

Synthesis and Polymerization of Novel Quinone Methide Ketals

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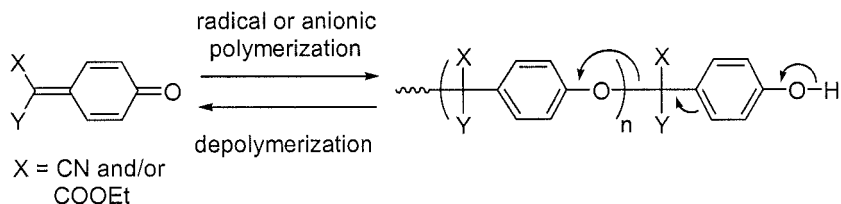
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Summary

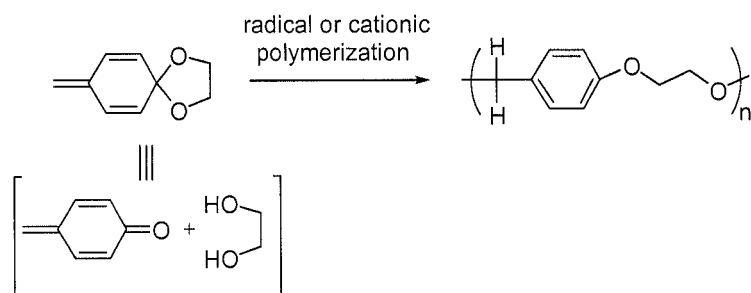
Novel quinone methide ketals, 8-[1'-cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]deca-6,9-diene (**1a**) and 8-(1',1'-dicyanomethylene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**1b**), were synthesized, and their polymerization behavior was investigated. Polymerizations of **1a** and **1b** initiated with BPO and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ gave corresponding novel ring-opening polymers, but no polymerization with BuLi. Copolymerization of **1a** with St in the presence of AIBN at 60 °C gave the monomer reactivity ratios $r_1(\mathbf{1a}) = 0.50 \pm 0.1$ and $r_2(\text{St}) = 0.1 \pm 0.02$, and Q and e values of **1a** were 2.46 and +0.93, indicating that **1a** is a highly conjugative, electron-accepting monomer. Homopolymers of **1a** and **1b** had better thermal stability than that of 7-cyano-7-(ethoxycarbonyl)-1,4-benzoquinone methide.

Introduction

Unsubstituted 1,4-benzoquinone methide spontaneously reacted at room temperature to give a dimeric compound coupled at the exocyclic position and oligomers [1]. Introduction of electron-withdrawing substituents on the exocyclic carbon induced the reduction of the reactivity and the substituted 1,4-benzoquinone methides became isolable as crystals at room temperature, for example, 7,7-dicyano-1,4-benzoquinone methide [2], 7-cyano-7-(alkoxycarbonyl)-1,4-benzoquinone methides [2,3], and 7,7-bis(alkoxycarbonyl)-1,4-benzoquinone methides [4], 7-cyano-7-phenyl-1,4-benzoquinone methide [5]. Polymerization behavior of these isolable substituted quinone methides has been investigated. Homopolymerizations initiated with radical and anionic initiators proceeded with reversion of ring to the stable aromatic structure (resonance stabilization) to give polymers with a head-to-tail monomer unit placement [2-5]. However, the obtained polymers were thermally less stable because of easy depolymerization which is induced by the presence of an acidic phenol-terminal end (Scheme 1). On the other hand, a ring-opening polymer of 8-methylene-1,4-dioxaspiro[4.5]deca-6,9-diene, regarded as a ketal derivative of unsubstituted 1,4-benzoquinone methide, initiated with radical and cationic initiators was thermally stable because of the absence of an acidic phenol-terminal end [6] (Scheme 2). Therefore, introduction of electron-withdrawing substituents such as cyano and ester groups on the exocyclic carbon of 8-methylene-1,4-dioxaspiro[4.5]deca-6,9-diene would provide novel monomers and polymers with better thermal stability.

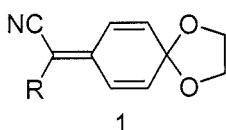


Scheme 1 Polymerization and depolymerization of substituted quinone methides



Scheme 2 Polymerization of unsubstituted quinone methide ketal

In this work, we describe the syntheses and polymerizations of novel quinone methide ketals, 8-[1'-cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]deca-6,9-diene (**1a**) and 8-(1',1'-dicyanomethylene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**1b**), and the thermal property of the polymers.



a: R = COOEt

b: R = CN

Experimental

Materials

Benzoyl peroxide (BPO) and 2,2'-azobis(isobutyronitrile) (AIBN) (Wako Pure Chem) were purified by recrystallization from methanol. Boron trifluoride etherate (Tokyo Kasei Kogyo) was distilled under reduced pressure under nitrogen. Butyl lithium (1.6 M in hexane) (Aldrich) was used as received. Styrene (St) and toluene were purified by conventional methods. Dichloromethane was distilled over calcium hydride.

Monomer Synthesis

8-[1'-Cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (**2a**). 1,4-Cyclohexanedione monoethylene ketal (10.0 g, 64.0 mmol) and ethyl cyanoacetate (7.2 g, 64.0 mmol) were refluxed in the presence of 0.5 g of ammonium acetate and 1.5 g of acetic acid in 38 mL of toluene using a Dean-Stark water separator to isolate water formed for 5 h. The reaction mixture was washed twice with 100 mL of water and dried over anhydrous magnesium sulfate. After toluene was removed under reduced pressure, the pale yellow residue was recrystallized from diethyl ether and **2a** was obtained as white needles (13.1 g, 81.1%): mp 75-76 °C; IR (KBr): $\nu_{\text{C-H}}$ 2978, ν_{CN} 2196, $\nu_{\text{C=O}}$ 1733, $\nu_{\text{C=C}}$ 1604, 1449, $\nu_{\text{C(=O)-O}}$ 1287, 1253, 1210, $\nu_{\text{C-O}}$ 1087 cm^{-1} ; $^1\text{H NMR}$: (CDCl_3): δ 4.27 (q, $J = 7.26$ Hz, 2H), 3.99 (s, 4H), 3.20 (t, $J = 6.93$ Hz, 2H), 2.88 (t, $J = 6.93$ Hz, 2H), 1.91 (t, $J = 6.92$ Hz, 4H), 1.35 (t, $J = 7.26$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ 176.6 (>C=), 161.6 (C=O), 115.3 (CN), 106.9 (>C<), 103.2 (>C=), 64.6 (CH_2), 61.8 (CH_2CH_3), 35.0 (CH_2), 34.7 (CH_2), 33.4 (CH_2), 27.8 (CH_2), 14.0 (CH_2CH_3). Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$: C, 62.14; H, 6.82; N, 5.57; O, 25.47. Found: C, 62.25; H, 6.90; N, 5.48; O, 25.37.

8-(1',1'-Dicyanomethylene)-1,4-dioxaspiro[4.5]decane (**2b**). **2b** was synthesized by the same method as the procedure of making **2a** (7.9 g, 88.6%): mp 109-110 °C; IR (KBr): $\nu_{\text{C-H}}$ 2976, 2900, ν_{CN} 2232, $\nu_{\text{C=C}}$ 1599, 1439, $\nu_{\text{C-O}}$ 1128 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 4.00 (s, 4H), 1.88 (t, $J = 6.93$ Hz, 4H), 2.85 (t, $J = 6.93$ Hz, 4H); $^{13}\text{C NMR}$ (CDCl_3): δ 182.0 (>C=), 111.4 (CN), 106.1 (>C<), 83.7 (>C=), 64.7 (CH_2), 34.4 (CH_2), 31.5 (CH_2). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$: C, 64.69; H, 5.93; N, 13.71; O, 15.67. Found: C, 64.56; H, 5.98; N, 13.80; O, 15.66.

8-[1'-Cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]deca-6,9-diene (**1a**). **2a** (1.0 g, 4.0 mmol) was dissolved in 500 mL of benzene and 17.4 g of activated manganese dioxide was added into this solution. After stirring for 3 min at reflux, the activated MnO_2 was removed by filtration and benzene of the filtrate was evaporated under reduced pressure. The pale yellow residue was recrystallized from hexane and **1a** was obtained as white needles (0.35 g, 34.9%): mp 97-98 °C; IR (KBr): $\nu_{\text{C-H}}$ 2944, 2856, ν_{CN} 2196, $\nu_{\text{C=O}}$ 1691, $\nu_{\text{C=C}}$ 1520, $\nu_{\text{C(=O)-O}}$ 1229, $\nu_{\text{C-O}}$ 1091 cm^{-1} ; $^1\text{H NMR}$: (CDCl_3): δ 7.86 (dd, $J = 10.23, 2.31$ Hz, 1H), 6.96 (dd, $J = 10.23, 2.31$ Hz, 1H), 6.37 (dd, $J = 10.23, 2.31$ Hz, 1H), 6.29 (dd, $J = 10.23, 2.31$ Hz, 1H), 4.34 (t, $J = 7.26$ Hz, 2H), 4.13 (s, 4H), 1.37 (t, $J = 7.26$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ 161.5 (C=O), 149.0 (>C=), 138.7 (CH), 138.0 (CH), 126.2 (CH), 123.0 (CH), 115.2 (CN), 104.9 (>C<), 98.4 (>C=), 65.6 (CH_2), 62.4 (CH_2CH_3), 14.0 (CH_2CH_3); UV (hexane): 294 ($\epsilon = 13600$) nm. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_4$: C, 63.14; H, 5.30; N, 5.67; O, 25.89. Found: C, 63.19; H, 5.46; N, 5.60; O, 25.75.

8-(1',1'-Dicyanomethylene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**1b**). **1b** was synthesized by the same method as the procedure of making **1a** (0.13 g, 13.2%): mp 138-139 °C; IR (KBr): $\nu_{\text{C-H}}$ 3024, ν_{CN} 2240, $\nu_{\text{C=C}}$ 1538, $\nu_{\text{C-O}}$ 1215, 1117 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 4.15 (s, 4H), 6.43 (d, $J = 9.90$ Hz, 2H), 6.88 (d, $J = 10.23$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3): δ 153.5 (>C=), 140.5 (CH), 122.9 (CH), 111.6 (CN), 98.3 (>C<), 84.8 (>C=), 65.6 (CH_2); UV (hexane): 293 ($\epsilon = 10870$) nm. Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$: C, 65.99; H, 4.04; N, 13.99; O, 15.98. Found: C, 65.20; H, 4.06; N, 14.00; O, 16.74.

Polymerization Procedure

For a radical polymerization, given amounts of monomer (**1a** or **1b**), styrene as a comonomer if necessary, AIBN or BPO as a radical initiator, and toluene as a solvent were placed in a glass ampule, and degassed by a freeze-thaw method (repeated three times). The ampule was sealed and placed in a bath thermostated at 60 or 90 °C for a given time of polymerization, and then opened. The reaction mixture was poured into an excess hexane to precipitate products, which were purified by three or more cycles of a redissolution and reprecipitation. Toluene and hexane were used as a solvent and a precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

For an ionic polymerization, polymerization was carried out in an apparatus reported previously [7]. A given amount of monomer (**1a** or **1b**) was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of solvent such as dichloromethane or toluene by a syringe. After the resulting solution was degassed by a freeze-thaw method (repeated twice), the apparatus was filled with nitrogen. It was sealed and set in a bath thermostated at 0 °C and a fixed amount of BF₃·Et₂O or BuLi was injected by a syringe. After a given time of reaction, the reaction mixture was poured into an excess hexane to deposit a polymeric product. The rest of procedure was carried out similarly to the above-mentioned radical polymerization.

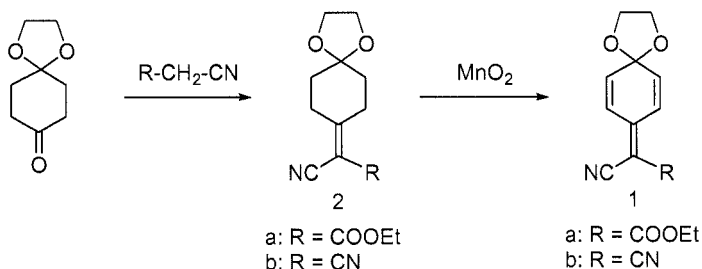
Measurements

Melting points were obtained with a Yanaco MP-53 melting point apparatus. Elemental analyses were performed on a Yanaco CHN Corder MT-5. Number-average molecular weights, M_n , of polymers were estimated by gel permeation chromatography (GPC) 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 of 5.0 × 10²-2.0 × 10⁶) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min and polystyrene standards for calibration at room temperature. ¹H- and ¹³C-NMR and IR spectra were recorded on a JEOL JNM-EX 270 FT NMR spectrometer using tetramethylsilane as an internal standard in chloroform-*d* and on a JASCO IR-700 spectrometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the homopolymers were measured on a Rigaku Denki DSC 8230 at a scanning rate of +10 °C/min in air for TGA and in nitrogen gas flow for DSC.

Results and Discussion

Monomer Synthesis

8-[1'-Cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]deca-6,9-diene (**1a**) and 8-(1',1'-dicyanomethylene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**1b**) were prepared by a synthetic route shown in Scheme 3. Knoevenagel condensation of 1,4-cyclohexanedione monoethylene ketal with ethyl cyanoacetate and malononitrile afforded **2a** (81% yield) and **2b** (89% yield), respectively. Oxidation of **2a** and **2b** with activated MnO₂ in refluxing benzene gave **1a** (35% yield) and **1b** (13% yield) as pale yellow needles, respectively. Both **1a** and **1b** were characterized by IR, ¹H- and ¹³C-NMR, and UV-vis spectroscopies and by elemental analysis.



Scheme 3. Synthetic route of monomers

Polymerization

The homopolymerizations of **1a** and **1b** were carried out using a radical initiator BPO in toluene at 90 °C, a cationic initiator boron trifluoride etherate in dichloromethane at 0 °C, and anionic initiator BuLi in toluene at 0 °C. Table 1 shows the results of the polymerizations. All polymerizations proceeded homogeneously. The polymers obtained as white solids were soluble in benzene, toluene, THF, chloroform and dichloromethane, but insoluble in hexane, diethyl ether and methanol. The polymerizations of **1a** and **1b** initiated by radical initiator gave relatively low molecular weight polymers ($1.0\text{--}1.3 \times 10^3$) in low yields and those initiated by cationic initiator gave high molecular weight polymers ($11.6\text{--}32.0 \times 10^3$) in high yields, but no polymerizations initiated by anionic initiator took place. This behavior was similar to that of 8-methylene-1,4-dioxaspiro[4.5]deca-6,9-diene except for the formation of high molecular weight polymer and the high yield by a radical initiator [6], and different from those of the 7-cyano-7-(alkoxycarbonyl)-1,4-benzoquinone methides [3] and 7,7-bis(alkoxycarbonyl)-1,4-benzoquinone methides [4], which were homopolymerizable with radical and anionic initiators, but not with a cationic one. Low yields and low molecular weight polymer formation for the polymerizations of **1a** and **1b** initiated by a radical initiator might be due to the steric hindrance at the exocyclic position.

Table 1. Homopolymerizations of **1a** and **1b** with various initiators

Initiator [I]	[1a or 1b] / [I]	Solvent	Temp./ °C	Time /h	Yield /%	$M_n/10^3$
1a						
BPO	30	toluene	90	48	15.5	1.2
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	10	CH_2Cl_2	0	24	85.7	32.0
BuLi	20	toluene	0	24	0	
1b						
BPO	30	toluene	90	48	24.0	1.0
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	10	CH_2Cl_2	0	24	99.0	11.6
BuLi	20	toluene	0	24	0	

[**1a**] = [**1b**] = 0.4 mol/L

The obtained polymers were characterized by $^1\text{H-NMR}$. Figure 1 shows the spectra of **1a** and the polymer of **1a** (poly(**1a**)) initiated with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, respectively, where each peak could be assigned to the respective protons of the chemical structure illustrated therein. The polymer obtained with BPO also showed a similar $^1\text{H-NMR}$

spectrum. In the Figure 1, absorption peaks at 7.86, 6.96, 6.37, and 6.29 ppm in the **1a** disappear and instead peaks due to aromatic protons are observed at 7.57 and 6.96 ppm in the poly(**1a**). For the case of **1b**, absorption peaks observed at 6.88 and 6.43 ppm disappeared and the aromatic proton peaks appeared at 7.59 and 6.98 ppm. It is, therefore, considered that the polymerization would proceed as shown in Scheme 4 like as 8-methylene-1,4-dioxaspiro[4.5]deca-6,9-diene [6].

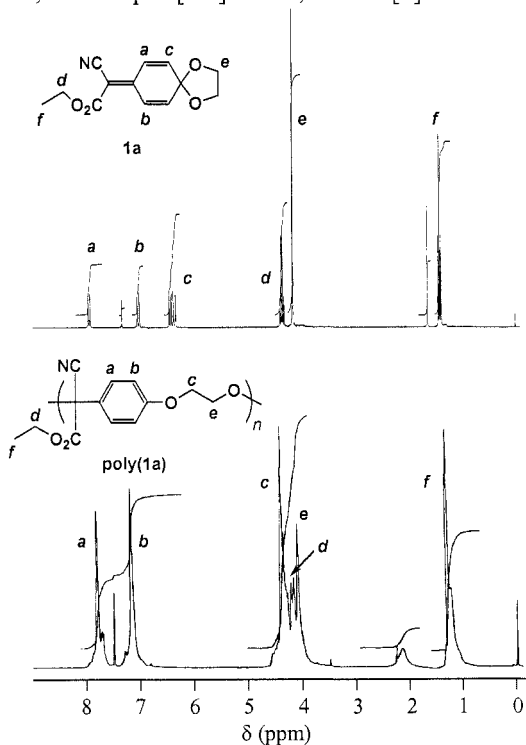
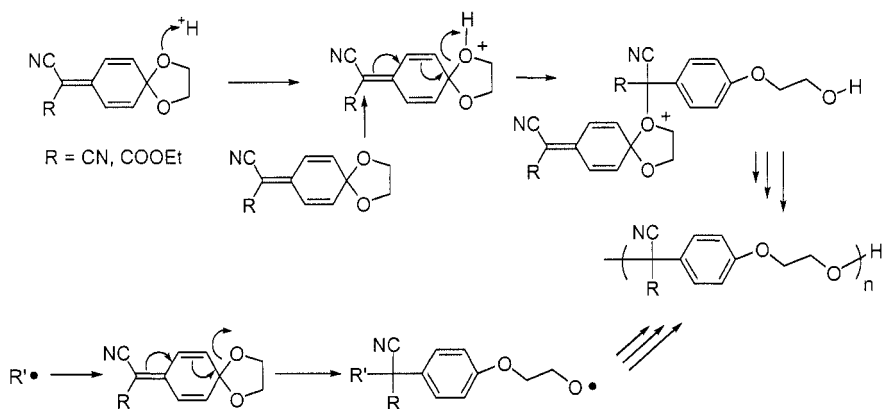


Figure 1. ¹H-NMR spectra of **1a** and poly(**1a**) obtained with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in chloroform-*d*



Scheme 4. Polymerization mechanism of **1a** and **1b** with cationic and anionic initiators

Copolymerization of **1a** with St in the presence of AIBN was carried out in toluene at 60 °C. Polymerizations proceeded homogeneously. Polymers obtained as white solids were soluble in benzene, toluene, chloroform, THF, but insoluble in hexane, diethyl ether and methanol. Table 2 shows the results of the copolymerization, and Figure 2 shows the copolymerization composition curves, together with that of the 7-cyano-7-(ethoxycarbonyl)-1,4-benzoquinone methide (CQM)-St system [3] for comparison. Monomer reactivity ratios of the copolymerization of **1a** with St were calculated, according to the intersection [8] and Kelen-Tüdös methods [9], to be $r_1(\mathbf{1a}) = 0.50 \pm 0.1$ and $r_2(\text{St}) = 0.1 \pm 0.02$ at 60 °C. Alfrey-Price's Q and e values of **1a** were determined on the basis of the monomer reactivity ratios to be 2.46 and +0.93, respectively, indicating that **1a** is a highly conjugative and electron-accepting monomer. The monomer reactivity ratios for the copolymerization of CQM with St were reported to be $r_1(\text{CQM}) = 3.40$ and $r_2(\text{St}) = 0.01$ at 60 °C [3]. The relative reactivity of the **1a** and the CQM towards a polymeric radical with a St terminal unit was estimated from the comparison with $1/r_2$ values to be CQM ($1/0.01 = 100$) > **1a** ($1/0.10 = 10$), indicating that the CQM is more reactive than the **1a**.

Table 2. Copolymerization^a of **1a** with St in toluene at 60 °C

Monomer Feed			Time /h	Yield /%	Anal.		Copolym 1a /mol%	M_n /10 ³
1a /mmol	St /mmol	1a /mol%			%C	%N		
0.20	3.84	5.0	1	5.0	76.53	2.63	26.7	15.3
0.40	3.67	9.9	2	7.5	75.05	3.16	34.7	5.8
0.40	2.67	15.1	3	8.2	73.75	3.45	39.6	3.3
0.40	1.22	24.9	4	10.8	73.40	3.92	48.6	2.2
0.41	0.39	51.0	6	9.1	68.62	4.35	58.2	1.2
0.61	0.22	73.6	12	6.1	67.30	4.78	69.3	0.8

^a [**1a**] = 0.3 mol/L; [**1a**]/[AIBN] = 10

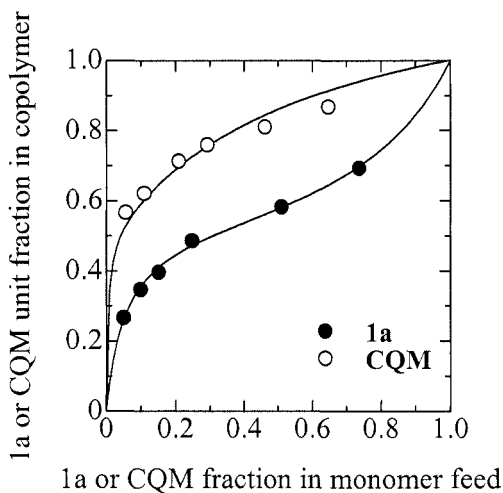


Figure 2. Copolymerization composition curves for the (●) **1a**-St and (○) CQM-St systems

Thermal behavior

Figure 3 shows the comparison of thermal stability of the poly(**1a**) and poly(**1b**) with that of CQM (poly(CQM)) by TGA measurement. The TGA curves are shown as a solid line for the poly(**1a**), a dashed dot line for the poly(**1b**), and a dashed line for the poly(CQM), respectively. The weight loss started at 256 °C and the 10% weight loss occurred at 324 °C for the poly(**1a**), 220 °C and 291 °C for the poly(**1b**), and 123 °C and 175 °C for the poly(CQM), respectively. Therefore, both poly(**1a**) and poly(**1b**) had better thermal stability than the poly(CQM). The glass transition temperatures of poly(**1a**) and poly(**1b**) were determined to be 70.3 °C and 58.3 °C, respectively.

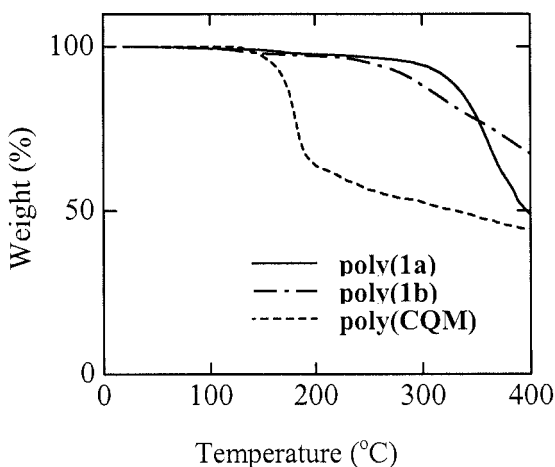


Figure 3. TGA curves of the poly(**1a**) (—), poly(**1b**) (---), and poly(CQM) (···) under air

In conclusions, **1a** and **1b** were successfully synthesized as pale needle crystals. Polymerizations of **1a** and **1b** initiated with BPO and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ afforded the novel ring-opening polymers, but no polymerization with BuLi. The copolymerization of **1a** with St indicated that **1a** is a highly conjugative, electron-accepting monomer. Thermal stability of both poly(**1a**) and poly(**1b**) was better than that of poly(CQM).

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