acetic acid in chloroform-*d*.

Scheme 1



formed first on mixing monomers as indicated by the color development, and then a zwitterionic intermediate is formed.

Here, it is possible for the zwitterionic intermediate to exist in two forms: gauche and trans forms. Probably, gauche-form zwitterionic intermediate would lead to the 1:2 cycloadduct by addition of another MeOSt to its cationic site and then cyclization, while the trans form one would lead to alternating copolymer by transformation to a phenoxytetramethylene zwitterionic intermediate with the formation of the corresponding stable aromatic structure, followed by the coupling reactions. For the experiments of the solvent effect on spontaneous reactions of CQM with MeOSt, the polymer yields increased with an increase in the solvent polarity (benzene < chloroform < THF), but on the contrary the yields of the 1:2 cycloadduct of CQM:MeOSt decreased. This suggests strongly that the zwitterionic intermediate exists in two forms, gauche and trans forms; that is, in more polar solvents, the zwitterionic intermediate takes mainly a trans form, but in less polar solvents, a gauche form. Similar solvent effect was observed in the spontaneous reaction of methyl 3,3-dicyanoacrylate with MeOSt,[24] though the intermediate is diradical one. The spontaneous reactions of CQM with MeOSt gave their alternating copolymers and 1:2 cycloadducts of CQM: MeOSt. In contrast, in the spontaneous reactions of more stronger electron-accepting QM-1 with MeOSt, 7-(4-methoxyphenyl)-8,8-dicyanoquinodimethane (QM-2) and methylene Meldrum's acid (MM) were formed by metathesis reaction via a zwitterionic intermediate, and QM-2 copolymerized with QM-1 to form copolymer and MM reacted with MeOSt to form 1:1 cycloadduct of MM: MeOSt.[16] The difference in polymerization behavior is observed between both systems although they have formed same zwitterionic intermediates, probably due to the difference in the electron-accepting property between CQM and QM-1. When the weaker electron-accepting CQM was used, electrostatic interaction between positive and negative charges in the zwitterionic intermediate should be weaker in comparison with the case of QM-1. Therefore, the zwitterionic intermediate might take predominantly a trans form, leading to the alternating copolymers. While in the gauche-form zwitterionic intermediate of CQM with MeOSt, weaker interaction between positive and negative charges might allow another MeOSt to add to the cationic site of the intermediate before forming cyclobutane ring, leading to a more stable 1:2 cycloadduct having a cyclohexane ring. On the other hand, in the case of QM-1, a gauche-form zwitterionic intermediate is more favorable because of stronger electrostatic interaction between positive and negative charges in the zwitterionic intermediate to form an unstable cyclobutane ring.

Conclusions

Spontaneous reactions of CQM with MeOSt were investigated in various conditions. On the basis of the analyses of the products obtained at different monomer feed ratios, in three different polarity solvents, and in the presence of additives such as TEMPO and acetic acid, the polymerization mechanism involving a zwitterionic intermediate, which exists in gauche and trans forms, and alternating copolymer formation of the CQM with MeOSt by coupling reaction of the trans-form zwitterionic intermediate were proposed.

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