Acid-Promoted Double Ring-Opening Reaction of Bicyclobis (γ-butyrolactone) with Alcohol and Its Application to Polyester Synthesis

Sousuke Ohsawa, Balaka Barkakaty, Atsushi Sudo, Takeshi Endo

Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka, 820-8555, Japan
Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

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ABSTRACT: Bicyclobis(γ-butyrolactone) (BBL) bearing methyl group **1a** reacted with benzyl alcohol (BnOH) in the presence of *p*-toluenesulfonic acid (*p*-TsOH) through the double ring-opening of the bislactone structure to afford the corresponding adduct **2a** bearing carboxyl group. The resulting carboxyl group underwent condensation with BnOH to afford the corresponding diester **3a**. The second step was quite slow at ambient temperature; however, it was efficiently accelerated by elevating temperature to 120 °C or performing under reduced pressure at 80 °C to afford **3a** in an excellent yield. Based on these results, the reaction of **1a** with xylene-α,α-diol (XyD) was carried out in chlorobenzene at 120 °C to obtain the corresponding polyester bearing ketone group in the side chain. The condensation reaction in the second step was effectively promoted by simultaneous removal of water under reduced pressure. BBLs **1b** and **1c** bearing reactive groups, isopropenyl and chloromethyl, respectively, were also employed as monomers efficiently. Their reactions with XyD gave the corresponding reactive polyesters bearing methacryloyl and chloroacetyl moieties, respectively. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1281–1289, 2012

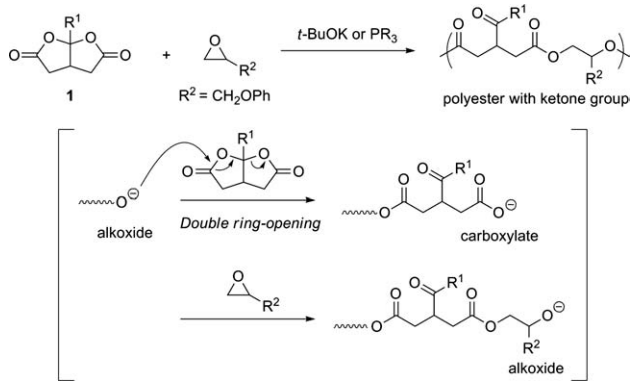
KEYWORDS: addition polymerization; bicyclobis(γ-butyrolactone); polyester; polycondensation; ring-opening polymerization

INTRODUCTION Lactones are an important class of cyclic monomers that have been intensively investigated so far. Considerable efforts have been devoted to the development of lactones and their efficient polymerization systems that affords various polyesters. In general, 4-, 6-, and 7-membered lactones readily undergo anionic and cationic polymerizations, whereas 5-membered ones are not likely to undergo the ring-opening polymerization due to the lack of ring distortion.[1] Aliphatic polyesters obtained by the ring-opening polymerizations of lactones have attracted much attention because of their flexibility[2–8] and their promising applications to biodegradable materials.[9–12]

So far, we have developed bicyclobis(γ-butyrolactone) (BBL),[13–16] consisting of two 5-membered lactones that are connected to form a 5–5 fused ring system. As can be expected from the thermodynamically disfavored ring-opening reaction of 5-membered lactone, BBL exhibits no homopolymerizability. Nevertheless, they undergo the anionic alternating copolymerization with epoxides using metal alkoxide and phosphines as initiators to afford the corresponding polyesters (Scheme 1). One of the features of this copolymerization process is the double ring-opening reaction accompanied by an isomerization process, which prevented the backward cyclization for reproducing the thermodynamic stable 5-membered lactone. Besides this anionic system, the cationic copolymerization of BBL and epoxide with using scandium triflate as a Lewis acid-type initiator has been reported.[17] Although the resulting polymer structure has been not fully clarified, incorporation of the BBL-derived ester moieties into the copolymer was confirmed at least, to demonstrate the potential use of BBL in various cationic systems.

Among various cationic systems, we focused on the acid-promoted ring-opening reaction of lactones with alcohols. In this reaction, lactones activated by acid readily undergo the nucleophilic attack of alcohols to afford the corresponding acyclic esters bearing hydroxyl group. This reactivity has allowed the development of ring-opening polymerizations of lactones based on the so-called "activated monomer mechanism," where alcohols employed as initiators attack lactones that are activated by acid, leading to the incorporation of the alcohol-derived moieties into the initiating end of the resulting polyesters.[18–24] For example, we have previously reported living ring-opening polymerizations of ε-caprolactone, δ-valerolactone, and cyclic carbonates by using $HCl{\cdot}Et_2O$ as an acid catalyst and alcohols as an initiator.[18,19] Utilization of trifluoromethanesulfonic acid and bis(trifluoromethanesulfonyl)imide as catalysts have been also reported.[20,21]

In this article, we disclose the details of our investigation on acid-promoted ring-opening reaction of BBL with alcohols as



SCHEME 1 The anionic ring-opening copolymerization of BBL with epoxide.

a nucleophilic reactant, which was motivated by the above-mentioned acid-promoted ring-opening polymerization of lactones. What we expected was a smooth cascade of ring-opening reactions of the two 5-membered lactone moieties to afford the corresponding acyclic structure with a ketone moiety, based on an analogy to the double ring-opening reaction of BBL observed in the anionic system. The highlight of this article is the application of this newly developed reaction system to a new polyester synthesis, which afforded polyesters bearing ketone group in the side chain successfully. A new BBL bearing chloromethyl group as a monomer for synthesizing a new reactive polyester is also reported herein.

RESULTS AND DISCUSSION

Synthesis of BBLs

BBLs were synthesized by the reaction of 1,2,3-propanetricarboxylic acid and carboxylic anhydride in the presence of basic catalysts such as pyridine and DMAP (Scheme 2). The substituent R of the carboxylic anhydride was introduced into the resulting BBL through the reaction.[13–16] Using acetic anhydride for this reaction, a methyl-substituted BBL **1a** was synthesized.[15] BBL bearing isopropenyl moiety **1b** was synthesized by using methacryloyl anhydride according to the reported procedure.[25] A new BBL bearing chloromethyl moiety **1c** was synthesized by using chloroacetic anhydride. In the initial attempt of the synthesis, we employed the standard conditions for the BBL synthesis, that is, using pyridine as a base and heating at 140 °C without solvent. However, **1c** was obtained only in an unsatisfactory yield (30%, Run 1 in Table 1). Employment of *N,N*-dimethyl-4-aminopyridine (DMAP), a more basic and nucleophilic catalyst than pyridine, resulted in more efficient formation of **1c** (Run 2). A more remarkable improvement was achieved by elevating reaction temperature to 180 °C (Run 3). In this case, **1c** was formed almost quantitatively. However, isolation of **1c** from the reaction mixture was quite difficult, due to the presence of a large excess amount of chloroacetic anhydride and chloroacetic acid formed by the reaction. To overcome this problem, the amount of chloroacetic anhydride was reduced (Run 4), and furthermore, the reaction was performed under reduced pressure (200 mmHg) to remove chloroacetic acid that formed during the reaction (Run 5). As a result, 1,2,3-propanetricarboxylic acid was converted to **1c** almost quantitatively to isolate of **1c** in 56% yield by crystallization. The structure of **1c** was confirmed by ^{1}H NMR and FTIR spectroscopy. The ^{1}H NMR spectrum of **1c** showed the singlet signal at 3.91 ppm, which was attributable to the methylene proton of the chloromethyl group. A strong IR absorption at 1791 cm^{-1} confirmed the lactone structure of **1c**.

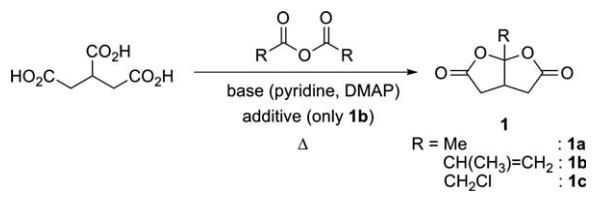
TABLE 1 Synthesis of BBL-Containing Chloromethyl Moiety[a]

Run	Catalyst	Amount of Chloroacetic Anhydride (eq)	Temp. (°C)	Time (h)	Yield (%)[b]
1	Pyridine	9	140	1	– (30[c])
2	DMAP	9	140	1	– (49[c])
3	DMAP	9	180	1	11 (99[c])
4	DMAP	3	180	3	43 (85[c])
5[d]	DMAP	3	180	3	56 (99[c])

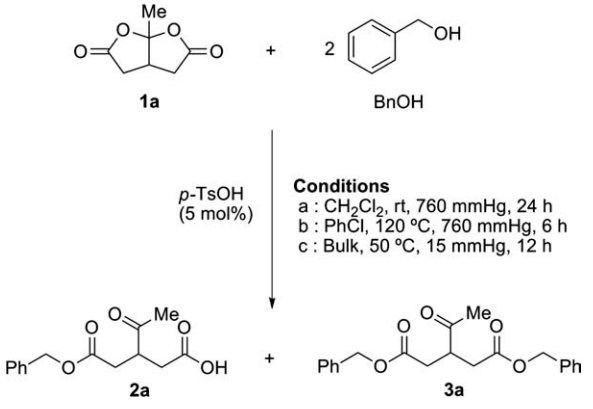
[a] Reaction conditions: Amount of catalyst = 2 mol %, in bulk.
[b] Isolated by crystallization.
[c] NMR-yield.
[d] Under reduced pressure (200 mmHg).

Acid-Promoted Reaction of 1a with BnOH

We carried out a reaction of **1a** with BnOH ([**1a**]$_0$/[BnOH]$_0$ = 1/2) in the presence of 5 mol % of *p*-TsOH as a catalyst in CH_2Cl_2 at rt (Scheme 3). Monitoring the reaction by ^{1}H NMR revealed that the intensity of the signal at 1.8 ppm attributable to the methyl protons of **1a** decreased gradually, implying the ring-opening reaction of **1a** smoothly proceeded. Figure 1 shows the changes of ^{1}H NMR spectra on the reaction.



SCHEME 2 Synthesis of BBLs **1**.



SCHEME 3 Acid-promoted reaction of **1a** and BnOH.

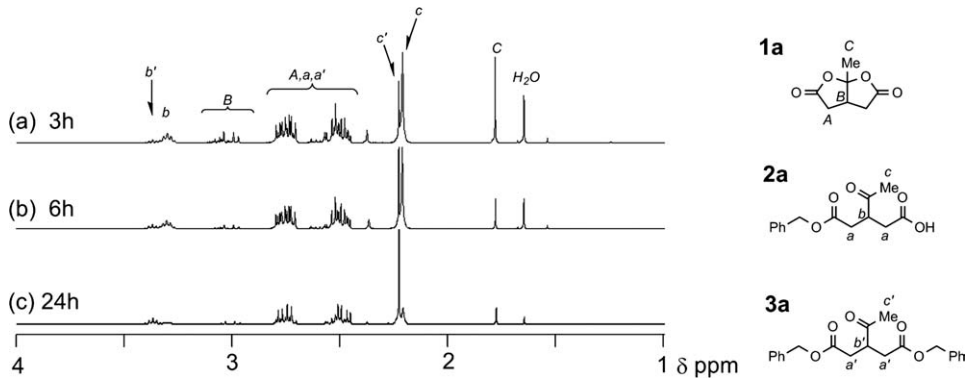


FIGURE 1 ^{1}H NMR of reaction mixture on the acid-promoted reaction of **1a** and BnOH measured at 3 h (a), 6 h (b), and 24 h (c) in $CDCl_3$ at rt.

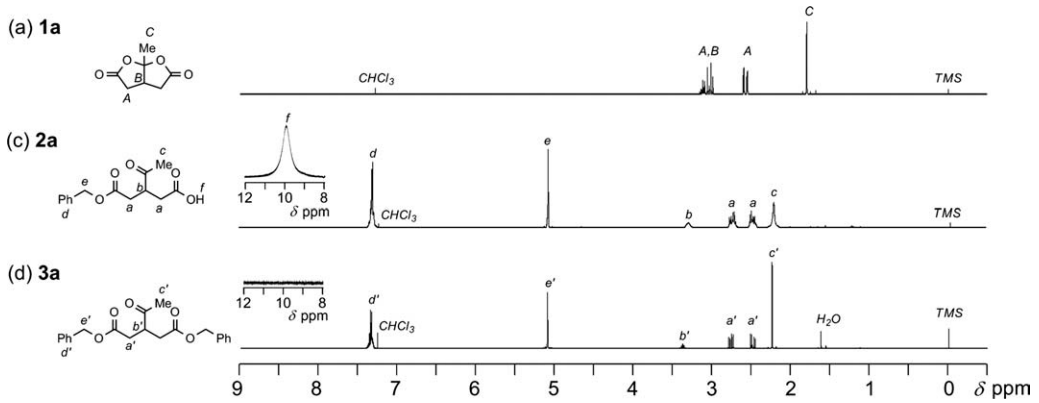


FIGURE 2 ^{1}H NMR spectra of isolated **1a** (a), **2a** (b), and **3a** (c) measured in $CDCl_3$ at rt.

Two signals were observed around 2.2 ppm, which represented the formation of acetyl moiety via the double ring-opening reaction of **1a**. After 24 h, 90% of **1a** was consumed with affording two products, 1:1 adduct **2a** and 1:2 adduct **3a**. These adducts were isolated by silica-gel column chromatography in 37 and 57% yield, respectively.

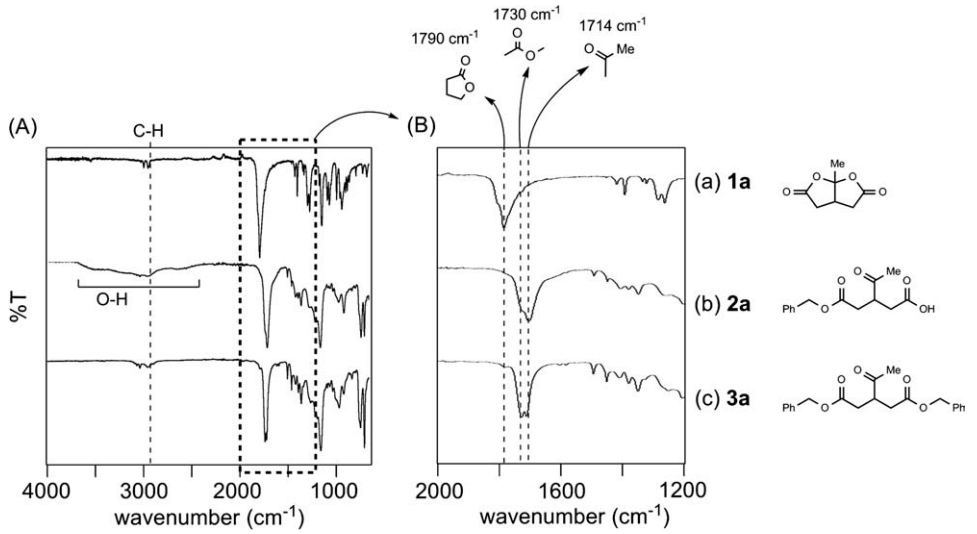


FIGURE 3 FTIR spectra of **1a** (a), **2a** (b), and **3a** (c) measured at rt. The magnified spectra from 1200 to 2000 cm^{-1} are shown in (B).

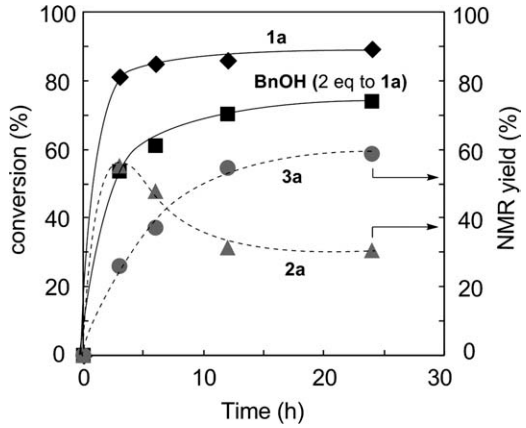


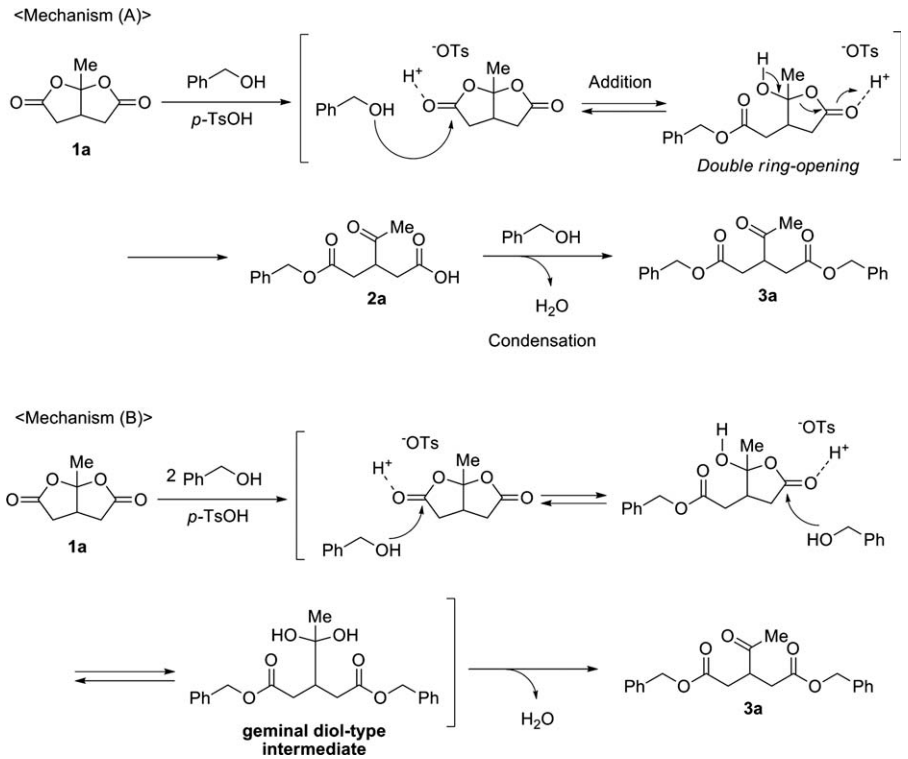
FIGURE 4 Time dependences of conversion of **1a** (—◇—), conversion of BnOH (—□—), yield of 1:1 adduct **2a** (---Δ---), and yield of 1:2 adduct **3a** (---○---) in the acid-promoted reaction of **1a** and BnOH monitored by ^{1}H NMR.

Figure 2(b) shows the ^{1}H NMR spectrum of isolated **2a**. The spectrum showed singlet signals at 2.2 and 5.1 ppm, which were attributable to the methyl protons of the acetyl group and the methylene protons of the benzyl group, respectively. The ratio of their intensities was 3:2, to confirm **2a** was a 1:1 adduct of **1a** and benzyl alcohol. Besides, a broad signal was observed at 10.0 ppm to confirm the presence of the carboxyl group. Interestingly, the signal of acetyl protons of **2a** was broad to suggest that conformation of the acetyl group would be restricted by an intramolecular hydrogen-bonding between carboxyl and ketone moieties. Figure 3(b) shows the FTIR spectrum of isolated **2a**. The carbonyl peaks at 1730 and 1714 cm^{-1}, which attributed to ester and ketone moieties, were observed with no signals of lactone carbonyl at 1790 cm^{-1}. A carbonyl peak of carboxylic acid moiety could not be clearly observed because of its overlapping with the carbonyl peaks of ester and ketone moieties.

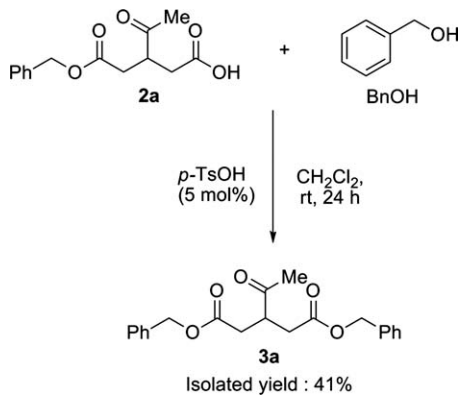
The ^{1}H NMR spectrum of **3a** is shown in Figure 2(c). The spectrum pattern of **3a** was quite similar to that of **2a**, while no signal was observed at 10.0 ppm. Integral ratio between the signal of benzyl proton at 5.1 ppm and that of acetyl group at 2.2 ppm was 4:3, indicating that **3a** contained two benzyl ester moieties. FTIR spectrum of **3a** showed carbonyl peaks at 1730 and 1714 cm^{-1}, which were attributed to the ester and ketone moieties [Fig. 3(c)].

Figure 4 shows the time dependences of (1) conversion of **1a**, (2) conversion of BnOH, (3) yield of 1:1 adduct **2a**, and (4) yield of 1:2 adduct **3a** in the reaction of **1a** and BnOH monitored by ^{1}H NMR. Within 3 h, 80% of **1a** was consumed, and accordingly, **2a** and **3a** were afforded in 55 and 26%, respectively. After that, conversion of **1a** reached a plateau, whereas the conversion of BnOH increased continuously until 12 h. Accordingly, conversion of **2a** gradually increased in parallel with the increase in the amount of **3a**.

These observations made us postulate a reaction mechanism (A) that involves the following steps (Scheme 4): (1) Nucleophilic attack of benzyl alcohol to the activated **1a** by protonation, (2) successive double ring-opening reaction of **1a** to afford the 1:1 adduct **2a**, and (3) condensation of the carboxyl moiety of **2a** with BnOH to afford the 1:2 adduct **3a**.



SCHEME 4 Plausible mechanisms for formation of **3a** through the acid-promoted reaction of **1a** and benzyl alcohol.



SCHEME 5 Condensation reaction of **2a** and BnOH.

The predominance of this mechanism was confirmed by the fact that the isolated **2a** reacted slowly with BnOH in the presence of *p*-TsOH to give **3a** in 41% yield (Scheme 5).

On the other hand, it is still possible to postulate another mechanism (B), which does not involve the formation of **2a** as an intermediate (Scheme 4). The reaction steps that compose this mechanism are: (1) Simultaneous nucleophilic attack of two BnOH molecules to **1a** activated by protonation, (2) subsequent ring-opening reactions of both the two lactone rings to form a germinal diol, and (3) elimination of water from the geminal diol to give a ketone moiety.

The fact that the reaction of **1a** with two equivalent amount of BnOH afforded the 1:2 adduct **3a** demonstrated the potential of **1a** as a bifunctional monomer for polyester synthesis. However, the efficiency was still unsatisfactory if one considers the possibility to apply this reaction to polyester synthesis with replacing BnOH (2.0 eq) by diol (1.0 eq). First, we attempted to improve the efficiency by elevating the reaction temperature. For this purpose, chlorobenzene (PhCl) was used as a solvent with less volatility. The reaction was performed at 120 °C with monitoring conversions of **1a** and BnOH by ^{1}H NMR. As a result, as being clarified by the resulting time-conversion relationships [Fig. 5(A)], both the reactants were consumed much more rapidly, leading to 95% conversions of them within 1 h. The corresponding 1:2 adduct **3a** was isolated in 88% yield by silica-gel column chromatography. Another efficient way to improve the reaction efficiency was performing the reaction under a reduced pressure to remove water that formed by the condensation reaction of **2a** and BnOH. When the reaction was performed in bulk under 15 mmHg, it proceeded smoothly at 50 °C [Fig. 5(B)]. These results suggested that the reaction could be also accelerated by effective removal of eliminated H_2O, which were in good agreement with the postulated mechanisms described above.

Synthesis of Polyester Using BBLs 1 as Bifunctional Monomers

We performed a reaction of **1a** and xylene-α,α-diol (XyD) using 5 mol % of *p*-TsOH as a catalyst (Scheme 6). The reaction conditions and the corresponding results are summarized in Table 2. When the reaction was carried out in CH_2Cl_2 at rt for 48 h, the conversion of **1a** reached 68%, which allowed only the formation of oligomers (Run 1). Elevating the reaction temperature to 40 °C brought no significant improvement (Run 2), while elevating the temperature to 80 °C with using PhCl as a solvent resulted in a much higher conversion of **1a**. Accordingly, the corresponding polymer **4a** isolable as a methanol-insoluble fraction was obtained in 59% (Run 3). Furthermore, by elevating the temperature to 120 °C, **4a** was obtained in a higher yield within a shorter reaction time (Run 4). Figure 6(a) shows the ^{1}H NMR spectrum of **4a**. Signals of acetyl and benzyl protons in the polymer side and main chains were observed at 2.2 and 5.1 ppm. The structure of **4a** was also confirmed by means of FTIR spectroscopy [Fig. 7(a)]. Two peaks were observed at 1728 and 1712 cm^{-1}, which were attributed to carbonyl of ester in the main chain and ketone in the side chain, respectively. These results revealed that polyester having ketone group in the side chain was obtained by the reaction of **1a** and XyD through the ring-opening reaction of **1a**, and the successive condensation of the resulting carboxylic group with hydroxyl group of XyD or the chain ends of the

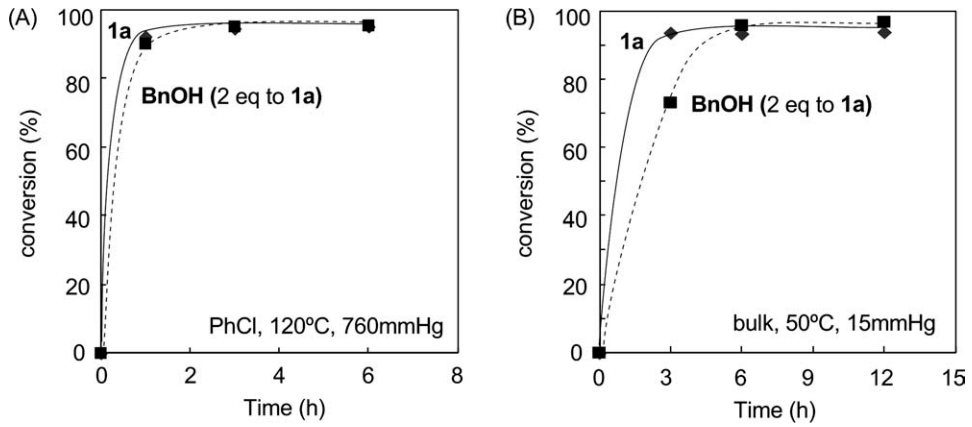
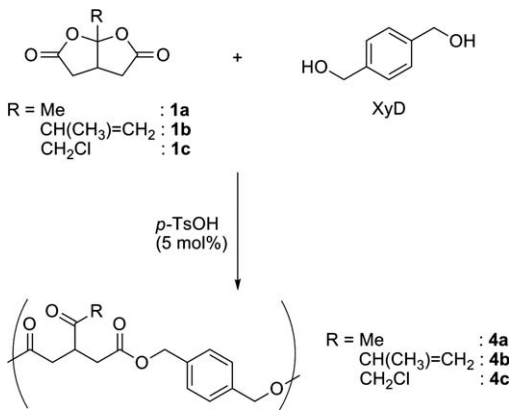


FIGURE 5 Time-conversion curves of **1a** (—◇—) and BnOH (---□---) on the reaction performed in PhCl at 120 °C under ordinary pressure (760 mmHg) (A), and at 50 °C without solvent under reduced pressure (15 mmHg) (B). The conversions were determined by ^{1}H NMR.



SCHEME 6 Acid-promoted reaction of **1** and XyD in the presence of *p*-TsOH.

propagating polymer. More effective formation of **4a** was achieved by conducting the reaction at 80 °C under reduced pressure (15 mmHg) without solvent (Table 2, Run 5).[26] The conversion of **1a** reached 94% within 3 h, to afford **4a** in 90% yield. M_n and M_w/M_n of the obtained polymer were 3.4 $\times$ 10^3 g/mol and 1.6, respectively. These results indicated that the effective removal of H_2O under reduced pressure was important for the effective formation of polyester **4a** as was observed in the reaction of **1a** and BnOH.

The other BBLs, **1b** and **1c** bearing reactive groups, were similarly utilized for polyester synthesis (Scheme 6). Reaction of **1b** and XyD was carried out at 80 °C under reduced pressure (15 mmHg) without solvent for 3 h (Table 2, Run 6). The reaction proceeded almost quantitatively, and the corresponding polyester **4b** was obtained in 79% yield. Figure 6(b) shows the ^{1}H NMR spectrum of **4b**. Some of the signals were identical with these observed in the ^{1}H NMR spectrum of **4a**, to imply these bears the same main chain. The presence of methacryloyl moieties in the side chains was confirmed by the signals at 5.8 and 6.1 ppm. In the FTIR spectrum of **4b** [Fig. 7(b)], the characteristic carbonyl peaks attributed to ester and methacryloyl moieties were observed at 1728 and 1674 cm^{-1}, respectively.

The reaction of **1c** and XyD under the same conditions gave the corresponding polyester **4c** (Table 2, Run 7). The structure of **4c** was confirmed by ^{1}H NMR spectroscopy [Fig. 6(c)]. The characteristic signal for the methylene protons of chloroacetyl group, which formed via double ring-opening reaction of **1c**, was observed at 4.44 ppm. The FTIR spectrum of **4c** showed a strong peak at 1723 cm^{-1} in which

TABLE 2 Addition Condensation of 1 with XyD in the Presence of *p*-TsOH as a Catalyst[a]

Run	Monomer	Solvent	Temp. (°C)	Pressure (mmHg)	Time (h)	Conv. (%)[b]	Yield (%)[c]	$M_n \times 10^{-3}$ (M_w/M_n)[d]
1	**1a**	CH_2Cl_2	rt	760	48	68	–	0.6 (1.4)
2	**1a**	CH_2Cl_2	40	760	48	78	–	0.7 (1.5)
3	**1a**	PhCl	80	760	48	94	59	3.0 (1.6)
4	**1a**	PhCl	120	760	18	88	88	3.5 (1.9)
5	**1a**	–	80	15	3	94	90	3.4 (1.6)
6	**1b**	–	80	15	3	99	79	5.0 (8.9)
7	**1c**	–	80	15	3	91	73	3.5 (2.1)

[a] Polymerization conditions: [*p*-TsOH] = 5 mol %, [**1**]/[XyD] = 1.
[b] Determined by ^{1}H NMR signals based on bislactone.
[c] Methanol-insoluble part.
[d] Estimated by GPC (eluent = THF, polystyrene standards).

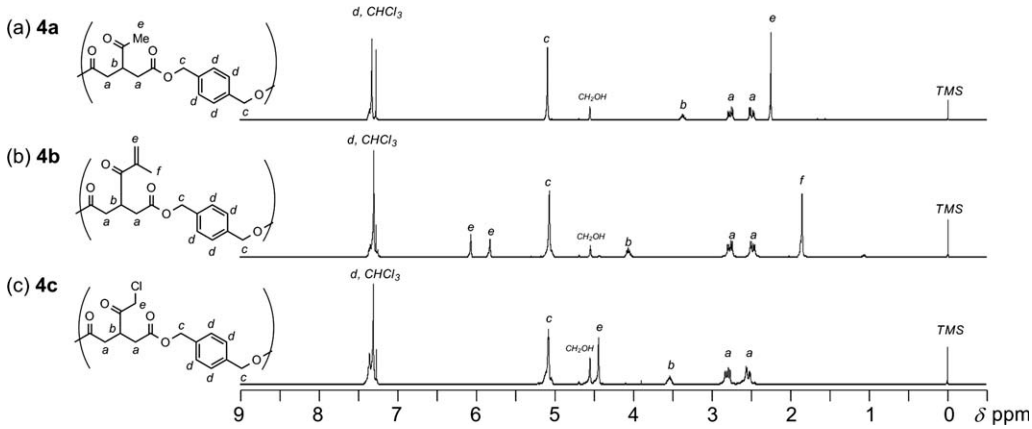


FIGURE 6 ^{1}H NMR spectra of **4a** (a), **4b** (b), and **4c** (c) measured in $CDCl_3$ at rt.

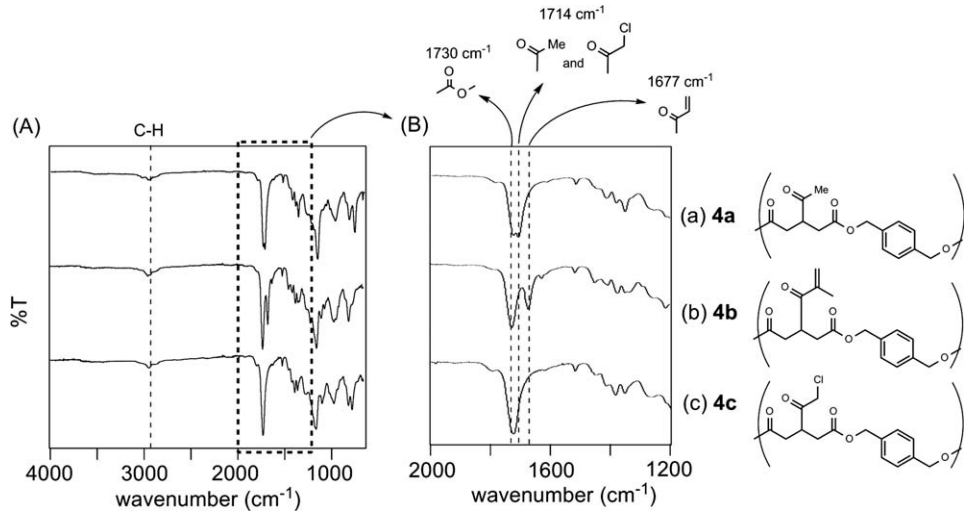


FIGURE 7 FTIR spectra of **4a** (a), **4b** (b), and **4c** (c) measured at rt. The magnified spectra from 1200 to 2000 cm^{-1} are shown in (B).

two absorptions for the main chain ester and side chain ketone would be superimposed [Fig. 7(c)].

CONCLUSION

We developed a novel synthetic approach to polyesters bearing ketone moiety in the side chain based on utilization of BBLs as potential bifunctional monomers that can react with diols. The process of the polyester formation involved (1) nucleophilic attack of alcohol to BBLs activated by acid, (2) successive double ring-opening reaction of BBLs with linking BBLs and alcohols thorough ester formation, and (3) condensation of the BBL-alcohol adducts bearing carboxylic acid with alcohol to form another ester linkage with releasing water. Employment of BBLs bearing functional groups such as isopropenyl and chloromethyl groups in this novel polyester synthesis afforded the corresponding functional polyesters bearing methacryloyl and chloroacetyl pendants, respectively. The structural diversity of BBLs as well as that of diols will give us opportunity to design and synthesize a wide variety of functional polyesters.

EXPERIMENTAL

Materials

1,2,3-Propanetricarboxylic acid (98%), DMAP (99%), trifluoroacetic acid (TFA) (99%), and trifluoromethane sulfonic acid (TfOH) (99%) were purchased from Tokyo Kasei (TCI, Tokyo Japan). Chloroacetic anhydride (95%) was purchased from Aldrich. *p*-Toluenesulfonic acid monohydride (*p*-TsOH) (99%), benzylalcohol (BnOH) (99%), chloroacetic acid (98%), xylene-α,α'-diol (99%), chlorobenzene (99%), and dichloromethane (99%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Chlorobenzene (PhCl) and dichloromethane (CH_2Cl_2) were dried over calcium hydride and distilled under nitrogen before use. 2,8-Dioxa-1-methylbicyclo[3.3.0]octane-3,7-dione (**1a**) and 2,8-dioxa-1-isopropenylbicyclo[3.3.0]octane-3,7-dione (**1b**) were prepared according to the previously reported methods (Scheme 2).[13–16]

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, respectively, with tetramethylsilane as an internal standard). IR spectra were recorded 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 an eluent at a flow rate of 0.6 mL/min at 40 °C, performed on a Tosoh chromatograph model HLC-8320 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–visible detector (254 nm). The molecular weight calibration curve was obtained with polystyrene standards.

Synthesis of 2,8-Dioxa-1-chloromethylbicyclo[3.3.0]octane-3,7-dione (1c)

The reaction is depicted in Scheme 2. A mixture of 1,2,3-propanetricarboxylic acid (16 g, 91 mmol), DMAP (2.2 g, 18 mmol), and chloroacetic anhydride (47 g, 0.27 mol) was stirred at 180 °C under reduced pressure (200 mmHg). After 3 h, chloroacetic acid was removed at 100 °C under reduced pressure (0.04 mmHg). To the residue, 500 mL of ethyl acetate was added and the resulting precipitates were filter off. The filtrate was washed with saturated aqueous solution of $NaHCO_3$. The organic layer was then dried over anhydrous $MgSO_4$, treated with active charcoal, and filtered off. The solution was evaporated under reduced pressure, and the residual solid was recrystallized from 200 mL of toluene two times to afford **1c** (9.7 g, 51 mmol; 56%) as a colorless crystal.

Spectroscopic Data of Obtained 1c

IR (neat): 3027 (C—H), 2962 (C—H), 1791 (C=O), 1012 (C—Cl) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.61 (q, 2H, OC(=O)—CH_2—CH), 3.15 (q, 2H, OC(=O)—CH_2—CH), 3.42 (m, 1H, CH_2—C*H*(—C)—CH_2), 3.91 (s, 2H, C—CH_2Cl). ^{13}C NMR

($CDCl_3$, 100 MHz): δ 36.1 (C(=O)—*C*H_2—CH, CH_2—*C*H(—C)—CH_2), 45.7 (C—*C*H_2Cl), 111.6 (O—*C*—O), 171.8 (CH_2—*C*(=O)—O). Anal. Calcd for $C_7H_7O_4Cl$: C, 44.12; H, 3.70. Found: C, 43.80; H, 4.00.

Reaction of 1a and BnOH

The reaction is depicted in Scheme 3. Compound **1a** (600 mg, 3.84 mmol), BnOH (0.2 mL, 7.68 mmol), *p*-TsOH (33 mg, 0.19 mmol), and 4.8 mL of CH_2Cl_2 was stirred at rt. After 24 h, the solvent was removed under reduced pressure. The resulting residue was fractionated by silica gel chromatography (eluent : chloroform/ethyl acetate = 5/1) to afford the corresponding 1 : 1 adduct **2a** (501 mg, 1.29 mmol; 37%) and the corresponding 1 : 2 adduct **3a** (777 mg, 1.98 mmol; 57%) as colorless viscous oils.

Spectroscopic Data of 2a

IR (neat): 3600–2300 (O—H), 3033 (C—H), 1730 [C=O (ester)], 1708 [C=O (ketone)] cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 3H, C*H*$_3$), 2.50 (m, 2H, C*H*$_2$COO), 2.76 (m, 2H, C*H*$_2$COO), 3.33 (br, 1H, C*H*), 5.12 (s, 2H, C*H*$_2$OCO), 7.37 (m, 5H, Ph), 9.99 (br, 1H, COO*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.2 (*C*H$_3$—C), 34.9 (CH—*C*H$_2$—C(=O)OH), 35.2 (CH—*C*H$_2$—C(=O)O), 43.7 (CH_2—*C*H(—C)—CH_2), 66.9 (COO—*C*H$_2$—Ph), 128.4 (Ph), 128.5 (Ph), 128.7 (Ph), 135.4 (Ph), 171.3 (CH_2—*C*(=O)—O—CH_2), 177.3 (CH_2—*C*(=O)—OH), 208.9 (CH_3—*C*(=O)—CH). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.34; H, 6.11.

Spectroscopic Data of 3a

IR (neat): 3033 (C—H), 2953 (C—H), 1730 [C=O (ester)], 1714 [C=O (ketone)] cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 3H, C*H*$_3$), 2.50 (q, 2H, C*H*$_2$COO), 2.75 (q, 2H, C*H*$_2$COO), 3.36 (m, 1H, C*H*), 5.10 (s, 4H, C*H*$_2$OCO), 7.35 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 29.4 (*C*H$_3$—C), 35.4 (CH—*C*H$_2$—C(=O)O), 44.0 (CH_2—*C*H(—C)—CH_2), 66.9 (COO—*C*H$_2$—Ph), 128.4 (Ph), 128.5 (Ph), 128.7 (Ph), 135.6 (Ph), 171.4 (CH_2—*C*(=O)—O—CH_2), 209.1 (CH_3—*C*(=O)—CH). Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.08; H, 6.32.

Reaction of 2a and BnOH

The reaction is depicted in Scheme 5. Compound **2a** (119 mg, 0.45 mmol), BnOH (49 mg, 0.45 mmol), *p*-TsOH (3.9 mg, 0.02 mmol), and 0.56 mL of CH_2Cl_2 was stirred at rt. After 24 h, the solvent was removed under reduced pressure. The resulting residue was purified by silica gel chromatography (eluent:chloroform/ethyl acetate = 5/1) to afford **3a** (66 mg, 0.18 mmol; 41%) as a colorless viscous oil.

Reaction of 1 and XyD

The reaction is depicted in Scheme 6. A typical procedure: **1a** (156 mg, 1.00 mmol), XyD (138 mL, 1.00 mmol), and *p*-TsOH (9.9 mg, 0.05 mmol) were stirred at 80 °C under reduced pressure (15 mmHg). After 3 h, the resulting mixture was dissolved in 2 mL of chloroform and poured into 50 mL of methanol. The resulting copolymer was collected by centrifugation, washed with methanol, and dried *in vacuo* to afford **4a** (264 mg, 94%) as a viscous oil. M_n and M_w/M_n of **4a** were 3.4×10^3 g/mol and 1.6, respectively.

Spectroscopic Data of 4a

IR (neat): 3033 (C—H), 1728 [C=O (ester)], 1712 [C=O (ketone)] cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 3H, C*H*$_3$—C(=O)—CH), 2.52 (m, 2H, CH—C*H*$_2$—COO), 2.76 (m, 2H, CH—C*H*$_2$—C(=O)—O), 3.38 (br, 1H, CH_2—C*H*(—C)—CH_2), 5.09 (br, 4H, C(=O)—O—C*H*$_2$— Ar), 7.32 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.3 (*C*H$_3$—C(=O)CH), 35.3 (CH—*C*H$_2$—C(=O)O), 44.0 (CH_2—*C*H(—C)—CH_2), 66.4 (COO—*C*H$_2$—Ar), 128.6 (Ar), 135.8 (Ar), 171.3 (CH_2—*C*(=O)—O—CH_2), 208.9 (CH_3—*C*(=O)—CH).

Compounds **4b** and **4c** were synthesized according to the same procedure for **4a** using **1b** and **1c** as a starting material, respectively.

Spectroscopic Data of 4b

IR (neat): 2956 (C—H), 1728 [C=O (ester)], 1674 [C=O (ketone)] cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.85 (s, 3H, C*H*$_3$—C(—C)=C*H*$_2$), 2.48 (m, 2H, CH—C*H*$_2$—COO), 2.77 (m, 2H, CH—C*H*$_2$—COO), 4.06 (br, 1H, CH_2—C*H*(—C)—CH_2), 5.06 (br, 4H, C(=O)—O—C*H*$_2$—Ar), 5.82 (s, 1H, C=C*H*$_2$), 6.06 (s, 1H, C=C*H*$_2$), 7.30 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.0 (*C*H$_3$—C(—C)=CH_2), 36.2 (CH—*C*H$_2$—C(=O)O), 37.8 (CH_2—*C*H(—C)—CH_2), 66.4 (COO—*C*H$_2$—Ar), 125.7 (CH_3—C=*C*H$_2$), 128.6 (Ar), 135.8 (Ar), 143.2 (CH_3—*C*=CH_2), 171.3 (CH_2—*C*(=O)—O—CH_2), 202.3(H_2C=C—*C*(=O)—CH).

Spectroscopic Data of 4c

IR (neat): 2943 (C—H), 1723 [C=O (ester and ketone)] cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.53 (m, 2H, CH—C*H*$_2$—COO), 2.79 (m, 2H, CH—C*H*$_2$—COO), 3.53 (br, 1H, CH_2—C*H*(—C)—CH_2), 4.44 (s, 2H, C(=O)—C*H*$_2$Cl), 5.08 (br, 4H, C(=O)—O—C*H*$_2$—Ar), 7.31 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.3 (Cl*C*H$_2$—C), 40.3 (CH—*C*H$_2$—C(=O)O), 49.3 (CH_2—*C*H(—C)—CH_2), 66.6 (COO—*C*H$_2$—Ar), 128.6 (Ar), 135.7 (Ar), 171.0 (CH_2—*C*(=O)—O—CH_2), 204.0 (ClCH_2—*C*(=O)—CH).

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26 While the reaction of **1a** and BnOH was performed at 50 °C under 15 mmHg because of the boiling point of BnOH, we carried out the reaction with XyD at 80 °C under 15 mmHg to accelerate the reaction.