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Spontaneous Addition Reaction of *N*,7,7-Tricyanobenzoquinone Methide Imine with 1-[(Trimethylsilyl)oxy]-1-cyclohexene

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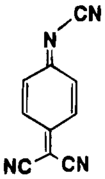
ABSTRACT: Spontaneous reaction of *N*,7,7-tricyanobenzoquinone methide imine (BMI) with 1-[(trimethylsilyl)oxy]-1-cyclohexene (**1**) was carried out at 60 °C in acetonitrile with the concentration of BMI below and above its equilibrium monomer concentration, and reaction products were analyzed. On the basis of the structure of the reaction products and ^{1}H NMR spectra observed in situ for the reactions of BMI with **1** and of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with **1**, the initiation mechanism and a driving force to determine the addition direction for the intermediate formation are discussed.

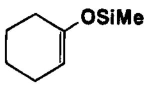
Introduction

Spontaneous polymerizations of electron-accepting quinodimethane derivatives such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, 2,5,7,7,8,8-hexacyanoquinodimethane, and 11,11,12,12-tetracyano-2,6-naphthoquinodimethane with donor monomers such as styrene, butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether were studied previously.[1–4] Styrene copolymerized in alternating fashion with these quinodimethane derivatives and vinyl ethers polymerized with these quinodimethanes in two modes of polymerization, namely, alternating copolymerization and cationic homopolymerization of the vinyl ethers. The polymerization mode for the vinyl ethers was greatly dependent upon the electron-accepting character of the quinodimethane derivatives and the electron-donating character of the vinyl ethers; that is, cationic polymerizations of vinyl ethers took place in the strong electron-accepting quinodimethane–strong electron-donating vinyl ether cases and alternating copolymerization occurred in the weak electron-accepting quinodimethane-weak electron-donating vinyl ether cases.[1–4] For the spontaneous reactions of TCNQ with alkyl vinyl ethers, Stille *et al.*[5] proposed that zwitterionic intermediates are formed through charge-transfer complex formation between TCNQ and alkyl vinyl ethers and a further electron-transfer reaction and that their cationic ends initiate the cationic polymerization of the alkyl vinyl ethers. Iwatsuki *et al.*[6] studied the spontaneous reactions of TCNQ with cyclic enol ethers such as 1-methoxy-1-cyclopentene, 1-methoxy-1-cyclohexene, 1-[(trimethylsilyl)oxy]-1-cyclopentene, and 1-[(trimethylsilyl)oxy]-1-cyclohexene (**1**). They found that zwitterionic intermediates were generated as well for the reactions of TCNQ with alkyl vinyl ethers. For the reaction of 1-[(trimethylsilyl)oxy]-1-cyclopentene or **1** with TCNQ, the trimethylsilyl group in the zwitterionic intermediates shifted to the anionic end, that is, to the dicyanomethylene anion of the TCNQ unit, to give organosilane intermediates.[6] Recently, Hall *et al.*[7] have proposed a mechanism, the bond-forming initiation theory, for the initiation of the spontaneous polymerizations of electron-poor olefins with electron-rich olefins involving tetramethylene intermediates, which can be zwitterionic or diradical depending on the nature of the substituents on their olefins. These authors also have extended this theory to the spontaneous reactions of donor monomers with electron-accepting quinodimethane derivatives.[8]

In this work, the spontaneous reaction of *N*,7,7-tricyanobenzoquinone methide imine (BMI) with **1** was investigated in order to elucidate the initiation mechanism. BMI (first reduction potential (E_1) = +0.17 V)[9] was found to be as strongly electron-accepting as TCNQ (E_1 = +0.19 V),[9] but it homopolymerized with radical and anionic initiators[9] and underwent a typical equilibrium polymerization,[10] greatly different from the polymerization behavior of TCNQ. Moreover, BMI contains different exocyclic atoms such as the dicyanomethylene carbon at the 7-position and the cyanoimine nitrogen at the 8-position. The difference should allow one to know the primary reaction site (the addition direction) by means of detailed structure analysis of the spontaneous reaction products between BMI and **1** as donor monomer.



BMI



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Experimental Section

N,7,7-Tricyanobenzoquinone methide imine (BMI) was prepared according to the method reported previously.[9] 1-[(Trimethylsilyl)oxy]-1-cyclohexene (**1**) was prepared from trimethylsilyl chloride and cyclohexanone according to the method reported by House *et al.*[11] Phenylcyanamide and phenylmalononitrile were prepared according to the methods reported by Kurzer *et al.*[12] and by Uno *et al.*,[13] respectively. Commercial 7,7,8,8-tetracyanoquinodimethane (TCNQ) was purified by recrystallization (twice) from acetonitrile. Acetonitrile (bp 82 °C) was refluxed over calcium hydride for 12 h and then distilled. Number-average molecular weight was determined without correction by gel permeation chromatography (GPC) using standard polystyrene as a reference and tetrahydrofuran as an eluent. ^{1}H NMR measurement was carried out in chloroform-*d* or dimethyl-d_6 sulfoxide with tetramethylsilane as an internal standard. A Büchi capillary melting point apparatus was used for melting point measurement, a JEOL JNM-EX270 FT NMR spectrometer for ^{1}H NMR spectroscopy, a Jasco IR-700 spectrometer for infrared spectroscopy, a Yanaco CHN corder MT-3 for elemental analysis,

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and a gel permeation chromatographic meter Tosoh HLC-803D with a series of two columns, Tosoh G2500H and G2000H, for number-average molecular weight measurement, respectively. Metrohm 665 Dosimat autotitrator, Metrohm E 536 potentiograph, and Horiba glass electrode were used for the potentiometry.

Reaction of BMI with 1. BMI (70.0 mg, 0.39 mmol), 85.0 mg (0.50 mmol) of **1**, and 10 mL of acetonitrile as solvent were placed in an ampule, which was degassed by the freeze–thaw method (repeated twice) and sealed. The concentration of BMI in this solution corresponds to 3.89×10^{-2} mol/L, which is above the equilibrium monomer concentration of BMI of 2.92×10^{-2} mol/L[10] at 60 °C. The ampule was set in a bath thermostated at 60 ± 0.1 °C for 10 h. White solid precipitated in the ampule during polymerization. The reaction mixture was poured into 100 mL of chloroform to precipitate the reaction product, which was collected by filtration and washed with chloroform and methanol. The chloroform- and methanol-insoluble product (118.0 mg) was taken as sample 1.

BMI (70.0 mg, 0.39 mmol), 66.0 mg (0.39 mmol) of **1**, and 40 mL of acetonitrile were placed in an ampule, which was degassed by the freeze–thaw method. The concentration of BMI corresponds to 9.71×10^{-3} mol/L, which is below the equilibrium monomer concentration of BMI of 2.92×10^{-2} mol/L at 60 °C. The ampule was set in a bath thermostated at 60 ± 0.1 °C for 10 h. The reaction mixture was poured into an excess of isopropyl ether to deposit the reaction product, which was dissolved in 10 mL of chloroform. The resulting solution was filtered to remove a small amount of insoluble product (about 10 mg), and the filtrate was poured again into an excess of isopropyl ether to give 92 mg of a white solid. The product soluble in chloroform and insoluble in isopropyl ether was taken as sample 2. ^1H NMR ($CDCl_3$): δ 7.40 (br, 1H), 7.54 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 3.17 (m, 1H), 2.54 (m, 1H), 2.40 (m, 1H), 2.14 (m, 1H), 1.96 (m, 2H), 1.66 (m, 3H).

Procedure for the Reaction of BMI with 1 in a NMR Tube. Chloroform-*d* without containing tetramethylsilane as an internal standard was used as a solvent, and each chemical shift was estimated relative to chloroform contained as an impurity which appeared at 7.26 ppm.

BMI (1.2 mg) in chloroform-*d* was mixed with **1** (4.6 mg) in 1 mL of chloroform-*d*, and 0.5 mL of the resulting solution was placed in a NMR tube which was purged with nitrogen gas and sealed. Concentrations of BMI and **1** in the resulting solution were 1.35×10^{-2} mol/L each. The NMR tube was set in a bath thermostated at 60 °C, and its NMR spectra were measured at room temperature in 30-min intervals. For the spontaneous reaction of TCNQ with **1** in a NMR tube, 0.9 mg of TCNQ was placed in a NMR tube and then 2.5 mg of **1** in 1 mL of chloroform-*d* was added. The rest of the procedure was similar to that for the reaction of BMI with **1**.

Measurements of pK_a for Phenylcyanamide and Phenylmalononitrile. The pK_a values of phenylcyanamide and phenylmalononitrile were determined using a potentiometer according to the method reported by Albert and Serjeant.[14] A given amount of phenylcyanamide or phenylmalononitrile was dissolved in ethanol, and into the resulting solution was added deionized water in order to obtain the 10 vol % or 50 vol % ethanol solutions. The solution was titrated with a 0.1 N potassium hydroxide aqueous solution at a temperature of 25 ± 1 °C using an automatic titrator. The mean of eight to nine values obtained for each compound was adopted as the pK_a value.

Results and Discussion

Sample 1, obtained from the reaction of **1** with BMI at a BMI concentration of 3.89×10^{-2} mol/L, which is above its equilibrium monomer concentration, was partially soluble in tetrahydrofuran. The molecular weight of the soluble part in tetrahydrofuran was about 1000 by the GPC measurement. The IR spectrum of sample 1 exhibited absorption bands at 3414 cm^{-1} due to the stretching vibration of the nitrogen–hydrogen bond, 2910–2832 cm^{-1} due to the carbon–hydrogen bond of aliphatic methylene, 2222 cm^{-1} due to the nitrile group, 1681 cm^{-1} due to the carbonyl group, 1595 and 1484 cm^{-1} due to the carbon–carbon double bonds of the aromatic ring, and 827 cm^{-1} due to out-of-plane deformation of substituted benzene, characteristic of a two-adjust-hydrogen system, respectively. The ^1H NMR spectrum of sample 1 measured in dimethyl-d_6 sulfoxide showed peaks at 8.2–7.2 ppm due to the NH and aromatic protons of the BMI unit, 4.0–3.9 ppm due to a methine proton at the 1-position of the 2-oxocyclohexyl group, and 2.6–2.4 and 2.0–1.5 ppm due to methylene protons at the 3-, 4-, 5-, and 6-positions of the 2-oxocyclohexyl group. The peak area ratio of the aromatic and NH protons (8.2–7.2 ppm) to methine proton (4.0–3.9 ppm) at the 1-position of the 2-oxocyclohexyl group was to be 9.6, corresponding well to the BMI/**1** unit ratio of 2.4. The elemental analysis values of sample 1 (H, 3.81; C, 72.57; N, 20.57) were in good agreement with the calculated ones (calcd for $C_6H_9O\text{-}(C_{10}H_4N_3)_{2.4}$: H, 3.98; C, 72.51; N, 20.29). BMI was homopolymerizable with anionic initiator butyllithium in toluene at a BMI concentration of 3.50×10^{-2} mol/L.[9] Therefore, it is pointed out that sample 1 is a compound composed of one **1** unit and more than two BMI units which reacted successively via an anionic addition, indicating that when the concentration of BMI in feed is above its equilibrium monomer concentration of 2.92×10^{-2} mol/L at 60 °C, anionic polymerization of BMI takes place.

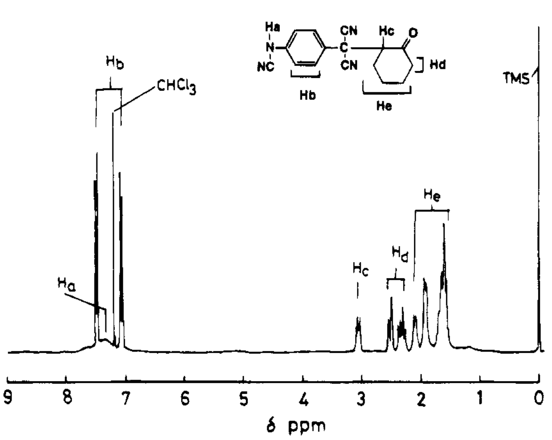
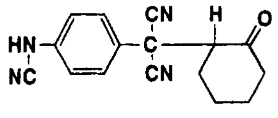


Figure 1. ^1H NMR spectrum of sample 2 in chloroform-*d*.

Sample 2, obtained from the reaction of **1** with BMI at a BMI concentration of 9.71×10^{-3} mol/L, which is below its equilibrium monomer concentration, melted at 120 °C with decomposition and was soluble in chloroform, ethyl acetate, and tetrahydrofuran and insoluble in hexane, benzene, and isopropyl ether. The IR spectrum of sample 2 exhibited absorption bands at 3392 cm^{-1} due to the stretching vibration of the nitrogen–hydrogen bond, 2912–2832 cm^{-1} due to the carbon–hydrogen bond of aliphatic methylene, 2220 cm^{-1} due to the nitrile group, 1675 cm^{-1} due to the carbonyl group, 1583 and 1489 cm^{-1} due to the carbon–carbon double bonds of the aromatic ring, and 822 cm^{-1} due to out-of-plane deformation of substituted benzene, characteristic of a two-adjust-hydrogen system, respectively. The ^1H NMR spectrum measured in chloroform-*d* is shown in Figure 1, where each peak is assignable to each proton in the chemical structure illustrated herein. Elemental analysis values of sample 2 (H, 5.21; C, 69.20; N, 19.82) are in good agreement with the calculated ones (H, 5.09; C, 69.05; N, 20.13) of compound **2**. Therefore, it could be concluded from the IR and ^1H NMR spectral data and elemental analysis data that sample 2 is



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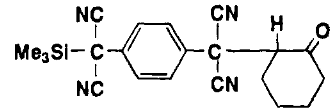
compound **2**, indicating that when the concentration of BMI in the feed is below its equilibrium monomer concentration, **2** derived from one BMI unit and one **1** unit is mainly formed.

The reaction of BMI with **1** in chloroform-*d* was carried out at 60 °C in a sealed NMR tube with each monomer concentration of 1.35×10^{-2} mol/L, and its ^{1}H NMR spectra were observed *in situ* in each 30-min interval. ^{1}H NMR spectra at reaction times of 0 and 120 min are shown in parts a and b of Figure 2, respectively. At the reaction time of 0 min, each peak in Figure 2a was assignable to each proton of BMI and **1** illustrated herein, and at the reaction time of 120 min (Figure 2b), new peaks in addition to peaks due to each proton of BMI and **1** appeared at 0.34, 1.74, 1.88, 2.18, 2.41, 2.57, 3.09, 7.07, and 7.48 ppm. These new signals increased in intensity as the reaction proceeded, whereas the signals due to each proton of BMI and **1** decreased. The new proton signals observed at 1.74, 1.88, 2.18, 2.41, 2.57, 3.09, 7.07, and 7.48 ppm except for a proton signal at 0.34 ppm correspond well to the chemical shift values of each proton of **2** illustrated in Figure 1. However, the proton signal assignable to NH in **2** was not observed and instead a signal due to the trimethylsilyl proton appeared at 0.34 ppm, indicating that trimethylsilyl group is attached to a lower electron-density part than that of **1**. Previously, it was reported that an organosilane **3**, where the trimethylsilyl group of **1** unit shifted to dicyanomethylene carbon of the TCNQ unit, could be generated in the reaction of TCNQ with **1** in chloroform-*d* in a sealed tube.[8] If a similar



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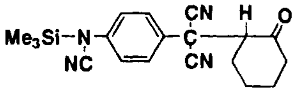
reaction would take place between BMI and **1**, the formation of two kinds of compounds is possible owing to the chemical structure of BMI with two different exocyclic atoms, i.e., organosilanes **4** and **5**. When the



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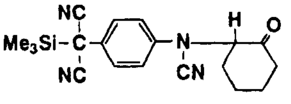

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reaction of TCNQ with **1** in chloroform-*d* was carried out in a sealed NMR tube at 60 °C, the signal due to the trimethylsilyl proton of **3** was observed at 0.15 ppm. The corresponding signal of the reaction mixture of BMI with **1** appeared at 0.34 ppm as a new signal, as shown in Figure 2b, and no signal at 0.15 ppm was observed, indicating that only **4** is generated in the reaction mixture of BMI with **1**. This is also supported by the formation of **2** as the main product in the reaction of BMI with **1** with the concentration of BMI below its equilibrium monomer concentration.

In analogy with the mechanism proposed for reactions of TCNQ with alkyl vinyl ethers[2] and cyclic enol ethers,[8] it can be postulated that the reaction of BMI with **1** takes place as shown in Scheme 1. One electron-transfer reaction between BMI and **1** takes place to form the anion radical of BMI and the cation radical of **1**, both of which linked up between the dicyanomethylene carbon of BMI and the β-carbon toward the trimethylsilyloxy group of **1** to form the zwitterionic intermediate **I**. In concentrations above its equilibrium monomer concentration, BMI is able to add to the phenylcyanamide anion of the zwitterionic intermediate **I** to provide an oligomer of BMI. When the concentration of BMI is below its equilibrium monomer concentration, BMI no longer adds and the phenylcyanamide anion of the

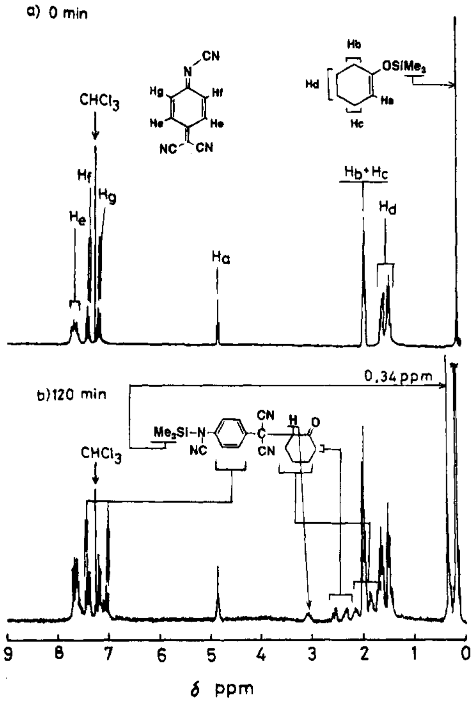
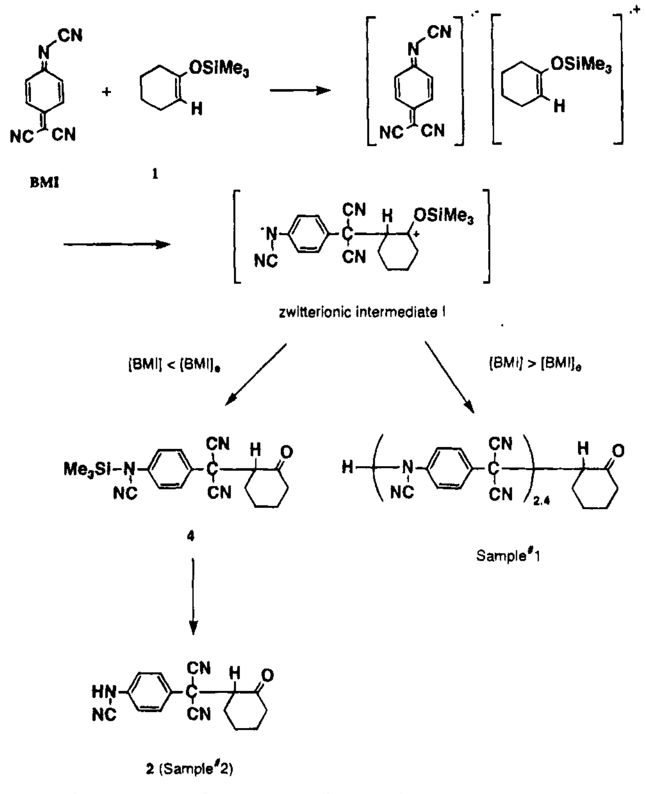


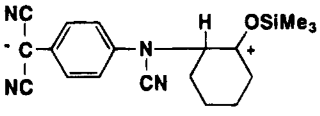
Figure 2. ^{1}H NMR spectra of the reaction mixture of BMI with **1** in chloroform-*d*: (a) reaction time, 0 min; (b) reaction time, 120 min.

Scheme 1



zwitterionic intermediate **I** may attack intramolecularly or intermolecularly the silicon atom in the zwitterionic intermediate **I** to result in the organosilane **4**. The trimethylsilyl group is so labile in water that it is readily subjected to hydrolysis during postreaction treatment to give **2**, that is, sample 2. From the difference of the products obtained above and below the equilibrium monomer concentration of BMI, the addition reaction of BMI to the phenylcyanamide anion is considered to take place more readily than the shift of the trimethylsilyl group.

In the bond formation between the anion radical of BMI and the cation radical of **1**, the stabilization of the resulting anion and cation and the energy of the bond formation should be considered. The cation of the zwitterionic intermediate due to the **1** unit is considered to exist on a carbon atom with the trimethylsilyloxy group because the trimethylsilyloxy group is more electron-donating than a hydrogen atom. For the anion of the zwitterionic intermediate due to the BMI unit, two forms are possible, i.e., phenylcyanamide anion or phenylmalononitrile anion. Therefore, in order to compare the stabilization of the phenylcyanamide anion with that of the phenylmalononitrile one, pK_a values of phenylcyanamide and phenylmalononitrile were measured in 10 vol % and 50 vol % ethanol solutions at 25 °C. The pK_a values for phenylcyanamide were estimated to be 8.42 in a 10 vol % ethanol solution and 9.45 in a 50 vol % ethanol solution, and the corresponding values for phenylmalononitrile were estimated to be 5.02 and 5.51. The pK_a values of phenylcyanamide were larger than those of phenylmalononitrile, indicating that stabilization of the phenylmalononitrile anion is larger than that of the phenylcyanamide anion. If the stabilization of the resulting anion is a driving force to determine the addition direction for the zwitterionic intermediate formation, zwitterionic intermediate **II** should be formed instead of zwitterionic intermediate **I**, which is not in agreement with the chemical structure of **2** (sample 2) obtained in this reaction, indicating that the stabilization of the resulting anion is not a driving force to determine the addition direction for the intermediate formation. For the energy of the bond formation, the bonding energies of a carbon–carbon single bond and a carbon–nitrogen one are reported to be 83–85 and 69–75 kcal/mol,[16] respectively, indicating that the bonding energy of a carbon–carbon single bond is larger than that of a carbon–nitrogen one. If the energy of bond formation is a driving force to determine the addition direction for the zwitterionic intermediate formation, zwitterionic intermediate **I** should be formed and is in good agreement with the chemical structure of **2**. It is concluded therefore that the energy of bond formation probably prevails over the stabilization of the resulting anion as a driving force to determine the addition direction for the intermediate formation.



zwitterionic intermediate II

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