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Polymerization of *o*-Quinodimethanes Bearing Electron-Donating Groups *in Situ* Formed by Thermal Isomerization of Benzocyclobutenes

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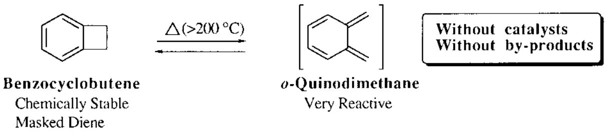
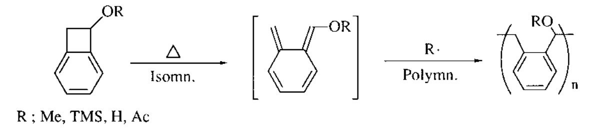
ABSTRACT: The substituent effect on the polymerization of *o*-quinodimethanes generated by thermal isomerization of benzocyclobutenes and the reaction of the obtained polymer is described. Polymerizations of 1-methoxybenzocyclobutene (**1**), 1-acetoxy benzocyclobutene (**2**), 1-hydroxybenzocyclobutene (**3**), and 1-((trimethylsilyl)oxy)benzocyclobutene (**4**) as benzocyclobutenes bearing electron-donating groups were examined. Although polymerization of **2** and **3** did not afford any polymer, polymerization of **1** and **4** in the presence of a radical initiator gave MeOH-insoluble polymer (M_n = 5000−11000) in moderate yields at temperatures above 90 °C, respectively. The structures of the obtained polymers were confirmed to be ring-opened polymer (**5**, **6**) by IR, ^{1}H-NMR, and ^{13}C-NMR. The yield of the polymer increased with increase of the concentration of the initiator. This polymerization was supported to proceed based on the driving force of aromatization stabilizing effect by semiempirical calculation. Radical copolymerizations of **1** with vinyl monomers were carried out to obtain the corresponding copolymers. Lastly, treatment of **3** with *p*-toluenesulfonic acid (10%) gave poly(*o*-phenylenevinylene) (**7**) quantitatively and its properties (UV absorption, T_g, Td_{10} (10% weight loss temperature)) were estimated.

Introduction

Scheme 1



Scheme 2



Benzocyclobutenes are the most convenient precursors of *o*-quinodimethanes (or *o*-xylylenes)[1] which are formed as reactive intermediates by solely heating *via* their simple isomerizations (Scheme 1). Polymerization of *o*-quinodimethane has never been reported in the literatures so far because the *o*-quinodimethane is highly unstable, in spite of the fact that *o*-quinodimethane can be regarded as a 1,3-diene with *cis* conformation. As reported in Oppolzer[2] and confirmed by our unpublished calculations,[3] introduction of an electron-donating substituent onto the cyclobutene ring of benzocyclobutenes effectively lowers the isomerization temperature to *o*-quinodimethane (unsubstituted benzocyclobutene; more than 200 °C). To overcome above difficulty, we have performed polymerization of *o*-quinodimethanes *in situ* produced through the thermal isomerization of the corresponding benzocyclobutenes. Recently, we have found 1-methoxy-*o*-quinodimethane can radically polymerize to give a corresponding ring-opened polymer *via* aromatization.[4] That is, the process can be regarded as one of the polymerizations containing monomer isomerization processes as outlined in Scheme 2. The work was the first example of the polymerization of *o*-quinodimethane itself and was very interesting. To follow up the above concept, we further investigated the substituent (electron-donating group) effect on the polymerization of *o*-quinodimethanes generated by ther-

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mal ring-opening isomerization of benzocyclobutenes and the polymer reaction of the obtained polymer in detail in this paper (Scheme 2).

Experimental Section

Materials. Benzoyl peroxide (BPO), 1,1′-azobis(cyclohexane-1-carbonitrile) (ACC), dicumyl peroxide (DCP), di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP), methyl methacrylate (MMA), methyl acrylate, acrylonitrile, and maleic anhydride were purchased and purified using conventional methods.

Semiempirical Molecular Orbital Calculation. Molecular orbital calculations and full geometrical optimization were performed on an Apple Macintosh IICi(40 MHz CXP coprocessor) using MOPAC version 6.02 (QCPE No.455)[5,6] with the restricted or unrestricted Hartree−Fock method with PM3 parameter.

1-Bromobenzocyclobutene.[7] Yield 62%. Bp 55 °C/1 mmHg (lit.[7] 90 °C/10.5 mmHg). IR(neat): 3069, 2976, 2930, 2829, 1458, 1423, 1342, 1321, 1278, 1205, 1180, 1163 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.3−6.9 (m, 4H, Ph), 5.29 (dd, J = 2.1 and 4.6 Hz, 1H, CH), 3.69 (dd, J = 4.6 and 14.7 Hz, 1H, CH$_2$), 3.35 (dd, J = 2.1 and 14.7 Hz, 1H, CH$_2$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 146.1, 142.1, 130.3, 128.4, 123.5, 122.7, 34.1, 33.2.

1-Methoxybenzocyclobutene (1). MeOH (20 mL) was slowly added to 2.0 g (0.083 mol) of NaH while continuously stirring. After cooling, 11.04 g (0.06 mol) of 1-bromobenzocyclobutene was dropwise added to the reaction mixture and refluxed for 5 h. After cooling, the solution was evaporated and 50 mL of water was added and extracted with ether three times (150 mL). The ether solution was dried over MgSO$_4$ and evaporated, and 5.79 g (72%) of 1-methoxybenzocyclobutene (**1**) was obtained by distillation as colorless oil. Bp 34 °C/2 mmHg (lit.[8] 50 °C/5 mmHg). IR(neat): 3067, 3022, 2984, 2928, 2876, 2822, 2367, 2083, 1911, 1800, 1721, 1661, 1599, 1458, 1422, 1352, 1279, 1209, 1171, 1152, 1136 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.18 (m, 4H, Ph), 4.92 (dd, J = 4.3 and 2.0 Hz, 1H, CH), 3.42 (s, 3H, OMe), 3.40 (dd, J = 13.8 and 4.3 Hz, 1H, CH$_2$), 3.06 (dd, J = 13.8 and 2.0 Hz, 1H, CH$_2$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 145.95, 142.50, 129.33, 127.01, 123.47, 122.70, 78.00, 56.00, 38.10.

1-Acetoxybenzocyclobutene (2).[9] Yield 70%. Bp 72−73 °C/3.5 mmHg (lit.[10] 55−56 °C/0.1 mmHg). IR(neat): 3385, 3069, 2934, 2832, 2361, 1738, 1660, 1603, 1458, 1426, 1373, 1348, 1238, 1181, 1152, 1136, 1113, 1084, 1040, 1009, 953 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.23 (s, 4H, Ph), 5.90 (dd, J = 10.8 and 4.5 Hz, 1H, CH), 3.56 (dd, J = 31.5 and 10.8 Hz, 1H, CH$_2$), 3.27 (dd, J = 31.5 and 10.8 Hz, 1H, CH$_2$), 2.05 (s, 3H, CH$_3$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 170.83, 144.30, 142.70, 130.00, 127.53, 123.56, 123.17, 98.84, 71.58, 20.83.

1-Hydroxybenzocyclobutene (3). A solution of **2** (33.9 g, 0.21 mol) and *p*-toluenesulfonic acid monohydrate (1.9 g, 0.01 mol) in MeOH (100 mL) was stirred at room temperature for 24 h. The solution was evaporated and 50 mL of water was added and extracted with ether three times (150 mL). The ether solution was dried over MgSO$_4$ and evaporated, and 21.4 g (85%) of 1-hydroxybenzocyclobutene (**3**) was obtained by recrystallization as white powder. Mp 86 °C (lit.[9] 85 °C). IR(neat): 3385, 3069, 2934, 2832, 2361, 1738, 1660, 1603, 1458, 1426, 1373, 1348, 1238, 1181, 1152, 1136, 1113, 1084, 1040, 1009, 953 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.16 (m, 4H, Ph), 5.10 (dd, J = 4.5 and 2.0 Hz, 1H, CH), 3.58 (s, 1H, OH), 3.47 (dd, J = 14.5 and 4.5 Hz, 1H, CH$_2$), 2.89 (dd, J = 14.5 and 2.0 Hz, 1H, CH$_2$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 147.82, 142.26, 129.33, 127.12, 123.49, 122.24, 70.64, 42.07.

1-((Trimethylsilyl)oxy)benzocyclobutene (4).[11] Yield 70%. Bp 46 °C/0.3 mmHg. IR(neat): 3069, 3024, 2950, 2926, 1599, 1456, 1424, 1352, 1252, 1209, 1140, 1120 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.12 (m, 4H, Ph), 5.23 (dd, J = 4.5 and 2.0 Hz, 1H, CH), 3.49 (dd, J = 14.0 and 4.5 Hz, 1H, CH$_2$), 3.04 (dd, J = 14.0 and 2.0 Hz, 1H, CH$_2$), 0.20 (s, 9H, SiMe$_3$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 141.12, 140.89, 127.96, 125.92, 122.30, 121.17, 69.10, 41.00, −0.87.

Radical Polymerization. Typical Procedure. A mixture of **1** (0.134 g, 1 mmol) and DTBP (4.39 mg, 0.03 mmol) was placed in an ampule, degassed, and sealed *in vacuo*. After being stirred at 120 °C for 24 h, the reaction mixture was dissolved in THF and poured into a large amount of methanol. The obtained white precipitate was separated by filtration, washed thoroughly with methanol, and dried under vacuum to obtain 0.03 g (23%) of poly(1-methoxybenzocyclobutene) (**5**). IR (KBr): 3061, 3024, 2974, 2932, 2822, 2361, 2087, 1925, 1715, 1603, 1580, 1490, 1451, 1362, 1261, 1221, 1159, 1103, 1050, 1030, 990, 950 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.1 (br, d, 4H, Ph), 4.9 (br, d, CH), 3.1 (br, s, 3H, OMe), 2.8 (br, s, 2H, CH$_2$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 141.65, 137.36, 130.61, 127.44, 52.50, 82.03, 56.35, 41.03

Poly(1-((trimethylsilyl)oxy)benzocyclobutene) (6). IR (KBr): 3063, 3025, 2595, 2247, 1929, 1827, 1698, 1638, 1603, 1578, 1489, 1451, 1410, 1373, 1252, 1213, 1179, 1159, 1074, 1009, 939, 909, 756, 735 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.3 (br, d, 4H, Ph), 5.4 (br, s, CH), 3.2 (br, d, 2H, CH$_2$), −0.2 (br, s, 9H, SiMe$_3$). ^{13}C-NMR (22.5 MHz, CDCl$_3$): δ 143.9, 136.2, 133.7, 130.0, 128.0, 126.4, 92.5, 72.8, 41.5, 19.2, 0.0.

Radical Copolymerization. Typical Procedure. A mixture of **1** (0.207 g, 1.49 mmol), methyl methacrylate (0.149 g, 1.49 mmol), and DTBP (di-*tert*-butyl peroxide) (0.131 g, 0.877 mmol) was placed in an ampule, degassed, and sealed *in vacuo*. After being stirred at 120 °C for 24 h, the reaction mixture was dissolved in THF and poured into a large amount of methanol. The white precipitate was separated by filtration, washed thoroughly with methanol, and dried under vacuum to obtain 0.11 g (31%) of poly(1-methoxybenzocyclobutene-*co*-methyl methacrylate). IR (KBr): 2994, 2951, 2826, 2359, 1732, 1636, 1487, 1451, 1387, 1242, 1148, 1103, 990 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.2 (br, d, Ph), 4.3 (br, d, CH), 3.6 (br, s, COOMe), 3.1 (br, d, OMe, CH$_2$), 1.9 (br, s, CH$_2$), 0.9 (br, d, CH$_3$).

Poly(1-methoxybenzocyclobutene-*co*-methyl acrylate). Yield: 41%. IR (KBr): 1148(OMe), 1730, 1241, 1190(COOMe) cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.1 (br, d, Ph), 4.3 (br, d, CH), 3.8 (br, s, CH), 3.5 (br, s, COOMe), 3.1 (br, s, OMe, CH$_2$).

Poly(1-methoxybenzocyclobutene-*co*-acrylonitrile). Yield: 36%. IR (KBr): 2321(CN), 1152(OMe) cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.3 (br, s, Ph), 4.3 (br, d, CH), 3.2 (br, s, OMe), 2.5 (br, s, CH$_2$), 2.1 (br, s, CH).

Poly(1-methoxybenzocyclobutene-*co*-maleic anhydride). Yield: 25%. IR (KBr): 1865, 1788(CO), 1152(OMe) cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.1 (br, d, Ph), 4.9 (br, d, CH), 3.7 (br, s, CH), 3.1 (br, s, OMe), 2.8 (br, s, CH$_2$).

Polymer Reaction of Poly(1-methoxybenzocyclobutene) (5). A mixture of **5** (0.011 g, 0.079 mmol) and *p*-toluenesulfonic acid monohydrate (0.0015 g, 0.0079 mmol) was heated at 60 °C for 3 h *in vacuo*. After 3 h, the reaction mixture was dissolved in THF and poured into a large amount of methanol. The obtained pale yellow precipitate was separated by filtration, washed thoroughly with methanol, and dried under vacuum to obtain poly(*o*-phenylene vinylene) (**7**) (0.0083 g, 75%). IR (KBr): 3676, 3650, 3545, 3100, 3017, 2922, 2850, 2600−2400, 2363, 2000−1650, 1545, 1487, 1452, 1263 cm^{-1}. ^{1}H-NMR (90 MHz, CDCl$_3$): δ 8.0−6.3 (br, s, Ph, HC=CH), 5.0−2.4 (br, CH, CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 128−124.

Measurements. GC analyses were performed on a Shimadzu GC8APF. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JNM EX-90 or JNM EX-400 spectrometers. Molecular weights were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCPD equipped with three polystyrene gel columns (Tosoh TSK-GEL G5000Hxl, G4000Hxl, and G2500Hxl) at 35 °C, using THF as an eluent. Thermogravimetric analyses (TGA) were carried out with a SEIKO TG/DTA200 at the heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) analyses were made on a SEIKO DSC220C at a heating rate of 10 °C/min.

Results and Discussion

Isomerization Behavior. As benzocyclobutenes bearing electron-donating groups, 1-methoxy benzocy-

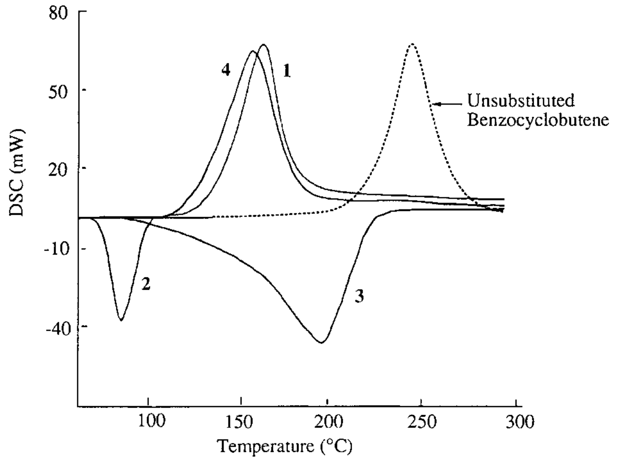
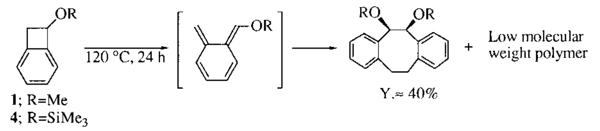


Figure 1. DSC curves of **1**, **2**, **3**, **4**, and unsubstituted benzocyclobutene (heating rate, 10 °C/min).

Scheme 3



Scheme 4

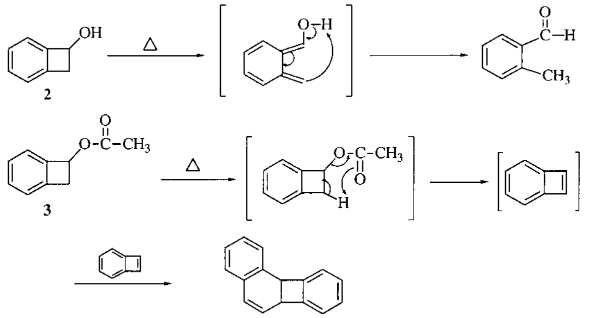


Table 1. Radical Polymerization of 1-Substituted Benzocyclobutenes[a]

run	monomer	yield (%)[b]	M_n (M_w/M_n)[c]
1	**1**	23	8700 (1.65)
2	**2**	0	
3	**3**	0	
4	**4**	20	6000 (1.40)

[a] DTBP 3 mol %, 120 °C, 24 h. [b] MeOH-insoluble part. [c] Estimated by GPC (THF-eluent, based on polystyrene standards).

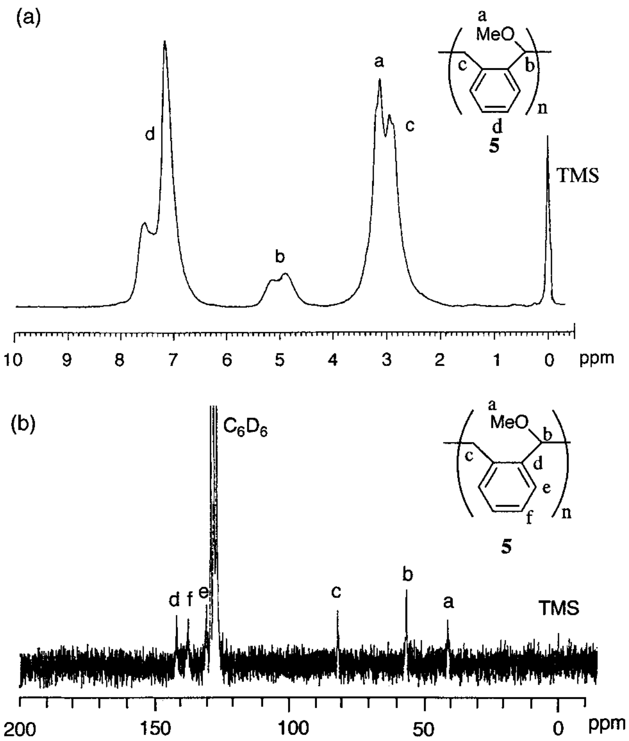


Figure 2. ^{1}H-NMR spectrum (90 MHz, $CDCl_3$) (a) and ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) (b) of **5**.

clobutene (**1**),[8] 1-acethoxybenzocyclobutene(**2**),[9] 1-hydroxybenzocyclobutene(**3**),[10] and 1-((trimethylsilyl)oxy)-benzocyclobutene (**4**)[11] were prepared with reference to the literature.[8-11] The isomerization temperatures of **1**–**4** were estimated by DSC, as shown in Figure 1.

In the cases of **1** and **4**, the exothermic peak by the self-Diels–Alder reaction of corresponding *o*-quinodimethane was observed; generation of *o*-quinodimethane was found to take place above 110 °C. On the other hand, some decomposition reactions seemed to undergo in the cases of **2** and **3** (endothermic peak).

All four compounds (**1**–**4**)were heated at 120 °C for 24 h without any polymerization initiator in a sealed tube respectively, but only two compounds (i.e., **1** and **4**) gave oligomeric products including the *cis*-dimer (ca. 40% yields) (Scheme 3). On the other hand, heating of **2** afforded mainly *o*-tolualdehyde generated by the sigmatropic reaction of 1-hydroxy-*o*-quinodimethane,[12] **3** afforded mainly benzobiphenylene generated by the dimerization of benzocyclobutadiene generated by the release of acetic acid from **3** (Scheme 4)[13].

These results would indicate that **1** and **4** can isomerize to the corresponding *o*-quinodimethanes, respectively, although **2** and **3** do not isomerize the *o*-quinodimethanes.

Polymerization. Radical polymerization of **1**–**4** was carried out using 3 mol % of DTBP at 120 °C for 24 h as summarized in Table 1. Although **1** and **4** gave the MeOH-insoluble polymer in ca. 20% yield, **2** and **3** gave no polymer as suggested above. The structures of the obtained polymers from **1** and **4** were confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR. In the ^{1}H-NMR spectra of the obtained polymer (**5**) from **1**, signals due to benzyl protons at 5.2, 4.9, and 2.8 ppm were observed (Figure 2a). The NMR signals of **5** supported structure of the simple ring-opened polymer. The presence of two broad peaks at 5.2 and 4.9 ppm may suggest some tacticity.

The ^{13}C-NMR spectra of the polymer showed signals due to benzyl carbons at 56.35 and 41.03 ppm (Figure 2b). As these peaks would be almost singlets, two broad peaks in the ^{1}H-NMR would be based on some tacticity. These spectral data supported the structure of **5** having head to tail linkage, as shown in Figure 2.

Temperature Effect. Radical polymerizations of **1** and **4** were carried out at 80–140 °C for 24 h in the presence of a radical initiator to examine the temperature dependence on the polymerization, as summarized in Table 2.

The bulk polymerizations of **1** and **4** were carried out at 80 °C in the presence of benzoyl peroxide (BPO) to recover the corresponding monomers completely (runs 1 and 8). Polymerizations of **1** and **4** above 90 °C afforded the corresponding polymers in moderate yields (runs 2–7 and 9-12). In the polymerization above 100 °C, monomers converted completely and the polymers with MW 5000–11000 were obtained in 20–40% yields. MeOH-soluble part was mainly composed of dimer (Y.35%) and oligomers which could be confirmed by gel

Table 2. Effect of Temperature on the Polymerization of 1[a]

run	monomer	temp (°C)	initiator[b]	conv (%)[c]	yield (%)[d]	M_n (M_w/M_n)[c]
1	**1**	80	BPO[f]	0	0	
2	**1**	90	ACC[g]	94	31	7200 (1.97)
3	**1**	100	ACC	100	33	7500 (1.97)
4	**1**	110	DCP[h]	100	35	7100 (1.80)
5	**1**	120	DTBP[i]	100	23	8700 (1.65)
6	**1**	120	DCP	100	27	5500 (1.64)
7	**1**	140	DTBP	100	27	7800 (1.53)
8	**4**	80	BPO	0	0	
9	**4**	90	ACC	90	20	11000 (1.31)
10	**4**	100	ACC	100	32	7300 (1.40)
11	**4**	120	DTBP	100	20	6000 (1.40)
12	**4**	140	DTBP	100	23	8000 (1.49)

[a] Polymerization time, 24 h. [b] 3 mol %. [c] Determined by ^{1}H-NMR. [d] MeOH-insoluble part. [e] Estimated by GPC (THF-eluent, based on polystyrene standards). [f] Benzoyl peroxide. [g] 1,1′-Azobis(cyclohexane-1-carbonitrile). [h] Dicumyl peroxide. [i] Di-*tert*-butyl peroxide.

Scheme 5. Possible Polymerization Mechanism

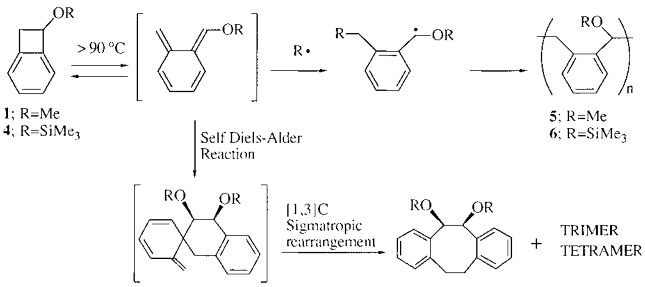


Table 3. Effect of Concentration of DTBP on the Polymerization of 1[a]

DTBP (mol%)	yield (%)[b]	M_n (M_w/M_n)[c]	dimer (%)[d]
0	0		38
10	34	6700 (1.68)	32
30	41	9700 (1.85)	16
50	60	8900 (3.74)	1

[a] 120 °C, 24 h. [b] MeOH-insoluble part. [c] Estimated by GPC (THF-eluent, based on polystyrene standards). [d] Determined by ^{1}H-NMR.

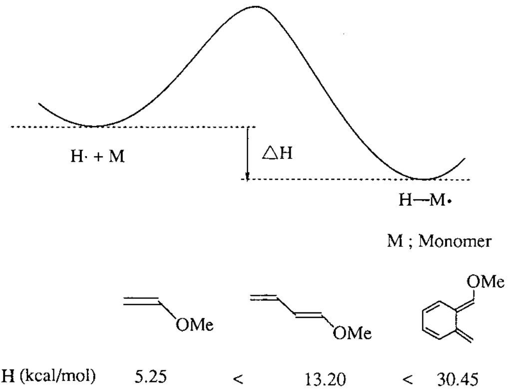


Figure 3. Comparison of the enthalpy change on the polymerization of some monomers by semiempirical molecular orbital calculation.

permeation chromatography (GPC). As the unimodal GPC curve seems to suggest the intervention of the single propagation species and the polymer would have a head-to-tail structure as presumed by the NMR, a possible polymerization mechanism would be speculated as shown in Scheme 5.

1 and **4** isomerize to *o*-quinodimethane above 90 °C and subsequently radical species will attack the methylene group of *o*-quinodimethane. The formed radical species will transfer to the benzyl position *via* aromatization and the radical species successive attack to the next monomer and afford the polymer. Side reactions were thought to be the self-Diels–Alder reaction, which generated dimer and low molecular weight polymers by successive [1,3]C sigmatropic rearrangement.

Concentration Effect of Radical Initiator. Since the self-Diels–Alder reaction of *o*-quinodimethane can proceed rapidly (Scheme 2), *o*-quinodimethane must be trapped by radical species before the self reactions to achieve the polymerization of **1** effectively. From such a view point, the polymerizations with 3 mol % of radical initiator seem not to be efficient enough to afford the polymer **3** in high yield, as shown in Table 1. If sufficient radical species attack the **2** before the self-Diels–Alder reaction of **2**, the polymer yield may increase. When *o*-quinodimethane will be trapped rapidly by radical species and the concentration will decrease, self-Diels–Alder reaction rate will decrease. Moreover, for the equilibrium between *o*-quinodimethane and benzocyclobutene, conversion rate of benzocyclobutene will increase. The effect of concentration of radical initiator (DTBP) on the polymerization of **1** was examined at 120 °C. The results are summarized in Table 3 in which yield of **3** certainly increases with the increase of concentration of DTBP according to decrease of yield of the dimer.

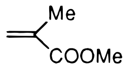
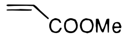
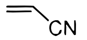
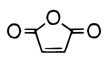
Use of 50% of DTBP vs **1** resulted in higher polymer yield (60%) in comparison with 3 mol % of DTBP (23%). Although the molecular weight of polymer usually decreases by using a large amount of initiator, the molecular weight did not decrease and the molecular weight distribution did not increase much. It indicated that the chain transfer reaction does not occur as far as expected. Stabilization effect by aromatization may make the polymerization proceed effectively and depress the chain transfer reaction.

Then, the stabilization effect on the polymerization of 1-methoxy-*o*-quinodimethane, methyl vinyl ether, and methoxybutadiene by the semiempirical molecular orbital calculation (MOPAC ver 6.02)[5,6] was examined. With the results based on heats of formation (kcal/mol) of the hydrogen radical (propagation end), each monomer and adducts are summarized in Figure 3.

The stabilization effect of methyl vinyl ether was lower and is consist with the low polymerizability.[14] Although methoxybutadiene has a polymerizability,[15] the stabilization effect was half of that of 1-methoxy-*o*-quinodimethane. It indicates that a larger stabilization effect by the aromatization[16] makes the polymerization of 1-methoxy-*o*-quinodimethane proceed effectively.

Copolymerization. This new type of radical polymerization of **1** was applied to the copolymerization with vinyl monomers. Radical copolymerizations of **1** with some vinyl monomers were carried out at 120 °C for 24

Table 4. Copolymerization of 1 with Vinyl Monomers[a]

run	comonomer[b]	*e* value	yield (%)[c]	M_n (M_w/M_n)[d]	*m*:*n*[e]
1		0.40	31	7400(1.57)	37:63
2		0.60	41	7400 (2.09)	47:53
3		1.20	36	1700 (1.70)	31:69
4		2.25	25	520 (1.16)	49:51

[a] DTBP 30 mol %, 120 °C, 24 h. [b] Feed ratio; **1**:comonomer = 1:1. [c] MeOH-insoluble part. [d] Estimated by GPC (THF-eluent, based on polystyrene standards). [e] *m*:*n* = 1-methoxybenzocyclobutene:comonomer, determined by ^{1}H-NMR.

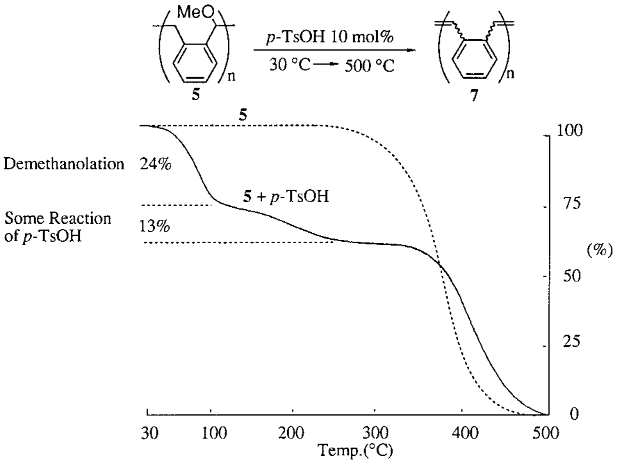


Figure 4. TGA curve of **5** in the presence of *p*-TsOH (10 mol %).

h using 30 mol % of DTBP as an initiator to obtain the corresponding copolymers (Table 4).

The structures of the obtained polymers were confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR. In the ^{1}H-NMR spectra of the obtained copolymers, broad three peaks attributed to **5** around 4.9, 3.4, and 3.1 ppm were observed. The molecular weights of the copolymers with methyl methacrylate or methyl acrylate were higher than those with acrylonitrile or maleic anhydride. The copolymerization behavior was similar to that of 1-methoxy-1,3-butadiene.[17] In the copolymerization of **1** with comonomers having higher *e* value, cycloaddition may precede polymerization predominantly.

Polymer Reaction. As the structure of **5** was suggested to be a head to tail structure, the conversion of **5** to poly(*o*-phenylenevinylene)[18] can be expected by the elimination reaction of methanol. Thermal gravimetric analyses of **5** with and without *p*-TsOH (10 mol %) were preliminary carried out to examine the decomposition behavior (Figure 4).

Although **5** was stable up to 300 °C in the absence of *p*-TsOH, **5** with *p*-TsOH (10 mol %) showed the TGA curve having three peaks. The first peak (60−100 °C) showed 24% weight loss by the release of methanol (theoretical, 23.9%), the second peak(140−240 °C) showed 13% weight loss probably by the some reaction of *p*-TsOH, and the third peak (380−500 °C) seemed to be thermal decomposition of the generated poly(*o*-phenylene vinylene). On the basis of these results, **5** was heated at 60 °C for 3 h in the presence of *p*-TsOH (10 mol %) *in vacuo* to give MeOH-insoluble polymer (pale yellow solid) quantitatively (Scheme 6). The obtained polymer was soluble in various solvents except for *n*-hexane and methanol. The molecular weight of the polymer decreased little. ^{1}H- and ^{13}C-NMR of the obtained polymer are shown in Figure 5.

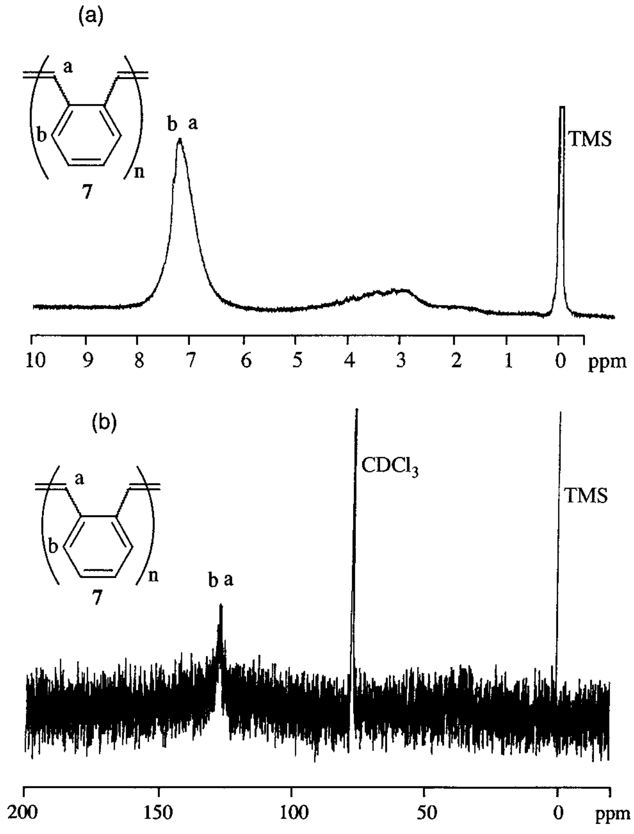
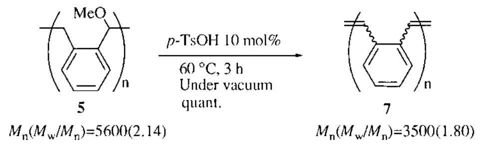
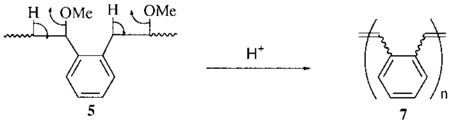


Figure 5. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) (a) and ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) (b) of polymer **7**.

Scheme 6



Scheme 7



In the ^{1}H-NMR, a broad peak around 7 ppm based on phenyl group and conjugated olefin was observed. Intramolecular Friedel−Crafts reaction of benzylic cation generated by the release of methoxy group as a side reaction may occur to generate the cyclobutene ring (4−2.5 ppm).

In the ^{13}C-NMR, only a broad peak based on a phenyl group and conjugated olefin existed around 130 ppm.

In the IR spectrum, absorption of the methoxy group (1221 cm^{-1}) completely disappeared, but broad absorption of conjugated olefin (1630 cm^{-1}) was observed. These results would support the elimination of methanol proceeded effectively as speculated mechanism in Scheme 7.

The UV spectrum supported the elongation of the conjugated system of **7** (Figure 6). Although λ_{max} of polymer **5** is observed at 265 nm, λ_{max} of polymer **7** shifted 40 nm to the long wavelength region (305 nm). As λ_{max} of polymer **7** is smaller than that of poly(*p*-

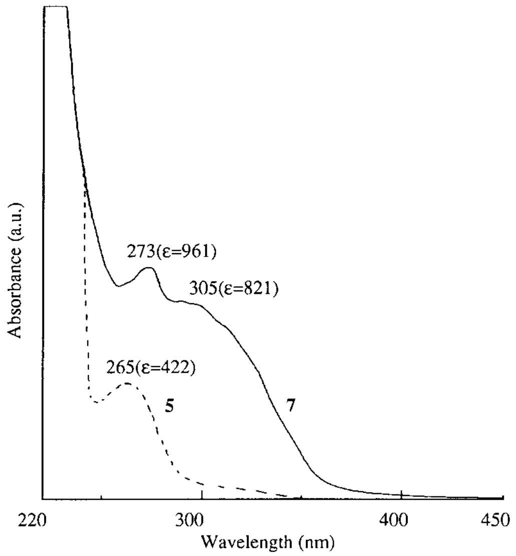


Figure 6. UV spectra of **5** and **7**.

Table 5. Thermal Properties of Polymers (5−7)

polymer	T_g (°C)[a]	T_d^{10} (°C)[b]
5	97	353
6	100	345
7	[c]	382

[a] Glass transition temperature, determined by DSC. [b] 10% weight loss temperature, determined by TGA under N_2. [c] No Observation.

phenylenevinylene) (407 nm), polymer **7** may not be completely in the plane due to steric hindrance of benzene ring. The absorption at 273 nm would be probably based on the deconjugated unit generated by the intramolecular Friedel−Crafts reaction.

Glass transition temperature (T_g) and 10% weight loss temperature (T_{d10}) of the obtained polymers were evaluated by DSC and TGA, respectively, as shown in Table 5.

T_g values of **5** and **6** were the same as that of polystyrene (100 °C). T_g of **7** did not show clearly. T_{d10} of **5** and **6** in N_2 showed about 350 °C, indicating little lower than that of polystyrene in N_2 (T_{d10} = 395 °C). T_{d10} of **7** was higher than those of **5** and **6**, which should indicate conjugated stabilization effect.

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