Macromolecules

ARTICLE

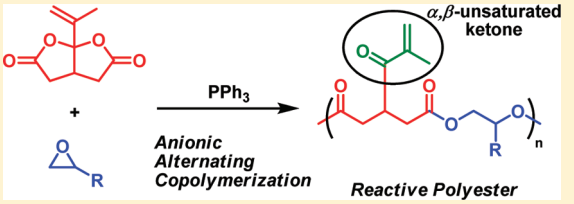
pubs.acs.org/Macromolecules

Synthesis of a Reactive Polyester Bearing α,β-Unsaturated Ketone Groups by Anionic Alternating Copolymerization of Epoxide and Bicyclic Bis(γ-butyrolactone) Bearing Isopropenyl Group

Sousuke Ohsawa, Kazuhide Morino, Atsushi Sudo, and Takeshi Endo*

Molecular Engineering Institute, Kinki University, Kayanomori, Iizuka, Fukuoka 820-8555, Japan

ABSTRACT: A novel bicyclic bis(γ-butyrolactone), 2,8-dioxa-1-isopropenylbicyclo[3.3.0]octane-3,7-dione (**2**), was successfully synthesized by the reaction of 1,2,3-propanetricarboxylic acid and methacrylic anhydride at 140 °C in the presence of *N*,*N*-dimethyl-4-aminopyridine and $CuCl_2$. Anionic ring-opening copolymerization of **2** with glycidyl phenyl ether (GPE) using PPh_3 as an initiator proceeded in a 1:1 alternating manner to give the corresponding polyester **3** bearing α,β-unsaturated ketone groups in the side chains. Prolongation of polymerization time resulted in the production of an insoluble networked copolymer due to reactions of the α,β-unsaturated ketone groups in the side chains. In order to demonstrate the potential of the copolymer **3** as a reactive polymer, Michael addition of thiols to the α,β-unsaturated ketone groups in the side chains was performed.



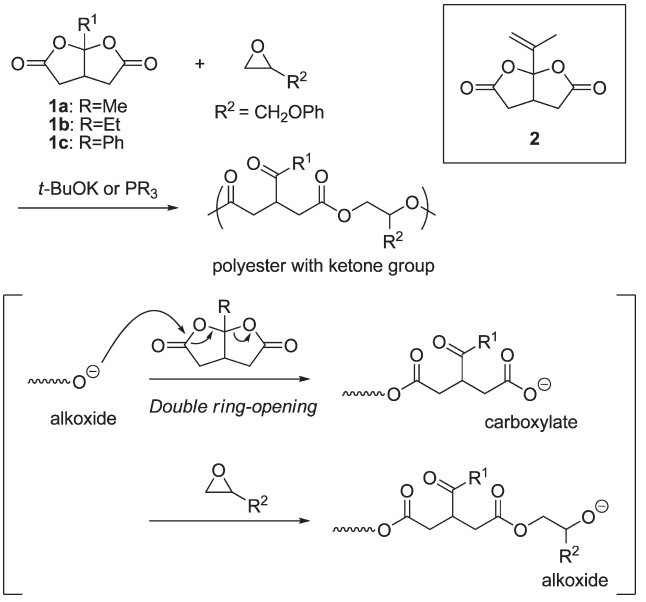
INTRODUCTION

Ring-opening polymerization of lactones is an attractive synthetic approach to polyesters, which has prompted many researchers to devote considerable efforts to the development of lactone-type monomers and their efficient polymerization systems to enable well-defined synthesis of polyesters with intriguing structures and the corresponding functions. Such efforts have involved those for the development of lactones having extra reactive groups and their successful ring-opening polymerizations, leading to reliable synthesis of reactive polyesters that can be used as polymeric precursors of functionalized polyesters. So far, there have been several reports on the ring-opening polymerizations of lactones bearing carbon−halogen bond,[1−3] carbon−carbon double bond,[2,4,6] acetylene,[5,7] and azide.[8] For example, Emrick et al. successfully introduced hydroxyl groups through oxidation of olefins.[2] They first carried out the ring-opening polymerization of δ-valerolactone bearing allyl and cyclopentenyl groups to give the corresponding polyesters having olefinic groups. The carbon−carbon double bonds of the obtained polymers were then oxidized by osmium tetroxide, resulting in the polyesters having hydroxyl moieties. Jérôme et al. reported the ring-opening polymerization of ε-caprolactone bearing allyl group followed by epoxidation of the olefins incorporated into the polymer side chains by using *m*-chloroperbenzoic acid as an oxidant.[6] Substitution of halogens using sodium azide following ring-opening polymerization of halogenated lactones was often performed to introduce azide groups in order to further functionalize by click reaction.[7] Halogens introduced into the side chains of polyesters were also successfully transformed into other reactive groups such as alcohol, carboxylic acid, and epoxide.[3]

Meanwhile, we have focused on another strategy for synthesizing polyesters based on alternating copolymerization of lactones with epoxides. The lactones we have developed so far can be categorized into three types of compounds, i.e., (1) spirobis(γ-butyrolactone) (SBL),[9] consisting of two five-membered lactones that are connected with each other in a spiro form, (2) bicyclic bis(γ-butyrolactone) (BBL),[11−13] consisting of two five-membered lactones that are connected to form a 5−5 fused ring system, and (3) 3,4-dihydrocoumain (DHCM),[13] an aromatic six-membered lactone. Although these compounds exhibited no homopolymerizability at all; however, they underwent the anionic alternating copolymerizations with epoxides to afford the corresponding polyesters. Scheme 1 depicts the anionic alternating copolymerization of BBL **1** with epoxide, through the selective reaction of the alkoxide-type propagating species with **1** and that of the carboxylate-type propagating species with epoxide. One of the features of this copolymerization process is the double ring-opening reaction accompanied by an isomerization process, which enables the formation of ketone moiety in the side chain of the polymer. In addition, this double ring-opening reaction is the origin of the volume expansion during polymerization, which has permitted the use of BBL as a "volume expandable monomer" to suppress the intrinsic shrinkage of epoxy curing systems.[10,12,14] Another advantage of BBL-type monomers is their straightforward and efficient synthesis by condensation of a citric acid-derived tricarboxylic acid (= 1,2,3-propanetricarboxylic acid) and acid anhydrides. For example, the employment of acetic anhydride, propionic anhydride, and benzoic anhydride resulted in the successful synthesis of BBLs **1a**−**c** bearing methyl, ethyl, and phenyl group, respectively.

Received: November 15, 2010
Revised: February 2, 2011
Published: March 04, 2011

Scheme 1. Copolymerization of Bicycle Bis(γ-butyrolactone) (BBL) with Epoxide



Herein, we report a new BBL-type monomer **2** bearing isopropenyl group, which can be readily synthesized from 1,2,3-propanetricarboxylic acid and methacrylic anhydride. Our expectation to this monomer was its copolymerization with epoxide in a 1:1 alternating manner to give the corresponding polyester, of which side chains are endowed with methacryloyl group through the double ring-opening reaction of **2**. Through the copolymerization, the isopropenyl group of **2** can be transformed into methacryloyl group, of which polymerizability and intrinsic high electrophilicity would permit various chemical modifications of the polymer side chains.

EXPERIMENTAL SECTION

Materials. 1,2,3-Propanetricarboxylic acid (98%), *N,N*-dimethyl-4-aminopyridine (DMAP) (99%), glycidyl phenyl ether (GPE) (99%), aluminum(III) chloride (98%), benzyl mercaptan (96%), and di-*tert*-butyl peroxide (DTBP) (94%) were purchased from Tokyo Kasei (TCI, Tokyo Japan). Methacrylic anhydride (94%) was purchased from Aldrich. Pottasium *tert*-butoxide (*t*-BuOK) (97%) was purchased from Tokyo Kasei (TCI, Tokyo Japan) and used as received. Triphenylphosphine (PPh_3) (97%), cupper dichloride ($CuCl_2$) (95%), and 1-dodecanethiol (98%) were obtained from Wako Pure Chemical Industries (Osaka, Japan). PPh_3 was recrystallized from ethanol. GPE was dried over calcium hydride and distilled under nitrogen. Tetrahydrofran (THF) was dried over sodium benzophenone ketyl and distilled under nitrogen just before use. 2,8-Dioxa-1-methylbicyclo[3.3.0]octane-3,7-dione (**1a**) was prepared according to previously reported method.[12,13]

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Varian NMR Unity Inova 400 (400 and 100 MHz for ^1H and ^{13}C with tetramethylsilane as the internal standard). IR spectra were taken on a Thermo Scientific Nicolet iS10 spectrometer. Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were estimated by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the eluent at a flow rate of 0.6 mL/min at 40 °C, performed on a Tosoh chromatograph model HLC-8120 system equipped with Tosoh TSKgel SuperHM-H styrogel columns (6.0 mm ϕ × 15 cm, 3 and 5 μm bead sizes), refractive index detector, and UV−vis detector (254 nm). The molecular weight calibration curve was obtained with polystyrene standards. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 using an aluminum pan under a 20 mL/min N_2 flow at the heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instruments Inc. TG-DTA 6200 using an alumina pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min.

Synthesis of 2,8-Dioxa-1-isopropenylbicyclo[3.3.0]octane-3,7-dione (2). A mixture of 1,2,3-propanetricarboxylic acid (38 g, 0.22 mol), DMAP (5.4 g, 0.043 mmol), $CuCl_2$ (0.98 g, 7.4 mmol), and methacrylic anhydride (100 mL, 12.0 mol) was stirred at 140 °C. After 6 h, unreacted methacrylic anhydride was removed at 60 °C under reduced pressure (0.04 mmHg). The residue was dissolved in 70 mL of chloroform and poured into 1000 mL of diethyl ether. The resulting precipitates were filter off, and the filtrate was washed with aqueous solution of $NaHCO_3$. The organic layer was then dried over anhydrous $MgSO_4$, treated with active charcoal, and filtered off. After evaporation of solvent, the residue was recrystallized from 30 mL of toluene three times to afford 20 g (51%) of **2** as a colorless crystal.

Spectroscopic data of obtained **2**: IR (neat): 3109 (C−H), 3018 (C−H), 2990 (C−H), 2935 (C−H), 1794 (C═O), 1655 (C═C), 1450, 1302, 1262, 1219, 1100, 988, 954, 922, 871, 780, 751, 675, 620 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.88 (s, 3H, CH_3), 2.60 (q, 2H, $OCOCH_2$), 3.02 (q, 2H, $OCOCH_2$), 3.26 (m, 1H, CH), 5.19 (q, 1H, $C═CH_2$), 5.35 (s, 1H, $C═CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.5 (CH_3), 35.2(CH), 37.1 (CH_2), 113.2 (O−C−O), 115.9 (=CH_2), 138.8 (C=), 172.6 (C═O).

Copolymerization of 2 with GPE. A typical copolymerization procedure for the synthesis of alternating copolymer **3** is described below. PPh_3 (8.5 mg, 0.32 mmol), **2** (0.15 g, 0.82 mmol), GPE (0.12 g, 0.82 mmol), and 0.4 mL of THF were placed in a glass ampule under a nitrogen atmosphere. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 5 h. After the reaction mixture was cooled to room temperature, a chloroform solution of acetic acid (1.0 vol %, 1.0 mL) was added. The resulting mixture was poured into 50 mL of methanol. The resulting copolymer was collected by centrifugation, washed with methanol, and dried in vacuo to afford 0.21 g (82%) of **3** as viscous oil. The M_n and M_w/M_n were 6.1 × 10^3 g/mol and 2.1, respectively.

Spectroscopic data of obtained copolymer: IR (neat): 2958 (C−H), 1740 (C═O (ester)), 1677 (C═O (ketone)), 1599 (phenyl), 1588 (phenyl), 1497, 1242, 1173, 1050, 814, 755, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.85 (s, 3H, CH_3), 2.45 (br, 2H, CH_2COO), 2.71 (br, 2H, CH_2COO), 3.97−4.14 (br, 1H, CH and 2H, CH_2OPh), 4.17−4.48 (m, 2H, CH_2OCO), 5.23−5.35 (br, 1H, COOCH), 5.81 (s, 1H, C═CH), 6.06 (s, 1H, C═CH), 6.84−7.31 (m, 5H, Ph).

Copolymerization of 2 with GPE in the Presence of $CuCl_2$. A procedure for the copolymerization of **2** with GPE in the presence of $CuCl_2$ is described below. Triphenylphosphine (12.8 mg, 0.48 mmol), **2** (0.15 g, 0.8 mmol), GPE (0.12 g, 0.8 mmol), $CuCl_2$ (10.8 mg, 0.08 mmol), and 0.4 mL of THF-d_8 were placed in a glass ampule under a nitrogen atmosphere.[13] The tube was cooled, evacuated, sealed off, and heated at 120 °C. The time−conversion curves are shown in Figure 4. After 18 h, the corresponding copolymer was obtained by the reprecipitation as methanol-insoluble part in 92% yield. The M_n and M_w/M_n were 4.2 × 10^3 g/mol and 3.1, respectively.

Cross-Linking Reaction of Isolated 3 by Heating. **3** (160 mg, 0.48 mmol) and 0.24 mL of THF were placed in a glass ampule under a nitrogen atmosphere. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 24 h. After the reaction mixture was cooled to room temperature, the resulting polymer was washed with chloroform; the insoluble part was corrected by filtration, affording 145 mg (90%) of corresponding networked polymer.

Cross-Linking Reaction of Isolated 3 Using DTBP. **3** (160 g, 0.48 mmol), di-*tert*-butyl peroxide (3.5 mg, 5 mol %), and 0.24 mL of chlorobenzene were placed in a glass ampule under a nitrogen

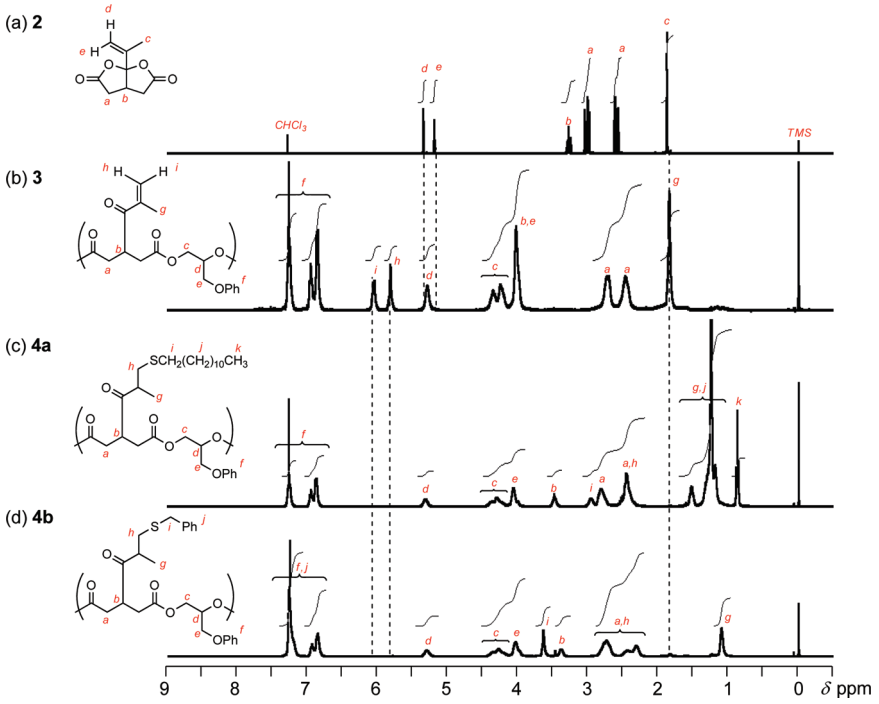


Figure 1. ^{1}H NMR spectra of **2** (a), **3** (b), and polymers obtained by the Michael addition with dodecanethiol (**4a**) (c) and with benzyl mercaptan (**4b**) (d), measured in $CDCl_3$ at rt.

atmosphere. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 24 h. After the reaction mixture was cooled to room temperature, the resulting polymer was washed with chloroform, and the insoluble part was corrected by filtration afforded 146 mg (91%) of corresponding networked polymer.

Cross-Linking Reaction of Isolated 3 Using *t*-BuOK. **3** (160 g, 0.48 mmol), *t*-BuOK (2.7 mg, 5 mol %), and 0.24 mL of THF were placed in a glass ampule under nitrogen atmosphere. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 24 h. After the reaction mixture was cooled to room temperature, the resulting polymer was washed with chloroform, and the insoluble part was corrected by filtration afforded 152 mg (95%) of corresponding networked polymer.

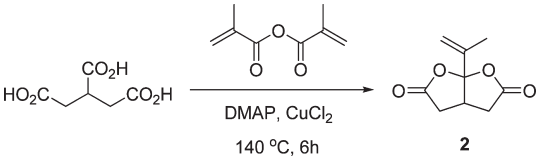
Michael Addition Reaction of Dodecanethiol to the α,β-Unsaturated Ketone Moieties of 3. A mixture of **3** (144 mg, 0.43 mmol), dodecanethiol (0.10 mL, 0.43 mmol), $AlCl_3$ (5.4 mg, 0.043 mmol), and $CHCl_3$ (0.87 mL) was stirred at ambient temperature. After 24 h solution was poured into 40 mL of methanol. The precipitated polymer was collected by centrifugation, washed with methanol, and then dried in vacuo to give 124 mg (78%) of **4a** as viscous oil. The M_n and M_w/M_n were 8.3×10^3 g/mol and 1.5, respectively. ^{1}H NMR and IR spectra are shown in Figures 1c and 5b, respectively.

Michael Addition Reaction of Benzyl Mercaptan to the α,β-Unsaturated Ketone Moieties of 3. A mixture of **3** (144 mg, 0.43 mmol), benzyl mercaptan (0.05 mL, 0.43 mmol), $AlCl_3$ (5.4 mg, 0.043 mmol), and $CHCl_3$ (0.87 mL) was stirred at ambient temperature. After 24 h solution was poured into 40 mL of methanol. The precipitated polymer was collected by centrifugation, washed with methanol, and then dried in vacuo to give 101 mg (73%) of **4b** as viscous oil. The M_n and M_w/M_n were 5.4×10^3 g/mol and 1.6, respectively. ^{1}H NMR and IR spectra are shown in Figures 1d and 5c, respectively.

RESULTS AND DISCUSSION

Synthesis of 2. To synthesize the novel bicyclic bis(γ-butyrolactone) bearing the isopropenyl group **2**, we first attempted the reaction of 1,2,3-propanetricarboxylic acid and methacrylic anhydride in the presence of pyridine at 140 °C in the same way for the synthesis of **1**.[12,13] However, the isolated yield of **2** was quite low (11%). This lower yield would be due to the consumption of methacrylic anhydride by its radical polymerization. Then we were conceived of two methods for improvement of reaction condition: (1) addition of radical inhibitor with expecting efficient suppression of the polymerization of methacrylic anhydride and (2) utilization of a more nucleophilic catalyst in order to accelerate the conversion of methacrylic anhydride into **2**. By optimizing of the reaction conditions, we found that employment of cupper dichloride ($CuCl_2$) as an inhibitor and *N,N*-dimethyl-4-aminopyridine (DMAP) as a catalyst resulted in successful synthesis of **2** in 51% isolated yield (Scheme 2). The structure of **2** was confirmed by ^{1}H NMR and IR spectroscopies; the ^{1}H NMR spectrum of **2** showed signals at 1.88, 5.19, and 5.35 ppm, which were attributable to methyl and olefinic protons of isopropenyl group (Figure 1a). In the IR spectrum, the peak assignable to lactone moiety was observed at 1794 cm^{-1} (Figure 2a).

Scheme 2. Synthesis of Bicyclic Bis(γ-butyrolactone) Bearing Isopropenyl Group 2



Copolymerization of 2 with GPE. We carried out the copolymerization of **2** with GPE using *t*-BuOK as an initiator in THF at 120 °C (Scheme 3). Figure 3 shows the corresponding time−conversion relationship, which suggested that the two

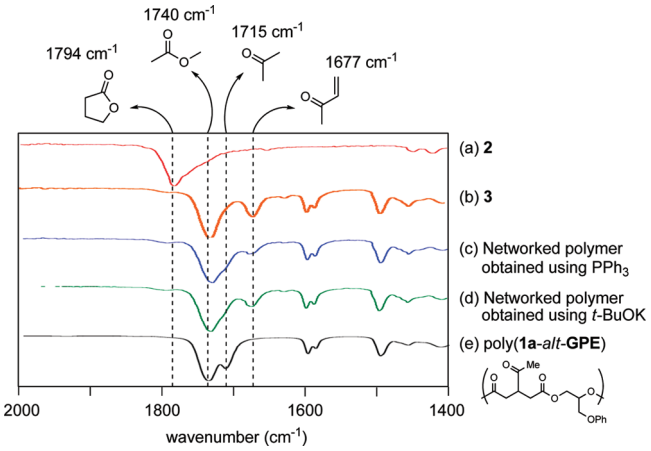
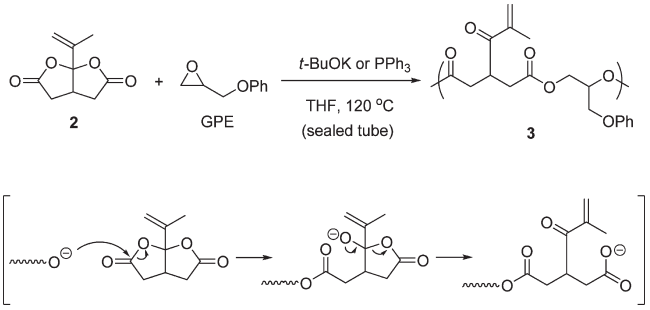


Figure 2. FT-IR spectra of **2** (a), **3** (b), networked copolymer using PPh_3 (c), networked copolymer using *t*-BuOK (d), and poly(**1a**-*alt*-**GPE**) (e).

Scheme 3. Copolymerization of 2 with GPE



monomers underwent the 1:1 alternating copolymerization. The copolymerization proceeded in a homogeneous solution until 48 h, but after that, insoluble polymer was formed (run 1 in Table 1). This phenomenon was probably due to the cross-linkage of polymer side chain due to heating for a long reaction time. On the other hand, we have reported that phosphines were efficient initiators for the copolymerization of **1a** with GPE, and the copolymerization was much faster than initiated by *t*-BuOK.[13] When PPh_3 was used as an initiator for the copolymerization of **2** and GPE, both the monomers were consumed much faster than in the *t*-BuOK-initiated copolymerization (Figure 3). The copolymerization proceeded smoothly in a homogeneous solution until 5 h, where the conversions reached 90%. At this point, the copolymer **3** was isolated as a methanol-insoluble fraction in 82% yield (run 2 in Table 1). **3** was soluble in chloroform, dichloromethane, ethyl acetate, acetone, and THF. Figure 1b shows the ^{1}H NMR spectrum of **3** obtained by the copolymerization using PPh_3 as an initiator. The integral ratio of the methyl protons at 1.85 ppm and the methylene proton at 5.35 ppm confirmed that the composition of the obtained copolymer was 50/50, which also supported that the copolymerization of **2** with GPE proceeded in a 1:1 alternating manner similarly to the alternating copolymerization of **1a** with GPE.[11−13] In addition, the ^{1}H NMR spectrum showed new signals at 5.81 and 6.06 assignable to olefinic protons of α,β-unsaturated ketone group while the signals assignable to the olefinic protons of **2** disappeared completely. We calculated the content of α,β-unsaturated

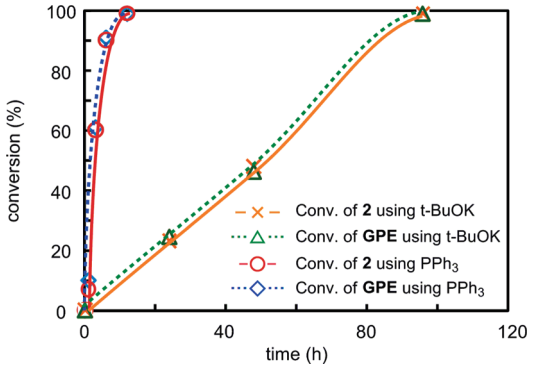


Figure 3. Time−conversion curves of **2** (×) using *t*-BuOK, GPE (Δ) using *t*-BuOK, **2** (○) using PPh_3, and GPE (◇) using PPh_3 on the copolymerization of **2** with GPE in THF-d_8 at 120 °C. The conversions were estimated by ^{1}H NMR spectra measured at rt.

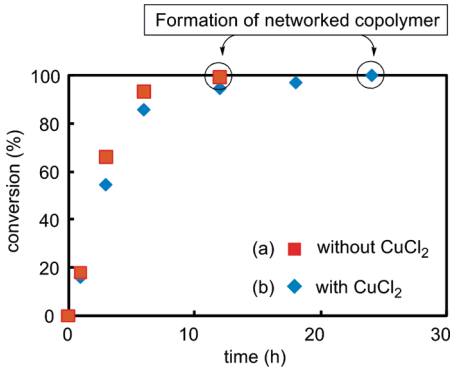


Figure 4. Time−conversion curves of **2** on the coplymerization of **2** and GPE in THF-d_8 at 120 °C using 4 mol % of PPh_3 without $CuCl_2$ (a) and using 6 mol % of PPh_3 with 1 mol % of $CuCl_2$ (b). The conversions were estimated by ^{1}H NMR based on **2**.

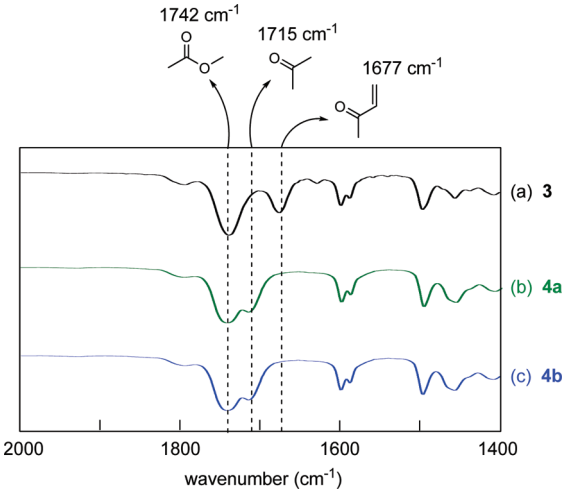


Figure 5. IR spectra of **3** (a) and polymers obtained by the Michael addition with dodecanethiol (**4a**) (b) and with benzyl mercaptan (**4b**) (c).

ketone groups incorporated into the polymer side chains based on the ^{1}H NMR spectrum, which was 90%, indicating that α,β-unsaturated ketone groups formed during the copolymerization were consumed by further reaction such as their thermal polymerization (vide infra). The structure of **3** was also

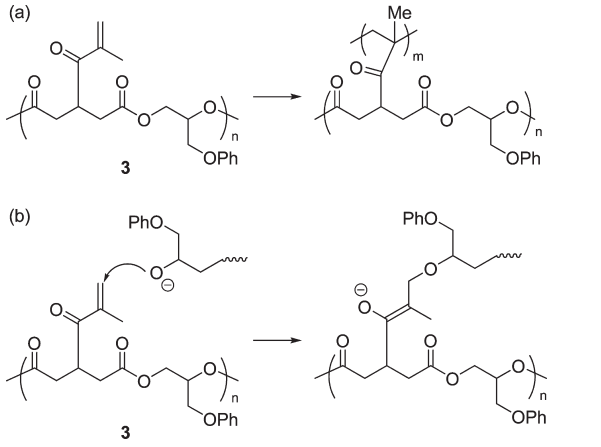
dx.doi.org/10.1021/ma102602e |*Macromolecules* 2011, 44, 1814–1820

Table 1. Copolymerization of 2 with GPE in THF at 120 °C[a]

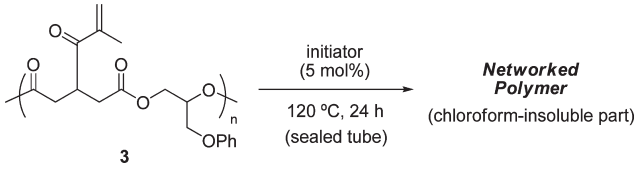
run	initiator	time (h)	yield (%)	M_n (M_w/M_n)[d]	unreacted vinyl moieties (%)	T_g (°C)[g]	T_{d10} (°C)[h]
1	*t*-BuOK	72	quant[b]		60[f]	29	277
2	PPh_3	5	82[c]	6.5×10^3 (2.1)	90[e]		
3	PPh_3	72	quant[b]		50[f]	29	326

[a] Polymerization conditions: [initiator] = 4.0 mol %, [**2**]/[GPE] = 50/50, 120 °C. [b] Chloroform-insoluble part. [c] Methanol-insoluble part. [d] Estimated by GPC (eluent = THF, polystyrene standards). [e] Determined by ^{1}H NMR. [f] Determined by FT-IR. [g] Determined by DSC. [h] Determined by TGA.

Scheme 4. Plausible Mechanisms for the Formation of the Networked Polymers through Thermal Polymerization of the α,β-Unsaturated Ketone Groups in the Side Chain (a) and Michael Addition of the Alkoxide of Growing Terminal into the α,β-Unsaturated Ketone Groups in the Side Chains (b)



Scheme 5. Cross-Linking Reaction of Isolated 3



confirmed by IR spectroscopy. In the IR spectrum of **3**, the peak at 1794 cm^{-1}, which assignable to lactone moiety of **2**, was not observed at all and the peaks due to the ester group appeared at 1740 cm^{-1} (Figure 2a,b). The peaks of the ketone groups in the side chains were observed at 1677 cm^{-1}, which was lower wavenumber by 38 cm^{-1} than that of the copolymer obtained by the copolymerization of **1a** with GPE (Figure 2b,e).[11] These results also demonstrated that the α,β-unsaturated ketone groups were formed upon the ring-opening process of **2** during the copolymerization. By prolonging polymerization time to 72 h, the corresponding networked copolymer was obtained quantitatively (vide infra).

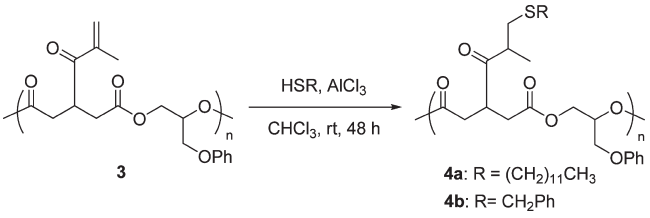
Formation of Networked Copolymer. As described above, insoluble networked polymers were obtained by prolonging polymerization time (Table 1, runs 1 and 3). Parts c and d of Figure 2 show the IR spectra of the networked copolymers obtained by copolymerization using PPh_3 and *t*-BuOK, respectively. From these spectra, the content of α,β-unsaturated ketone groups in the networked copolymers obtained with PPh_3 and

Table 2. Cross-Linking Reaction of Isolated 3 at 120 °C for 24 h[a]

run	initiator	yield (%)[b]	unreacted vinyl moieties (%)[c]	T_g (°C)[d]	T_{d10} (°C)[e]
1		91	55	31	315
2	DTBP[f]	90	60	41	324
3	*t*-BuOK	95	53	43	279

[a] Reaction conditions: [initiator] = 5.0 mol %, 120 °C, 24 h. [b] Chloroform-insoluble part. [c] Estimated by FT-IR. [d] Determined by DSC. [e] Determined by TGA. [f] Di-*tert*-butyl peroxide.

Scheme 6. Reaction of 3 with Thiols



t-BuOK was roughly estimated to be 50 and 60%, respectively, which suggested that the α,β-unsaturated ketone groups formed during the copolymerization were consumed for the networked formation. For this phenomenon, two mechanisms can be postulated: one is the radical polymerization of the methacryloyl group in the side chain (Scheme 4a), and the other is the Michael addition of the alkoxide-type propagating species and the methacryloyl group (Scheme 4b). We attempted suppression of possible radical polymerization of the methacryloyl group by adding $CuCl_2$ as an inhibitor. We first carried out the copolymerization in the presence of 4 mol % of PPh_3 and 3 mol % of $CuCl_2$; however, the copolymerization scarcely proceeded because of deactivation of PPh_3 by the coordination to $CuCl_2$. Therefore, the copolymerization was carried out by using 6 mol % of PPh_3 and 1 mol % of $CuCl_2$. As a result, the copolymerization rate was not affected by the presence of $CuCl_2$, while the formation of the networked polymer was retarded successfully (Figure 4): it took 24 h for the formation of networked copolymer in the presence of $CuCl_2$, whereas networked copolymer was formed after 12 h in the absence of $CuCl_2$. These results implied that the cross-linking process would involve radical polymerization of methacryloyl group in the side chain, although the anionic mechanism (b) cannot be denied.

The thermal properties of the obtained networked polymers are summarized in Table 1 (runs 1 and 3). The decomposition temperature (T_{d10}) of the networked copolymer obtained with PPh_3 was 326 °C, which was higher than that obtained with *t*-BuOK (277 °C) although the grass transition temperatures

Table 3. Michael Addition of Thiols into the α,β-Unsaturated Ketone Groups of 3

run	thiol	isolated yield (%)[a]	M_n (M_w/M_n)[b]	unreacted vinyl moieties (%)[c]	modified ratio (%)[c]
1	$CH_3(CH_2)_{11}SH$	78	8300 (1.5)	trace	>99
2	BnSH	73	5400 (1.6)	3	97

[a] Methanol-insoluble part. [b] Estimated by SEC (eluent = THF, polystyrene standards). [c] Estimated by ^{1}H NMR spectra.

(T_g) were identical. The lower T_{d10} value might be attributed to the small amount of residual *t*-BuOK which accelerated the decomposition of the networked polymers.

We demonstrated cross-linking reactions of the isolated copolymer **3** under several conditions (Scheme 5). When **3** was heated at 120 °C for 24 h in THF, a chloroform insoluble networked polymer was obtained in 91% yield (Table 2, run 1). Besides, **3** was efficiently cross-linked by heating in the presence of 5 mol % of di-*tert*-butyl peroxide as a radical initiator at 120 °C (Table 2, run 2). Both the obtained networked polymers showed high T_{d10} similar to the networked polymer obtained by the copolymerization using PPh_3. A cross-linking reaction of **3** under anionic condition was also performed (Table 2, run 3). In the presence of 5 mol % of *t*-BuOK, **3** was heated at 120 °C in THF. Although the corresponding networked copolymer was obtained in 95% yield, its thermal stability was much lower than the networked polymers obtained by the thermally and radically induced cross-linking reactions. The presence of a small amount of residual *t*-BuOK may be a possible reason for this low thermal stability.

Polymer Reaction. Finally, Michael reaction of thiols to the methacryloyl group in the side chain of **3** was examined. As thiols, dodecanethiol and benzyl mercaptan were employed. The reactions were carried out in chloroform at ambient temperature for 48 h in the presence of $AlCl_3$ (Scheme 6).[16] The reaction proceeded smoothly to give the corresponding adducts (**4a** and **4b**) in high yields (Table 3). Figure 1c,d shows the ^{1}H NMR spectra of the obtained copolymers. In both the spectra, the signals at 5.81 and 6.06 ppm assigned to the olefinic protons disappeared and the signals derived from the methyl protons shifted from 1.85 ppm to around 1.2 ppm. The integral ratio of these signals confirmed that the conversion was almost quantitative. The IR spectra also supported these results; the peaks of saturated ketone groups were observed at 1742 cm^{-1} in the IR spectra of **4a** and **4b**, which was identical to the copolymer of **1a** with GPE, whereas the peaks at 1682 cm^{-1} assignable to the α,β-unsaturated ketone moieties were completely disappeared (Figure 5). These results indicate that the reactive α,β-unsaturated ketone in the copolymer side chains was successfully converted to the corresponding functional groups through the Michael addition of thiols.

SUMMARY

A novel bicyclic bis(γ-butyrolactone) **2** bearing isopropenyl group was successfully synthesized. The copolymerization of **2** with glycidyl phenyl ether (GPE) by using PPh_3 as an initiator smoothly proceeded to give the corresponding alternating copolymer **3** bearing α,β-unsaturated ketone groups in the polymer side chains. Prolongation of the polymerization time resulted in the quantitative formation of the insoluble networked copolymer due to the reactions of the α,β-unsaturated ketone groups involving their radical polymerization. In addition, we successfully demonstrated Michael addition of thiols to the α,β-unsaturated ketone groups in the side chains of **3**.

AUTHOR INFORMATION

Corresponding Author

*Fax +81-948-22-7210; e-mail tendo@mol-eng.fuk.kindai.ac.jp.

ACKNOWLEDGMENT

This work was financially supported by JSR Corporation.

REFERENCES

(1) (a) Mecerreyes, D.; Atthoff, K.; Boduch, K. A.; Trollsas, M.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 5175–5182. (b) Lenoir, S.; Riva, R.; Lou, X.; Detrembleur, C.; Jérôme, R.; Lecomte, Ph. *Macromolecules* **2004**, *37*, 4055–4061. (c) Detrembleur, C.; Mazza, M.; Halleux, O.; Lecomte, Ph.; Mecerreyes, D.; Hedrick, J. L.; Jérôme, R. *Macromolecules* **2000**, *33*, 14–18. (d) Riva, R.; Rieger, J.; Jérôme, R.; Lecomte, Ph. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6015–6024.

(2) (a) Parrish, B.; Emrick, T. *Macromolecules* **2004**, *37*, 5863–5865. (b) Parrish, B.; Quansah, J. K.; Emrick, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1983–1990.

(3) Riva, R.; Lenoir, S.; Jérôme, R.; Lecomte, Ph. *Polymer* **2005**, *46*, 8511–8518.

(4) (a) Zhou, J.; Schmidt, A. M.; Ritter, H. *Macromolecules* **2010**, *43*, 939–942. (b) Chen, W.; Yang, H.; Wang, R.; Cheng, R.; Meng, F.; Wei, W.; Zhong, Z. *Macromolecules* **2010**, *43*, 201–207. (c) Mecerreyes, D.; Lee, V.; Hawker, C. J.; Hedrick, J. L.; Wursch, A.; Volksen, W.; Magbitang, T.; Huang, E.; Miller, R. D. *Adv. Mater.* **2001**, *13*, 204–208. (d) Mecerreyes, D.; Humes, L.; Miller, R. D.; Hedrick, J. L.; Detrembleur, C.; Lecomte, P.; Jérôme, R.; SanRoman, J. *Macromol. Rapid Commun.* **2000**, *21*, 779–784. (e) Jing, F.; Hillmyer, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 13826–13827. (f) Rieger, J.; Butsele, K. V.; Lecomte, P.; Detrembleur, C.; Jérôme, R.; Jérôme, C. *Chem. Commun.* **2005**, 274–276.

(5) van der Ende, A. E.; Harrell, J.; Sathiyakumar, V.; Meschievitz, M.; Karz, J.; Adcock, K.; Harth, E. *Macromolecules* **2010**, *43*, 5665–5671.

(6) Mecerreyes, D.; Miller, R. D.; Hedrick, J. L.; Detrembleur, C.; Jérôme, R. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 870–875.

(7) (a) Cooper, B. M.; Emrick, T. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 7054–7065. (b) Parrish, B.; Breitenkamp, R. B.; Emrick, T. *J. Am. Chem. Soc.* **2005**, *127*, 7404–7410.

(8) (a) Li, H.; Riva, R.; Kricheldorf, H. R.; Jérôme, R.; Lecomte, Ph. *Chem.—Eur. J.* **2008**, *14*, 358–368. (b) Xu, N.; Wang, R.; Du, F.-S.; Li, Z.-C.; Jérôme, R. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3583–3594. (c) Riva, R.; Schmeits, S.; Stoffelbach, F.; Jérôme, C.; Jérôme, R.; Lecomte, Ph. *Chem. Commun.* **2005**, 5334–5336.

(9) (a) Takata, T.; Tadokoro, A.; Chung, K.; Endo, T. *Macromolecules* **1995**, *28*, 1340–1345. (b) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 1711–1713.

(10) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1997**, *30*, 2532–2538.

(11) Takata, T.; Tadokoro, A.; Endo, T. *Macromolecules* **1992**, *25*, 2782–2783.

(12) (a) Tadokoro, A.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 4400–4406. (b) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 3048–3054.

(13) Ohsawa, S.; Morino, K.; Sudo, A.; Endo, T. *Macromolecules* **2010**, *43*, 3585–3588.

(14) (a) Uenishi, K.; Sudo, A.; Endo, T. *Macromolecules* **2007**, *40*, 6535–6539. (b) Uenishi, K.; Sudo, A.; Endo, T. *J. Polym. Sci., Part A:*

Polym. Chem. **2008**, *46*, 4092–4102. (c) Uenishi, K.; Sudo, A.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1661–1672. (d) Uenishi, K.; Sudo, A.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3662–3668.

(15) Takata, T.; Chung, K.; Tadokoro, A.; Endo, T. *Macromolecules* **1993**, *26*, 6686–6687.

(16) Chu, C.-M.; Huang, W.-J.; Lu, C.; Wu, P.; Liu, J.-T.; Yao, C.-F. *Tetrahedron Lett.* **2006**, *47*, 7375–7380.