Synthesis and Radical Polymerization of Methacrylate Endowed with Bicyclobis(γ-butyrolactone) Moiety through Methylene Linker

Ryu Yamasaki, Atsushi Sudo, Takeshi Endo

Molecular Engineering Institute, Kinki University, Fukuoka 820-8555, Japan
Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

ABSTRACT: A series of methacrylates bearing bicyclobis(γ-butyrolactone) (BBL) moiety were synthesized and radically polymerized to afford the corresponding poly(methacrylate)s bearing BBL moiety in the side chain, with expecting that the high polarity and rigidity of BBL would be inherited by the polymers. The resulting polymers were soluble in polar aprotic solvents such as dimethyl sulfoxide and N,N-dimethylformamide because of the high polarity of the BBL moiety. The glass transition temperatures (T_g) of the polymers depended on the length of methylene linker that tethered the methacrylate and BBL moieties, making the use of shorter linkers lead to higher T_gs. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, 53, 2462–2468

KEYWORDS: bicyclic bislactone; glass transition; monomers; radical polymerization

INTRODUCTION Polymers bearing rigid lactone moieties are potentially useful as photoresist materials in photolithography, an indispensable process for the production of integrated circuits. One of the attractive characteristics of such lactone-containing polymers is their high glass transition temperatures owing to the high polarity and rigidity of lactone moieties. In addition, the high polarity gives those polymers good adhesion property and high dry-etching resistance.[1–4]

For the recent few decades, we have focused our attention on bicyclobis(γ-butyrolactone)s (BBLs). In general, γ-butyrolactone, a 5-membered lactone, does not undergo ring-opening polymerization. BBLs are also quite stable and thus heating them at above 100 °C in the presence of anionic initiators does not lead to their polymerization. In contrast, BBLs undergo anionic copolymerization with epoxide quite efficiently.[5,6] The copolymerization can be initiated by potassium alkoxide or phosphines[7] and proceeds in a 1:1 alternating manner to afford polyesters bearing ketone moiety in the side chain. The facile access to BBLs through condensation of 1,2,3-propanetricarboxylic acid (PTA) with acid anhydride has allowed the synthesis of BBLs bearing functional groups such as C=C bond.[8] During the copolymerization, BBLs undergo the double ring-opening reactions with isomerization, leading to the efficient prevention of the backward ring-closure process that takes place significantly in the ring-opening polymerization of γ-butyrolactone. In addition, the double ring-opening accompanies volume expansion and thus the copolymerization is shrinkage free.[9,10] Recently, an acid-catalyzed reaction of BBL with alcohols has been developed and applied successfully to a new polyaddition system that yielded polyesters.[11]

On the other hand, BBLs have another interesting aspect as highly rigid and polar molecules. As it can be expected from the 5-5 fused ring system that forms the framework of BBLs, only limited freedom is given to BBLs in their conformational changes. At the same time, the restricted conformational change of the BBL skeleton gives it a large dipole moment. These structural characteristics of BBL moiety prompted us to envisage its use as a rigid and polar component in designing monomers for polymers with high polarity and high T_g.

Herein, we report a series of methacrylate-type monomers **1** bearing BBL moiety, where the methacrylate and BBL moieties are connected through a methylene linker (Scheme 1). Free radical polymerization of **1** was performed to obtain the corresponding poly(methacrylate)s, whose thermal properties and their dependence on the chain length of the methylene linker were investigated.
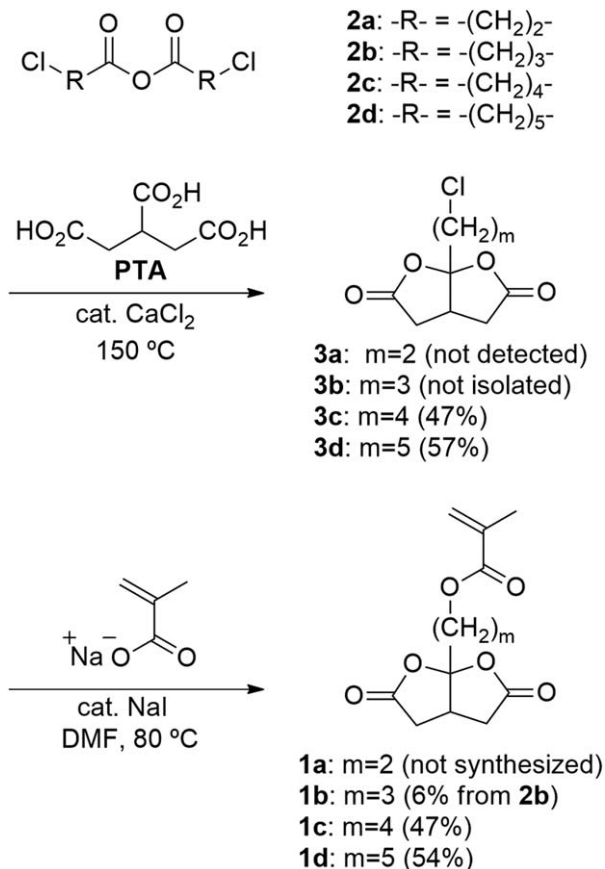
EXPERIMENTAL

Materials

2,2-Azobis(isobutironitrile) (AIBN), sodium iodide, thionyl chloride, oxalyl chloride, N,N'-dicyclohexylcarbodiimide

---

Additional Supporting Information may be found in the online version of this article.

2a: -R- = -(CH₂)₂-
2b: -R- = -(CH₂)₃-
2c: -R- = -(CH₂)₄-
2d: -R- = -(CH₂)₅-

3a: m=2 (not detected)
3b: m=3 (not isolated)
3c: m=4 (47%)
3d: m=5 (57%)

1a: m=2 (not synthesized)
1b: m=3 (6% from **2b**)
1c: m=4 (47%)
1d: m=5 (54%)

SCHEME 1 Synthesis of methacrylates **1b–1d** bearing BBL moiety.

(DCC), lithium hydroxide, methacryloyl chloride, 1,4-dioxane, chloroform, methanol, and hexane were purchased from Wako Pure Chemical Industries (Osaka, Japan). AIBN was recrystallized from MeOH. N,N-dimethylformamide (DMF) was purchased from Wako Pure Chemical Industries (Osaka, Japan), and dried over calcium hydride and distilled under nitrogen. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen prior to use. PTA and 1 M of SnCl₄ solution in dichloromethane were purchased from TCI Chemicals (Tokyo, Japan). Details of the synthesis of acid anhydrides **4** are described in Supporting Information material. 3-Benzyloxypropionic acid (BPA) was synthesized as reported earlier.[12] The details of the synthesis of BPA are described in Supporting Information material.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian NMR Unity Inova 400 or JEOL-ECS400 (400 and 100 MHz for ^{1}H and ^{13}C with tetramethylsilane as the internal standard). IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMN-700 spectrometer in an electron impact ionization mode. Number average molecular weight (M_n) and polydispersity index (M_w/M_n) were estimated by size exclusion chromatography (SEC) on a Tosoh chromatograph model HLC-8220 system equipped with three connec-

tive polystyrene gel columns (Tosoh TSKgel SuperAW2500, SuperAW3000, and SuperAW4000) (6.0 mm $\varphi \times$ 15 cm) and refractive index detector at 40 °C. The system was operated at a flow rate of 0.5 mL/min, and DMF containing 10 mM of LiBr was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument. DSC-6200 using an aluminum pan under a flow rate of 20 mL/min N₂ at the heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instrument. TG-DTA 6200 used an alumina pan under a flow rate of 50 mL/min N₂ at a heating rate of 10 °C/min.

Synthesis of BBLs 3b-3d
A Typical Procedure

Anhydride **2d** (3.89 g, 13.7 mmol), PTA (804 mg, 4.56 mmol), and calcium chloride (35 mg, 316 μmol) were placed in 100-mL round flask and the mixture was heated at 150 °C for 8 h. The mixture was cooled to room temperature (RT) and dissolved with AcOEt (60 mL). The solution was washed with saturated aqueous solution of sodium bicarbonate (30 mL, twice), brine (30 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent = AcOEt + n-hex 2/1) to afford bislactone **3d** (642 mg, 57%) as a brown solid.

Bislactones **3b** and **3c** were synthesized and isolated in a similar manner.

Bislactone 3b
This was obtained as a mixture with γ-butyrolactone.

^{1}H NMR (400 MHz, CDCl₃, δ): 3.64 (t, 2H, J = 6.0 Hz; ClCH₂—), 3.12 (m, 1H; —CH₂CH(—C)CH₂—), 3.03 (dd, 2H, J = 18.3, 9.6 Hz; —CH₂CH(—C)CH₂COO—), 2.57 (dd, 2H, J = 18.3, 4.2 Hz; —CH₂CH(—C)CH₂COO—), 2.17 (m, 2H), 2.06 (m, 2H); ^{13}C NMR (100 MHz, CDCl₃, δ): 172.0, 114.0, 44.1, 37.9, 35.4, 34.9, 25.9.

Bislactone 3c
This is a pale brown oil.

^{1}H NMR (400 MHz, CDCl₃, δ): 3.57 (t, J = 6.4 Hz, 2H; ClCH₂—), 3.13 (m, 1H; —CH₂CH(—C)CH₂—), 3.02 (dd, 2H, J = 18.4, 9.6 Hz; —CH₂CH(—C)CH₂COO—), 2.57 (dd, 2H, J = 18.3, 4.2 Hz; —CH₂CH(—C)CH₂COO—), 2.03 (m, 2H), 1.87 (m, 2H), 1.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl₃, δ): 172.2, 114.4, 44.3, 37.4, 36.4, 35.6, 31.8, 20.3; IR (neat): ν = 2957 (m), 2873 (w), 1788 (s), 1731 (w), 1427 (w), 1279 (w), 1237 (m), 1145 (m), 976 (m), 944 (m), and 895 (w). HRMS (m/z): calcd for C₁₀H₁₄O₄Cl, 233.0581; found, 233.0578 [M + H]⁺.

Bislactone 3d
M_p = 75.1–76.4 °C.

^{1}H NMR (400 MHz, CDCl₃, δ): 3.54 (t, 2H, J = 6.6 Hz; ClCH₂—), 3.11 (m, 1H; —CH₂CH(—C)CH₂—), 3.01 (dd, 2H,

$J = 18.3$, 9.3 Hz; —CH_2CH(—C)CH_2COO—), 2.48 (dd, 2H, $J = 18.3$, 4.4 Hz; —CH_2CH(—C)CH_2COO—), 2.01 (m, 2H), 1.81 (m, 2H), 1.52 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.2, 114.5, 44.6, 37.5, 37.2, 35.6, 32.1, 26.5, 22.2; IR (neat): $v = 2940$ (m), 2866 (w), 1783 (s), 1426 (w), 1269 (m), 1229 (m), 1144 (m), 979 (m), 940 (m), 895 (w), 865 cm^{-1} (w). HRMS (m/z): calcd for C$_{11}$H$_{16}$O$_4$Cl, 247.0737; found, 247.0733 [M + H]$^+$.

Synthesis of Methacrylates 1b–1d
A typical procedure: Bislactone **3d** (160 mg, 649 μmol), sodium iodide (20 mg, 133 μmol), and sodium methacrylate (168 mg, 1.55 mmol) were dissolved in dry DMF (1.6 mL) and heated at 80 °C under N$_2$ for 15 h. The mixture was concentrated under reduced pressure and the resulting residue was dissolved in AcOEt (30 mL). The solution was washed with saturated aqueous solution of ammonium chloride (20 mL), dried over sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent = AcOEt + hexane 3/1) to give **1d** (103 mg, 54%).

Methacrylates **1b** and **1c** were synthesized from bislactones **3b** and **3c**, respectively, and isolated in a similar manner.

Bislactone 1b
It is colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.10 (s, 1H; CH_2=C), 5.59 (s, 1H; CH_2=C), 4.23 (t, 2H, $J = 6.2$ Hz; —COOCH_2—), 3.10 (m, 1H; —CH$_2$CH(—C)CH$_2$−), 3.02 (dd, 2H, $J = 18.4$, 9.3 Hz; —CH_2CH(—C)CH_2COO—), 2.57 (dd, 2H, $J = 18.3$, 4.2 Hz; —CH_2CH(—C)CH_2COO—), 2.09 (m, 2H), 1.95 (m, 5H; CH_3−C=C−, and —COO—CH$_2$—CH_2—); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.0, 167.3, 136.1, 125.8, 114.1, 63.5, 37.7, 35.5, 34.2, 22.5, 18.3; IR (neat): $v = 2958$ (w), 2927 (w), 2853 (w), 1784 (s), 1709 (s), 1635 (m), 1451 (w), 1425 (w), 1379 (m), 1321 (m), 1297 (w), 1160 (s), 1139 (s), 972 (s), 939 (s), 896 (m), 855 (m), 855 cm^{-1} (w). HRMS (m/z): calcd for C$_{13}$H$_{17}$O$_6$, 269.1025; found, 269.1027 [M+H]$^+$.

Bislactone 1c
It is pale yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.10 (s, 1H; CH_2=C), 5.57 (s, 1H; CH_2=C), 4.18 (t, 2H, $J = 6.3$ Hz; —COOCH_2—), 3.57 (t, 2H, $J = 6.4$ Hz; ClCH_2—), 3.11 (m, 1H; —CH$_2$CH(—C)CH$_2$—), 3.00 (dd, 2H, $J = 18.2$, 9.4 Hz; —CH_2CH(—C)CH_2COO—), 2.56 (dd, 2H, $J = 18.3$, 4.4 Hz; —CH_2CH(—C)CH_2COO—), 2.04 (m, 2H), 1.94 (s, 3H; CH_3−C=C—), 1.76 (m, 2H), 1.63 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.2, 167.4, 136.2, 125.6, 114.4, 63.8, 37.5, 36.8, 35.5, 28.2, 19.5, 18.3; IR (neat): $v = 2957$ (m), 1790 (s), 1713 (m), 1635(w), 1428 (w), 1322 (w), 1298 (w), 1261 (w), 1167 (m), 982 (m), 944 (m), 864 cm^{-1} (w). HRMS (m/z): calcd for C$_{14}$H$_{18}$O$_6$, 282.1103; found, 282.1105 [M]$^+$.

Bislactone 1d
It is colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.10 (s, 1H; CH_2=C), 5.56 (s, 1H; CH_2=C), 4.15 (t, 2H, $J = 6.5$ Hz; —COOCH_2—), 3.10 (m, 1H; —CH$_2$CH(—C)CH$_2$—), 3.01 (dd, 2H, $J = 18.2$, 9.4 Hz; —CH_2CH(—C)CH_2COO—), 2.56 (dd, 2H, $J = 18.3$, 4.3 Hz; —CH_2CH(—C)CH_2COO—), 2.01 (m, 2H), 1.71 (m, 2H), 1.47–1.56 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.3, 167.5, 136.4, 125.4, 114.6, 64.2, 37.4, 37.2, 35.6, 28.4, 25.7, 22.5, 18.3; IR (neat): $v = 2949$ (w), 1785 (s), 1708 (s), 1634 (m), 1454 (w), 1427 (w), 1322 (m), 1297 (m), 1243 (m), 1161 (s), 1060 (w), 983 (m), 935 (m), 893 (w), 867 (w), 816 (m), 786 cm^{-1} (w). HRMS (m/z): calcd for C$_{15}$H$_{21}$O$_6$, 297.1338; found, 297.1341 [M + H]$^+$.

Synthesis of Bislactone 5
To a solution of BPA (2.92 g, 16.2 mmol) in CHCl$_3$ (15 mL), DCC (1.67 g, 8.09 mmol) was added at RT, and the mixture was stirred for 3 h. The mixture was filtered by washing the precipitate with dichloromethane (10 mL), and the filtrate was concentrated under reduced pressure. The resulting oil was dissolved with toluene (20 mL), and the solution was filtered and concentrated under reduced pressure to obtain anhydride **4** (2.75 g).

Anhydride **4** was dissolved in 1,4-dioxane (15 mL), and to the resulting solution, 4-dimethylaminopyridine (DMAP) (16 mg, 131 μmol) and PTA (476 mg, 2.70 mmol) were added. The mixture was heated with refluxing for 3 h at 120 °C. After cooling to RT, the solution was concentrated under reduced pressure. The residue was dissolved with chloroform (30 mL), washed with saturated aqueous solution of sodium bicarbonate (20 mL, twice), 1 M of hydrochloric acid (20 mL), and brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column (eluent = AcOEt + hexane 1/1) to afford **5** (374 mg, 17%) as a viscous oil.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.33 (m, 5H; ArH), 4.46 (s, 2H; Ar—CH_2−O—), 3.68 (t, 2H, $J = 5.7$ Hz; BnO—CH_2—), 3.44 (m, 1H; —CH$_2$—CH(C) —CH$_2$—), 2.95 (dd, 2H, $J = 18.6$, 10.0 Hz; —CH_2CH(—C)CH_2COO—), 2.44 (dd, 2H, $J = 18.7$, 4.5 Hz; —CH_2CH(—C)CH_2COO—), 2.35 (t, 2H, $J = 5.7$ Hz; BnOCH$_2$CH_2—); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.8, 137.2, 128.6, 128.1, 127.9, 114.0, 73.6, 64.9, 37.8, 36.6, 35.6; IR (neat): $v = 2933$ (w), 2875 (w), 1791 (s), 1496 (w), 1453 (w), 1423 (w), 1367 (w), 1306 (w), 1261 (w), 1214 (m), 1137 (m), 1016 (w), 978 (m), 944 (m), 892 (w), 865 (m), 742 cm^{-1} (w). HRMS (m/z): calcd for C$_{15}$H$_{16}$O$_5$, 276.0998; found, 276.0998 [M]$^+$.

Synthesis of Methacrylate 1a
To a mixture of bislactone **5** (184 mg, 835 μmol) and methacryloyl chloride (86 μL, 837 μmol), a 1-M solution of SnCl$_4$ in dichloromethane (84 μL, 84 mmol) was added and stirred for 1 h at 0 °C, then warmed to RT, and then stirred for additional 3 h. To the reaction mixture, saturated aqueous solution of ammonium chloride (10 mL) was added, and the mixture was extracted with dichloromethane (20 mL). The organic layer was dried over sodium sulfate, filtered, and

concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent = AcOEt + hexane 2/1) to afford **1a** (122 mg, 74%) as colorless prisms: M_p 96.3–97.6 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.10 (s, 1H; CH_2=C), 5.62 (s, 1H; CH_2=C), 4.38 (t, 2H, J = 6.0 Hz; —COOCH_2—), 3.31 (m, 1H; —CH$_2$CH(—C)CH$_2$—), 3.02 (dd, 2H, J = 18.4, 9.7 Hz; —CH_2CH(—C)CH_2COO—), 2.60 (dd, 2H, J = 18.3, 4.2 Hz; —CH_2CH(—C)CH_2COO—), 2.45 (m, 2H; BnOCH$_2$CH_2—), 1.94 (s, 3H; CH_3—C(—C)—=CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 172.3, 166.9, 135.7, 126.2, 113.0, 58.9, 37.5, 35.8, 35.2, 18.1; IR (neat): v = 2961 (w), 2930 (w), 2855 (w), 1786 (s), 1711 (s), 1635 (m), 1454 (w), 1424 (w), 1375 (m), 1321 (m), 1297 (w), 1263 (w), 1215 (m), 1157 (s), 1115 (m), 1085 (m), 1029 (m), 965 (m), 934 (s), 891 (m), 863 (m), 815 cm^{-1} (m). HRMS (m/z): calcd for C$_{12}$H$_{15}$O$_6$, 255.0869; found, 255.0869 [M + H]$^+$.

Polymerization of Methacrylate 1

A Typical Procedure

Methacrylate **1d** (240 mg, 810 μmol) and AIBN (2.6 mg, 15.8 μmol) were placed in a glass ampule tube and were dissolved in DMF (0.81 mL). The solution was degassed with three freeze–pump–thaw cycles and the tube was sealed off. The solution was stirred at 80 °C for 6 h and was poured into MeOH (80 mL). The resulting precipitate was collected by filtration with suction, washed with MeOH, and dried under reduced pressure to afford the corresponding polymethacrylate **6d** (158 mg, 66%) as colorless powder.

The other monomers **1a–1c** were polymerized and the resulting polymers **6a–6c** were isolated according to the typical procedure.

Polymethacrylate 6a

It is colorless powder.

^{1}H NMR (400 MHz, dimethyl sulfoxide [DMSO]-d_6, δ): 4.09 (2H; —COOCH_2—), 3.23 (1H; —CH$_2$—CH(C)—CH$_2$—), 3.04 (2H; —CH_2CH(—C)CH_2COO—2.73 (2H; —CH_2CH(—C)CH_2COO—), 2.39 (2H; —C—CH_2), 1.75–1.95 (br, 2H; β-CH_2), 0.7–1.1 (m, 3H; —C—CH_3); IR (KBr): v = 3547 (s), 2988 (m), 1794 (s), 1724 (s), 1425 (w), 1228 (m), 1145 (m), 1027 (m), 941 (s), 893 (w), 866 (w).

Polymethacrylate 6b
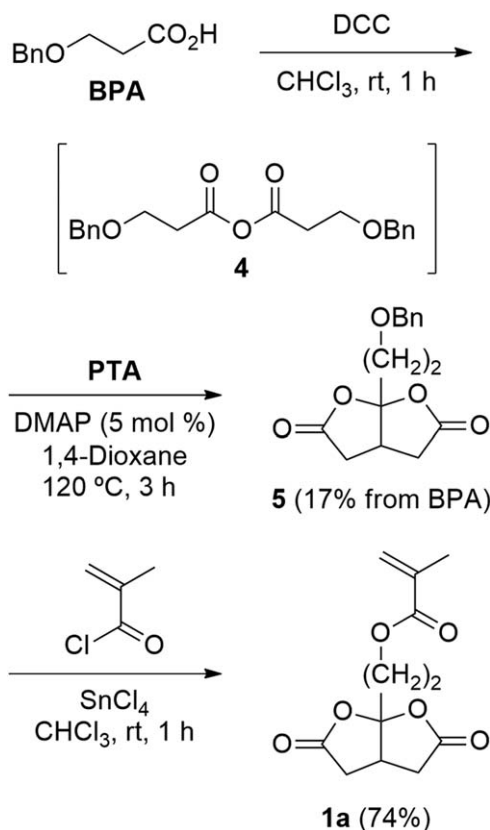
It is colorless powder.

^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.96 (brs, 2H; —COOCH_2—), 3.24 (brs, 1H; —CH$_2$—CH(C)—CH$_2$—), 3.01 (m, 2H; —CH_2CH(—C)CH_2COO—), 2.73 (m, 2H; —CH_2CH(—C)CH_2COO—), 2.06 (br, 2H; —C—CH_2), 1.74 (br, 4H; —CH$_2$—CH_2—CH$_2$— and β-CH_2), 0.77 (m, 3H; C—CH_3); IR (KBr): v = 2957 (w), 1794 (s), 1721 (s), 1426 (w), 1268 (m), 1163 (s), 1033 (s), 978 (s), 945 (m), 898 (w).

Polymethacrylate 6c

It is colorless powder.

SCHEME 2 Synthesis of monomer **1a**.

^{1}H NMR (400 MHz, DMSO-d_6, δ): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.92 (brs, 2H; —COOCH_2—), 3.22 (brs, 1H; —CH$_2$—CH(C)—CH$_2$—), 3.01 (m, 2H; —CH_2CH(—C)CH_2COO—), 2.70 (d, 2H, J = 19.0 Hz; —CH_2CH(—C)CH_2COO—), 2.02 (brs, 2H; —C—CH_2), 1.46–1.63 (m, 6H; —CH_2—CH_2— and β-CH_2), 0.76–0.93 (m, 3H; C—CH_3); IR (KBr): v = 2954 (m), 1793 (s), 1724 (s), 1637 (w), 1427 (w), 1264 (s), 1163 (s), 1061 (w), 1061 (w), 983 (w), 946 cm^{-1} (w).

Polymethacrylate 6d

It is colorless powder.

^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.89 (2H; —COOCH_2—), 3.21 (1H; —CH$_2$—CH(C)—CH$_2$—), 3.00 (dd, 2H, J = 18.5, 9.9 Hz; —CH_2CH(—C)CH_2COO—), 2.70 (d, 2H, J = 22.0 Hz; —CH_2CH(—C)CH_2COO—), 1.99 (brs, 2H; —C—CH_2), 1.40–1.60 (m, 8H; —CH$_2$—CH_2—CH$_2$— and β-CH_2), 0.76–0.93 (m, 3H; —C—CH_3); IR (KBr): v = 2949 (w), 1793 (s), 1721 (s), 1429 (w), 1389 (w), 1268 (s), 1158 (s), 1033 (s), 988 (s), 939 (s), 815 (w), 682 cm^{-1} (w).

RESULTS AND DISCUSSION

Synthesis of Monomers

The designed methacrylate monomers were attempted to synthesize as shown in Scheme 1. In the first step, the precursor bislactones **2** bearing chloroalkyl moieties were synthesized by the condensation reaction of the corresponding
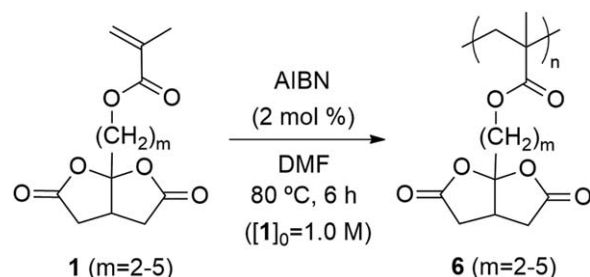
SCHEME 3 Radical polymerization of methacrylates **1**.

acid anhydrides with PTA.[12,13] The acid anhydrides were synthesized from the corresponding chloroalkyl carboxylic acids (Supporting Information Scheme S1). The yields of bislactones **2c** and **2d** were moderate, whereas that of **2b** was low owing to the predominant formation of γ-butyrolactone. When anhydride **2a** was used as the substrate, the desired bislactone was not observed, presumably because the elimination of hydrogen chloride was preferred.[14] Bislactones **3b–d** bearing chloroalkyl groups were treated with sodium methacrylate to afford the target methacrylate monomers **1b–1d**.

For the efficient synthesis of methacrylate **1a**, an alternative synthetic route was developed (Scheme 2). As a starting material, BPA was used. BPA was synthesized from 3-benzyloxypropionitrile (Supporting Information Scheme S2).[15] BPA was condensed into the corresponding anhydride **4** by the effect of DCC, and the anhydride prepared *in situ* was used for the reaction with PTA in the presence of a catalytic amount of DMAP. The reaction gave bislactone **5**, which was then treated with methacryloyl chloride and SnCl₄ to afford the target monomer **1a**.

Radical Polymerization of 1

Free radical polymerization of methacrylate **1** bearing BBL moiety was conducted in DMF (1 M) using AIBN (Scheme 3) as a radical initiator. The polymerization proceeded smoothly, leading to the high conversions of the monomers more than 90%. The resulting polymers **6a–6d** were isolated as MeOH-insoluble fractions. The number average and weight average molecular weights (M_n and M_w, respectively) were estimated by SEC. The SEC traces are shown in Supporting
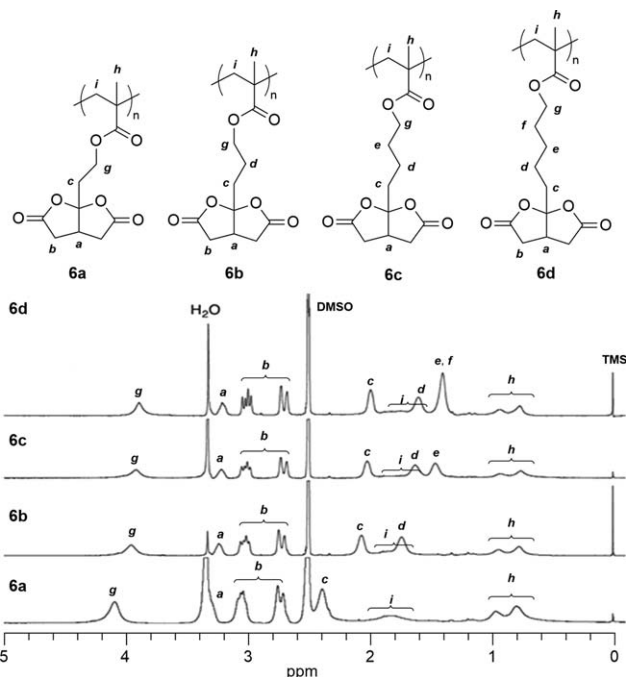
FIGURE 1 ^{1}H-NMR spectra of polymethacrylates **6a–6d** (in CDCl₃, at RT).

Information Figure S1. The yields of the polymers and their molecular weights are listed in Table 1.

The molecular weight of polymer **6a** was remarkably higher than those of the other polymers. For the higher M_n of **1a** that was estimated by SEC, the higher rigidity of the main chain of **1a** and consequent behavior of **1a** as a rigid rod-like polymer rather than a random coil one would be possible reasons: In **1a**, conformational change of the main chain would be more restricted because the bulky BBL groups are located closer to the main chain and to each other owing to the shorter distance between the BBL moiety and the main chain. For minimizing steric repulsion, the bulky BBL groups tend to keep away from each other. Consequently, the main chain can be stretched rather than folded in a coil, leading to the overestimation of molar mass by SEC.

The structures of the obtained polymers were confirmed by ^{1}H-NMR spectroscopy. The resulting spectra are shown in

TABLE 1 Polymerization of Methacrylates **1** and Properties of the Resulting Polymers **6**

Monomer	Polymer	Conversion[a] (%)	Yield (%)[b]	M_n (M_w/M_n)[c]	T_g (°C)[d]	T_{d5} (°C)[e]
1a	**6a**	96	71	15,000 (3.1)	138	279
1b	**6b**	97	59	9,500 (3.4)	118	296
1c	**6c**	94	59	8,200 (2.2)	76	305
1d	**6d**	93	66	9,200 (2.2)	67	304

[a] Determined by 1H NMR.
[b] MeOH-insoluble part.
[c] Estimated by SEC (eluent: solution of LiBr in DMF, PSt standards).
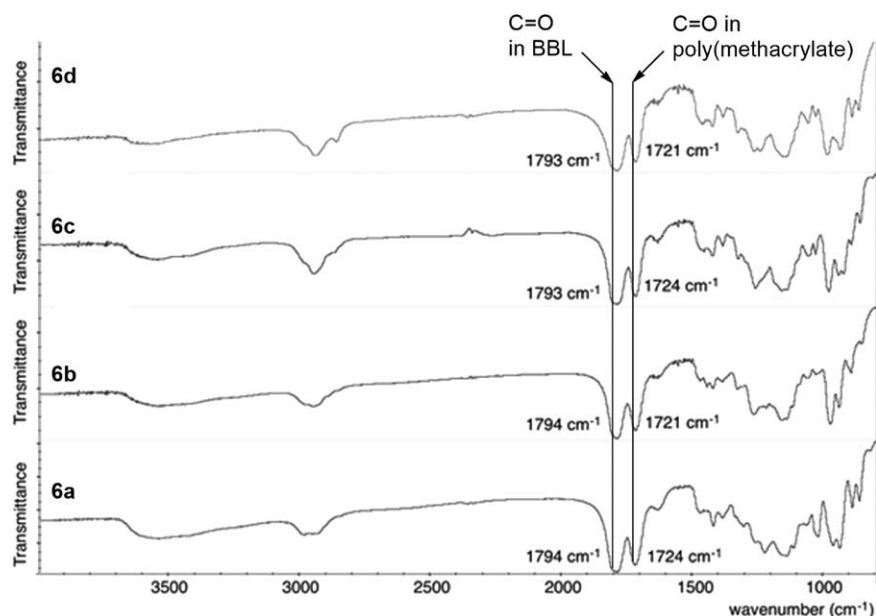[d] Determined by DSC.
[e] Determined by TGA.

FIGURE 2 FTIR Spectra of poly(methacrylate)s **6**.

Figure 1 which demonstrate the successful incorporation of the BBL moiety in the side chains of the polymers. The signals attributable to the BBL moiety were clearly observed and their relative intensities were in good agreement with the expected ones. When the chain length of the linker increased, the signal g attributable to the CH$_2$ located in the linker and attached directly to the ester group shifted to a lower magnetic field accordingly.

IR analysis of the polymers also supported their structural features (Fig. 2). Two characteristic peaks appeared at around 1790 and 1720 cm^{-1} and these were attributed to C=O bond in the BBL moieties and that in the polymethacrylate backbone, respectively.

Properties of Polymers 6

Polymers **6** inherited the high polarity of the BBL moiety and thus insoluble in less polar solvents such as CH$_2$Cl$_2$, CHCl$_3$, AcOEt, and THF. In contrast, **6** were soluble in aprotic polar solvents such as DMF and DMSO. Water and MeOH

were not good solvents for **6**; the poor solubility in MeOH enabled the facile isolation of the polymers. There was no significant difference in solubility among the polymers **6a–d**. Thermal properties of **6** were investigated with TGA and DSC. The resulting thermograms are shown in Figures 3 and 4, respectively. From the thermograms, temperatures for 5% of weight loss by thermal degradation (T_{d5}) and glass temperatures (T_g) were extracted and listed in Table 1. The TGA thermograms demonstrated that polymers do not exhibit weight loss below 260 °C. The residual weight% of polymer **6a** dropped steeply in the range between 270 and 295 °C, and this first step of weight loss was followed by much less steep weight loss continuing until 420 °C. The weight loss (ca. 70% of the initial weight) in the first step was in good accordance with the content of the BBL moieties, implying that the BBL moieties can be detached from the polymer **6a** below 300 °C. Polymers **6b–6d** exhibited higher thermal stability than that of **6a**. Their TGA profiles were quite similar
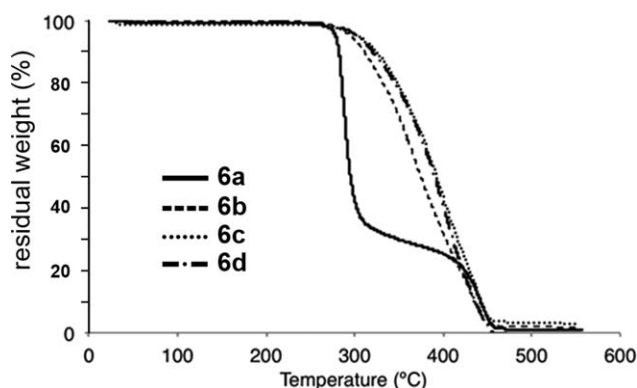

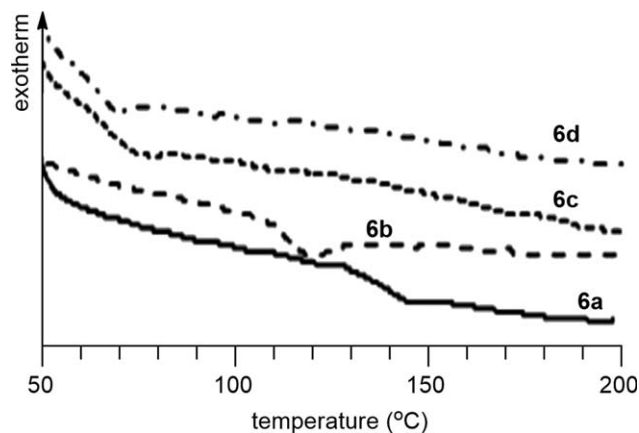**FIGURE 3** TGA thermograms of poly(methacrylate)s **6**.

FIGURE 4 DSC thermograms of poly(methacrylate)s **6**.

to each other, with showing one-step weight loss starting from 280 °C and completing at 450 °C. The relatively lower thermal stability of **6a** could be owing to the higher steric repulsion between the neighboring side chains carrying BBL moieties caused by the shorter distance between the poly(-methacrylate) main chain and BBL moieties than in the other polymers. On the other hand, T_g increased by reducing length of the alkyl linker. Polymer **6a** with the shortest linker exhibited the highest T_g (138 °C). A similar dependence of T_g on length of linker has been reported for poly(methacrylate)s bearing 2-methyl-2-adamantyloxycarbonyl moiety in the side chain.[16]

CONCLUSIONS

BBL moiety, which has been investigated so far as a structure that can undergo ring-opening reaction in the copolymerization with epoxide, was employed as a rigid and polar building block for designing a new series of methacrylate monomers. The radical polymerization of these methacrylates afforded the corresponding poly(methacrylate)s, which have BBL moiety in the side chain and thus inherited its rigidity and high polarity leading to the high T_g and solubility in aprotic polar solvents. These characteristics as well as the reactive nature of BBL in the side chain would guarantee polymers with BBL moiety in the side chain to be a promising candidate as photoresist materials.

REFERENCES AND NOTES

1 K. Nozaki, *J. Photopolym. Sci. Technol.* **2010**, *23*, 795–801.

2 K. Maeda, K. Nakano, M. Shirai, *J. Photopolym. Sci. Technol.* **2006**, *19*, 699–703.

3 K. Takeda, H. Asahara, T. Hanawa, K. Tsujita, H. Okumura, N. Hishinuma, *J. Photopolym. Sci. Technol.* **2003**, *16*, 511–516.

4 K. Nozaki, E. Yano, *J. Photopolym. Sci. Technol.* **1997**, *10*, 545–550.

5 A. Tadokoro, T. Takata, T. Endo, *Macromolecules* **1993**, *26*, 4400–4406.

6 T. Takata, A. Tadokoro, T. Endo, *Macromolecules* **1992**, *25*, 2782–2783.

7 S. Ohsawa, K. Morino, A. Sudo, T. Endo, *Macromolecules* **2010**, *43*, 3585–3588.

8 S. Ohsawa, K. Morino, A. Sudo, T. Endo, *Macromolecules* **2011**, *44*, 1814–1820.

9 K. Chung, T. Takata, T. Endo, *Macromolecules* **1997**, *30*, 2532–2538.

10 K. Chung, T. Takata, T. Endo, *Macromolecules* **1995**, *28*, 3048–3054.

11 S. Ohsawa, B. Barkakaty, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1281–1289.

12 W. L. Parker, F. Johnson, *J. Org. Chem.* **1973**, *38*, 2489–2496.

13 J. Martin, P. C. Watts, F. Johnson, *J. Org. Chem.* **1974**, *39*, 1676–1681.

14 M. K. Eberhardt, K. Soto, *Tetrahedron Lett.* **1987**, *28*, 3439–3440.

15 T. R. Krishna, N. Jayaraman, *J. Org. Chem.* **2003**, *68*, 9694–9704.

16 I. Takemoto, Y. Fuji, I. Yoshida, K. Hashioto, T. Miyagawa, S., Yamaguchi, K. Takahashi, S. Konishi, Y. Lee, *J. Photopolym. Sci. Technol.* **2005**, *18*, 399–406.