

Synthesis of Poly(ether)s with Pendant Ester Groups by the Polyaddition of Bis(oxetane)s with Active Bis(ester)s

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ABSTRACT: Polyadditions of certain bis(oxetane)s such as 1,4-bis[(3-ethyl-3-oxetanylmethoxymethyl)]benzene (BEOB), 1,4-bis[(3-ethyl-3-oxetanyl)methoxy]benzene (1,4-BEOMB), 4,4'-bis[(3-ethyl-3-oxetanyl)methoxy]benzene (4,4'-BEOBP), 2,2'-bis[(3-ethyl-3-oxetanyl)methoxy]biphenyl (2,2'-BEOBP), 3,3',5,5'-tetramethyl-[4,4'-bis(3-ethyl-3-oxetanyl)methoxy]biphenyl (TM-BEOBP) with such active bis(ester)s as 4,4'-isopropylidenebis(2,6-dichlorophenyl diacetate) (IBDPA), 4,4'-isopropylidene-bis(2,6-dichlorophenyl dibenzoate) (IBDPB) and 4,4'-isopropylidenebis(2,6-dichlorophenyl di-2,4-dichlorobenzate) (IBDPD) were examined in the presence of tetraphenylphosphonium chloride (TPPC) as a catalyst in DMAc at 160 °C for 96 h, and it was found that corresponding polyethers with M_n s in the range 7200–17400 were obtained in 91–99% yields. The all obtained polymers would soluble in common organic solvents. [DOI 10.1295/polymj.36.841]

KEY WORDS Polyaddition / Bis(oxetane) / Active Bis(ester) / Synthesis of Poly(ether) / Pendant Ester Group / Catalyst /

It is well known that epoxy compounds have high chemical reactivity to many organic reagents^{1–4} such as amines, phenols, thiols, carboxylic acids, acyl halides, aryl esters, and thioesters, carbon dioxide as well as cationic catalysts^{5–7} and anionic catalysts^{8–10} due to the high strain energy. Therefore, epoxy resins and polymers with pendant epoxide groups have been used^{1,2} as starting materials for the synthesis of functional polymers by the addition reaction of the epoxide groups with carboxylic acids, phenols, or amines. The above reaction systems of the epoxy resins and the polymers containing epoxide groups have also been applied as an important key technology in such industries as coatings, paintings, elastomers, adhesions, and electronics.

Meanwhile, oxetanes as 4-membered cyclic ether have the mostly same strain energy¹¹ (107 kJ/mol) as oxiranes. However, we could not found useful reactions of oxetanes in the synthetic organic chemistry or in the polymer synthesis excepting old cationic ring-opening polymerization,¹² and of recent cationic isomerization by Motoi and co-workers.^{13–15}

Therefore, the authors have been of great interest to develop new reactions of oxetanes, and found certain new addition reactions of oxetanes with carboxylic acids,¹⁶ phenols,^{17,18} and thiophenols,¹⁹ using quaternary onium salts or crown ether complexes as catalysts. Since these addition reactions proceed smoothly without any side reactions even at higher temperatures than those of the reaction of oxiranes, the reactions can be used as suitable reaction for the polymer syn-

thesis. More recently, our research group found anionic ring-opening alternating copolymerization²⁰ of oxetane with carboxylic anhydride, and anionic ring-opening polymerization^{21–23} of 3-ethyl-3-hydroxymethyl oxetane. However, we do not have development of the addition reaction of oxetanes with phenyl esters until now, although we have found the addition reactions of oxetane with acyl chloride^{15–24} or *S*-aryl thioesters.^{26,27}

From these backgrounds, in this article, we examined the polyaddition of bis(oxetane)s with active bis(ester)s, which were prepared by the reaction of bis(phenol)s with carboxylic acid derivatives, for the synthesis of poly(ether)s containing pendant ester groups under appropriate reaction conditions.

EXPERIMENTAL

Materials

The reaction solvents, such as *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), methylethylketone (MEK), and tetrahydrofuran (THF) were dried with P₂O₅, or CaH₂, and purified by distillation before use. Reagent grade tetrabutylphosphonium bromide (TBPB), tetrabutylphosphonium chloride (TBPC), tetraphenylphosphonium chloride (TPPC), tetraphenylphosphonium bromide (TPPB), 18-crown-6 ether (18-C-6), potassium chloride (KCl), potassium bromide (KBr), cesium fluoride (CsF), cesium chloride (CsCl), cesium bromide (CsBr), potassium *tert*-butoxide (*t*-BuOK), and potassium phenoxide (PhOK) were dried

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in vacuo, and used without further purification. Commercial 4,4'-isopropylidenebis(2,6-dichlorophenol) (IBDP), acetyl chloride, benzoyl chloride, 2,4-dichlorobenzoyl chloride, and triethylamine (TEA) were used without further purification. Commercial 4,4'-isopropylidenebisphenyl diacetate (BPAA) was recrystallized twice from methanol. Bis(oxetane)s, 1,4-bis[(3-ethyl-3-oxetanyl)methoxymethyl]benzene (BEOB), 1,4-bis[(3-ethyl-3-oxetanyl)methoxy]benzene (1,4-BEOMB), 4,4'-bis[(3-ethyl-3-oxetanyl)methoxy]benzene (4,4'-BEOBP), 2,2'-bis[(3-ethyl-3-oxetanyl)methoxy]biphenyl (2,2'-BEOBP), 3,3',5,5'-tetramethyl-[4,4'-bis(3-ethyl-3-oxetanyl)methoxy]biphenyl (TM-BEOBP) were donated from Toagosei Co., Ltd. and were purified by recrystallization from appropriate solvents. 4,4'-Isopropylidenebisphenyl diacetate (BPAA) was recrystallized twice from methanol.

Measurement

Melting points were determined with a Yanako MP-500D hot-stage microscope. Infrared (IR) absorption spectra were measured on a Jasco model FT/IR-420 spectrometer. The NMR spectra were recorded on JNM FX-200 (200 MHz for ^1H NMR and 50 MHz for ^{13}C NMR) or JNM α -500 (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) in CDCl_3 with Me_4Si (TMS) as an internal standard. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated by size exclusion chromatography (SEC; TOSOH model HLC-8020) on TSK gel Multipore Hxl-M columns calibrated by narrow molecular weight polystyrene standards and with tetrahydrofuran (THF) as an eluent without correction using a refractive index detector.

Synthesis of Active Bis(ester)

A typical procedure for the synthesis of active bis(ester) 4,4'-isopropylidenebis-(2,6-dichlorophenyl diacetate) (IBDPA) is as follows. Acetyl chloride (12.8 mL, 180 mmol) in THF (50 mL) was added slowly to the solution of IBDP (28.48 g, 80 mmol) and TEA (30 mL, 216 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 8 h. The resulting mixture was poured into water to remove reaction solvent, TEA, and TEA salts. The precipitated solid product was filtered, washed with water and dried *in vacuo*. The obtained product was purified by the recrystallization from the mixed solvent of MEK/hexane ($v/v = 5/2$) to obtain a colorless solid IBDPA; yield 56%; mp = 136.8–137.2 °C. IR (KBr): 1772 (ν C=O of ester), 1468 (ν C=C of aromatic), 1187 cm^{-1} (ν C–O–C). ^1H NMR (200 MHz, CDCl_3 , TMS) $\delta = 1.64$ (s, 6.0H, CH_3), 2.39 (s, 6.0H, CO– CH_3), 7.18 ppm (s, 4.0H, aromatic H).

^{13}C NMR (50 MHz, CDCl_3 , TMS) $\delta = 20.22$ ($\underline{\text{C}}\text{H}_3$ –CO), 30.38 ($\underline{\text{C}}\text{H}_3$), 42.85 (–C–), 127.00, 128.67, 142.30, 148.56 (aromatic C), 167.33 ppm ($\underline{\text{C}}=\text{O}$). *Elem. Anal.* Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_4\text{Cl}_4$: C, 50.70%; H, 3.58%. Found: C, 50.60%; H, 3.31%.

4,4'-Isopropylidenebis-(2,6-dichlorophenyl dibenzoate) (IBDPB)

Yield = 45%. Mp = 203.6–204.1 °C. IR (KBr): 1750 (ν C=O of ester), 1469 (ν C=C of aromatic), 1242 cm^{-1} (ν C–O–C), 809 cm^{-1} (ν C–Cl). ^1H NMR (200 MHz, CDCl_3 , TMS) $\delta = 1.57$ (s, 6.0H, CH_3), 7.26 (s, 4.0H, aromatic H in bisphenol), 7.48–7.79 (m, 6.0H, aromatic H in benzoate), 8.29 ppm (d, $J = 6.8$ Hz, 4.0H, aromatic H in benzoate). ^{13}C NMR (50 MHz, CDCl_3 , TMS) $\delta = 30.44$ ($\underline{\text{C}}\text{H}_3$), 42.97 (–C–), 127.06, 128.19, 128.70, 128.95, 129.63, 130.53, 134.09, 148.71 (aromatic C), 163.18 ppm ($\underline{\text{C}}=\text{O}$). *Elem. Anal.* Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{Cl}_4$: C, 60.65%; H, 3.51%. Found: C, 60.48%; H, 3.22%.

4,4'-Isopropylidenebis-(2,6-dichlorophenyl di-2,4-dichlorobenzoate) (IBDPD)

Yield = 56%. Mp = 189.4–189.9 °C. IR (KBr): 1775 (ν C=O of ester), 1473 (ν C=C of aromatic), 1234 cm^{-1} (ν C–O–C), 810 cm^{-1} (ν C–Cl). ^1H NMR (200 MHz, CDCl_3 , TMS) $\delta = 1.69$ (s, 6.0H, CH_3), 7.26 (s, 4.0H, aromatic H in bisphenol), 7.42 (dd, $J_{bc} = 2.0$ Hz, $J_{bd} = 8.3$ Hz, 2.0H, aromatic H in 2,4-dichlorobenzoate), 7.58 (d, $J_{cb} = 2.0$ Hz, 2.0H, aromatic H in 2,4-dichlorobenzoate), 8.16 ppm (d, $J_{db} = 8.3$ Hz, 2.0H, aromatic H in 2,4-dichlorobenzoate). ^{13}C NMR (50 MHz, CDCl_3 , TMS) $\delta = 30.39$ ($\underline{\text{C}}\text{H}_3$), 43.03 (–C–), 126.06, 127.14, 127.29, 127.43, 128.84, 131.47, 133.48, 136.28, 139.76, 149.02 (aromatic C), 160.76 ppm ($\underline{\text{C}}=\text{O}$). *Elem. Anal.* Calcd for $\text{C}_{29}\text{H}_{16}\text{O}_4\text{Cl}_8$: C, 48.92%; H, 2.27%. Found: C, 49.12%; H, 2.03%.

Polyaddition of Bis(oxetane)s with Active Bis(ester)s

A typical procedure for the polyaddition of BEOB with IBDPA is as follows: BEOB (0.334 g; 1.0 mmol), IBDPA (0.450 g; 1.0 mmol), TPPB (0.021 g; 0.05 mmol), and DMAc (0.3 mL) were charged to a glass tube in a dry box, after which the tube was evacuated and sealed using a gas torch. The reaction was performed at 160 °C for 96 h in the sealed tube under stirring, and the tube opened. The resulting solution was diluted with a small amount of CHCl_3 and poured into methanol (100 mL) to precipitate the polymer. The resulting polymer was precipitated twice from CHCl_3 into excess methanol, and dried *in vacuo* at 60 °C for 24 h. The yield of poly(BEOB–IBDPA) was 0.737 g (94%). The number-average molecular weight (M_n) of the polymer estimated by SEC was 7200

($M_w/M_n = 1.67$). IR (film): 1740 (ν C=O, ester), 1472 (ν C=C of aromatic), 1274 (ν C=O, ester), 1098 (ν C–O–C, ether), 801 cm^{-1} (ν C–Cl). ^1H NMR (500 MHz, CDCl_3 , TMS) $\delta = 0.95$ (t, $J = 7.5$ Hz, 6.0H, CH_2CH_3), 1.57 (s, 6.0H, C– CH_3), 1.63 (q, $J = 7.5$ Hz, 4.0H, CH_2CH_3) 2.02 (s, 6.0H, COCH_3), 3.52–3.56 (m, 4.0H, O– CH_2 –C), 3.96 (s, 4.0H, O– CH_2 –Ar– CH_2 –O), 4.20–4.23 (m, 4.0H, C– CH_2 –O–Ar–O– CH_2 –C), 4.50 (s, 4.0H, C– CH_2 –O–CO), 7.06 (s, 4.0H, aromatic H in bisphenol), 7.28 ppm (s, 4.0H, CH_2 – C_6H_4 – CH_2). ^{13}C NMR (125 MHz, CDCl_3). $\delta = 7.6$ (CH_2CH_3), 20.9 (C– CH_3), 22.7 (CH_2 – CH_3), 30.3 (COCH_3), 42.4 (quaternary carbon in bisphenol unit), 42.7 (quaternary carbon in methylene unit), 64.6 (C– CH_2 –O–bisphenol), 69.8 (C– CH_2 –O– CH_2 –Ar– CH_2 –O– CH_2 –C), 72.8 (C– CH_2 –O–CO), 73.2 (O– CH_2 –Ar– CH_2 –O), 127.3, 127.4, 129.1, 137.8, 146.7, 149.1 (aromatic C), 170.9 ppm (O–CO– CH_3). *Elem. Anal.* Calcd for $\text{C}_{33}\text{H}_{49}\text{O}_8\text{Cl}_4$: C, 59.69%; H, 5.92%. Found: C, 59.67%; H, 5.83%.

Poly(1,4-BEOMB-IBDPA)

Yield = 0.745 (99%). $M_n = 11200$, $M_w/M_n = 1.88$. IR (film): 1743 (ν C=O, ester), 1508 (ν C=C, aromatic), 1127 (ν C–O–C ester), 1034 (ν C–O–C, ether), 801 cm^{-1} (ν C–Cl). ^1H NMR (500 MHz, CDCl_3 , TMS) $\delta = 1.01$ (t, $J = 7.0$ Hz, 6.0H, CH_2 – CH_3), 1.57 (s, 6.0H, C– CH_3), 1.77 (q, $J = 7.0$ Hz, 4.0H, CH_2CH_3) 2.06 (s, 6.0H, COCH_3), 4.00–4.05 (m, 8.0H, Ar–O– CH_2 –C– CH_2 –O–bisphenol unit), 4.30 (s, 4.0H, C– CH_2 –O–CO), 6.84 (s, 4.0H, O– C_6H_4 –O), 7.06 ppm (s, 4.0H, aromatic H in bisphenol). ^{13}C NMR (125 MHz, CDCl_3). $\delta = 7.6$ (CH_2CH_3), 20.9 (C– CH_3), 22.7 (CH_2 – CH_3), 30.3 (COCH_3), 42.4 (quaternary carbon in bisphenol unit), 42.5 (quaternary carbon in methylene unit), 64.3 (C– CH_2 –O–bisphenol), 68.0 (C– CH_2 –O–Ar–O– CH_2 –C), 72.5 (C– CH_2 –O–CO), 115.3, 127.3, 129.1, 146.8, 149.0, 153.3 (aromatic C), 170.9 ppm (O–CO– CH_3). *Elem. Anal.* Calcd for $\text{C}_{37}\text{H}_{42}\text{O}_8\text{Cl}_4$: C, 58.73%; H, 5.61%. Found: C, 58.52%; H, 5.56%.

Poly(4,4'-BEOBP-IBDPA)

Yield = 0.791 (95%). $M_n = 17400$, $M_w/M_n = 1.78$. IR (film): 1742 (ν C=O, ester), 1499 (ν C=C, aromatic), 1237 (ν C–O–C ester), 1038 (ν C–O–C, ether), 801 cm^{-1} (ν C–Cl). ^1H NMR (500 MHz, CDCl_3 , TMS) $\delta = 1.03$ (t, $J = 7.3$ Hz, 6.0H, CH_2 – CH_3), 1.57 (s, 6.0H, C– CH_3), 1.78 (q, $J = 7.3$ Hz, 4.0H, CH_2CH_3) 2.06 (s, 6.0H, COCH_3), 4.08 (s, 4.0H, C– CH_2 –O–biphenyl unit), 4.10 (s, 4.0H, C– CH_2 –O–bisphenol unit), 4.28–4.33 (m, 4.0H, C– CH_2 –O–CO), 6.96 (d, $J = 8.7$ Hz, 4.0H, C_{12}H_4 –O), 7.06 (s, 4.0H, aromatic H in bisphenol), 7.46 ppm (d, $J = 8.7$ Hz, 4.0H, C_{12}H_4 –O). ^{13}C NMR (125

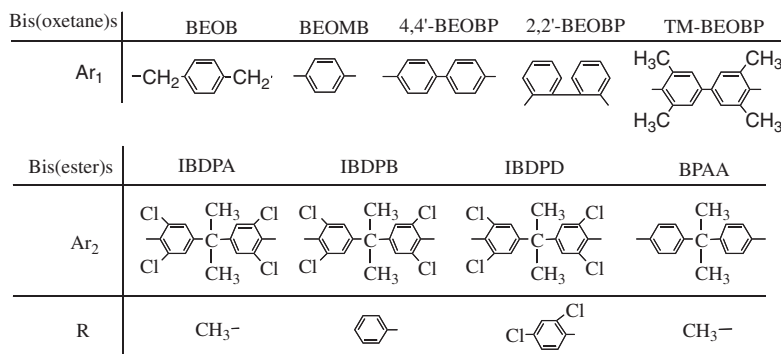
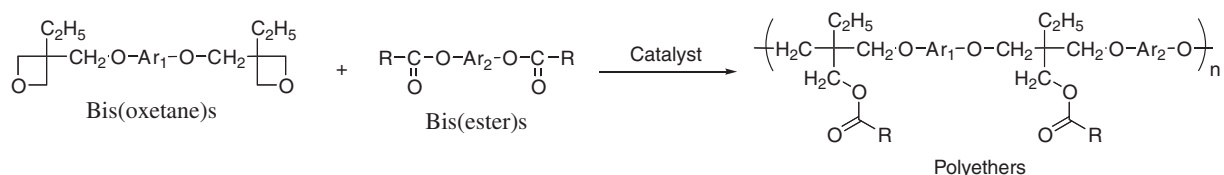
MHz, CDCl_3). $\delta = 7.7$ (CH_2CH_3), 20.9 (C– CH_3), 22.7 (CH_2 – CH_3), 30.3 (COCH_3), 42.4 (quaternary carbon in bisphenol unit), 42.5 (quaternary carbon in methylene unit), 64.3 (C– CH_2 –O–bisphenol), 64.5 (C– CH_2 –O–biphenyl–O– CH_2 –C), 72.4 (C– CH_2 –O–CO), 114.8, 127.3, 127.7, 129.2, 133.6, 146.8, 149.0, 158.1 (aromatic C), 170.9 ppm (O–CO– CH_3). *Elem. Anal.* Calcd for $\text{C}_{42}\text{H}_{46}\text{O}_8\text{Cl}_4$: C, 62.05%; H, 5.57%. Found: C, 62.04%; H, 5.47%.

Poly(2,2'-BEOBP-IBDPA)

Yield = 0.750 (90%). $M_n = 11400$, $M_w/M_n = 1.69$. IR (film): 1742 (ν C=O, ester), 1498 (ν C=C, aromatic), 1236 (ν C–O–C ester), 1034 (ν C–O–C, ether), 801 cm^{-1} (ν C–Cl). ^1H NMR (500 MHz, CDCl_3 , TMS) $\delta = 0.78$ (t, $J = 6.9$ Hz, 6.0H, CH_2 – CH_3), 1.45–1.57 (m, 10.0H, C– CH_3 and CH_2CH_3), 1.98 (s, 6.0H, COCH_3), 3.77 (s, 4.0H, C– CH_2 –O–biphenyl unit), 3.95 (s, 4.0H, C– CH_2 –O–bisphenol unit), 4.06 (s, 4.0H, C– CH_2 –O–CO), 6.87–6.94 (m, 4.0H, C_{12}H_4 –O), 7.04 (s, 4.0H, aromatic H in bisphenol), 7.12–7.21 ppm (d, 4.0H, C_{12}H_4 –O). ^{13}C NMR (125 MHz, CDCl_3). $\delta = 7.5$ (CH_2CH_3), 20.8 (C– CH_3), 22.7 (CH_2 – CH_3), 30.3 (COCH_3), 42.4 (quaternary carbon in bisphenol unit), 42.5 (quaternary carbon in methylene unit), 64.6 (C– CH_2 –O–bisphenol), 68.1 (C– CH_2 –O–biphenyl–O– CH_2 –C), 72.7 (C– CH_2 –O–CO), 112.1, 120.3, 127.2, 128.1, 128.4, 129.1, 131.2, 146.7, 149.0, 156.1 (aromatic C), 170.7 ppm (O–CO– CH_3). *Elem. Anal.* Calcd for $\text{C}_{42}\text{H}_{46}\text{O}_8\text{Cl}_4$: C, 62.05%; H, 5.57%. Found: C, 61.87%; H, 5.49%.

Poly(TM-BEOBP-IBDPA)

Yield = 0.809 (91%). $M_n = 12500$, $M_w/M_n = 1.88$. IR (film): 1739 (ν C=O, ester), 1471 (ν C=C, aromatic), 1234 (ν C–O–C ester), 1022 (ν C–O–C, ether), 800 cm^{-1} (ν C–Cl). ^1H NMR (500 MHz, CDCl_3 , TMS) $\delta = 1.11$ (t, $J = 6.9$ Hz, 6.0H, CH_2 – CH_3), 1.60 (s, 6.0H, C– CH_3), 1.88 (q, $J = 6.9$ Hz, 4.0H, CH_2CH_3), 2.09 (s, 6.0H, COCH_3), 2.32 (s, 12.0H, Ar– CH_3), 3.89 (s, 4.0H, C– CH_2 –O–biphenyl unit), 4.14 (s, 4.0H, C– CH_2 –O–bisphenol unit), 4.46 (s, 4.0H, C– CH_2 –O–CO), 7.09 (s, 4.0H, aromatic H in bisphenol), 7.14 ppm (s, 4.0H, aromatic H in biphenyl). ^{13}C NMR (125 MHz, CDCl_3). $\delta = 7.9$ (CH_2CH_3), 16.5 (Ar– CH_3), 21.0 (C– CH_3), 23.0 (CH_2 – CH_3), 30.3 (COCH_3), 42.4 (quaternary carbon in bisphenol unit), 43.0 (quaternary carbon in methylene unit), 65.0 (C– CH_2 –O–bisphenol–O– CH_2 –C), 71.4 (C– CH_2 –O–biphenyl), 72.9 (C– CH_2 –O–CO), 127.4, 127.6, 131.0, 136.5, 146.7, 149.1, 154.5, (aromatic C), 170.9 ppm (O–CO– CH_3). *Elem. Anal.* Calcd for $\text{C}_{46}\text{H}_{54}\text{O}_8\text{Cl}_4$: C, 63.36%; H, 6.52%. Found: C, 63.07%; H, 6.34%.



Scheme 1.

RESULTS AND DISCUSSION

It has been found that addition reactions of oxetanes with carboxylic acids, thiols, phenols, and *S*-phenyl thioesters proceed selectively and smoothly without any side-reaction under appropriate reaction conditions using certain quaternary onium salts or crown ether complexes as catalysts. Therefore, we examine to develop new addition reaction of oxetanes with phenyl esters in this article.

Active esters IBDPA, IBDPB, and IBDPD were obtained in 56, 45, and 56% yields, respectively, by the reaction of IBDP with acetyl chloride, benzoyl chloride, and 2,4-dichlorobenzoyl chloride. Then, the resulting products were confirmed by IR and NMR spectra, and elemental analysis. Commercial BPAA was also examined as an active bis(ester).

Since the polyaddition¹⁴ of bis(oxetane)s with di(*s*-phenyl thioester)s proceeded at higher temperature than 150 °C to produce corresponding polyesters with high molecular weight, the polyaddition of bis(oxetane)s with the above active bis(ester)s were performed at 160 °C using the same catalyst system. The reaction of bis(oxetane) 4,4'-BEOBP with IBDPA did not proceed without catalyst in DMAc at 160 °C for 96 h. However, the polyaddition proceeded smoothly, and corresponding poly(ether)s with M_n 's = 9200–17400 were obtained in 92–95% yields when 5 mol % of TBPC, TBPB, TPPC or TPPB were used as catalysts (Table I). In this reaction system, tetraphenylphosphonium salts TBPB and TBPC showed higher catalytic activity than tetrabutylphosphonium salts TBPC and TBPB, because the former catalysts have good thermal stabilities.^{26–29}

The structure of the obtained polymer was confirmed by the IR, ¹H NMR and ¹³C NMR spectroscopy, and the elemental analysis. In the IR spectrum of the polymer film, the absorption peaks at 1772 and 1187 cm⁻¹ assignable to the C=O and C–O–C stretching from aryl ester linkage disappeared, and shows new appearance of characteristic absorption peaks at 1742 and 1237 cm⁻¹ assignable to the C=O and C–O–C (ester) from alkyl ester linkage, respectively. The ¹H NMR spectrum of this polymer shows signals at $\delta = 1.03, 1.57$ due to both –CH₃, 1.78 due to –CH₂CH₃, 2.06 due to COCH₃, 4.08 due to C–CH₂–O–biphenyl unit, 4.10 due to C–CH₂–O–bisphenol unit, 4.28–4.33 due to C–CH₂–O–CO, and 6.96, 7.06 and 7.46 ppm due to aromatic protons. These results show that the polyaddition of bis(oxetane) 4,4'-BEOBP with active bis(ester) IBDPA proceeded to afford the poly(ether) poly(4,4'-BEOBP–IBDPA), whose structure is shown in Scheme 1. The ¹³C NMR spectrum also supported this structure.

We also examined the catalytic activity of crown ether complexes such as 18-C-6/KCl, 18-C-6/KBr, 18-C-6/CsF, 18-C-6/CsCl, 18-C-6/CsBr, 18-C-6/*t*-BuOK, and 18-C-6/PhOK under the same conditions. As summarized in Table I, the polyaddition of 4,4'-BEOBP with IBDPA proceeded when these crown ether complexes were used as catalysts. However, molecular weights and yields of the resulting poly(ether)s were not high enough. In addition, SEC of these obtained polymers showed multimodal curves. Although the complexes 18-C-6/CsF, 18-C-6/*t*-BuOK and 18-C-6/PhOK showed relatively higher activity than other crown ether complexes, the activities of these crown ether complexes were lower than those of the above quaternary phosphonium salts under the same

Table I. The polyaddition of 4,4'-BEOBP with IBDPA using certain catalysts^a

Run no.	Catalyst	Yield (%) ^b	M_n^c	M_w/M_n
1	No catalyst	0	—	—
2	TBPC	92	9200	1.45
3	TBPB	92	10800	1.82
4	TPPC	93	13400	1.59
5	TPPB	95	17400	1.78
6	18-C-6/KCl	49	3800, 2400, 1800	multimodal
7	18-C-6/KBr	39	2700, 1800, 1300	multimodal
8	18-C-6/CsF	80	5000, 2600, 1800	multimodal
9	18-C-6/CsCl	27	2900, 1900, 1300	multimodal
10	18-C-6/CsBr	24	2600, 1900, 1300	multimodal
11	18-C-6/ <i>t</i> -BuOK	73	4000, 2300, 1800	multimodal
12	18-C-6/PhOK	82	4800, 2900, 2300	multimodal

^aThe reaction was carried out with 4,4'-BEOBP (1.0 mmol) and IBDPA (1.0 mmol) using certain catalyst (5 mol %) in DMAc (2 mol/L) at 160 °C for 96 h. ^bInsoluble part in methanol. ^cEstimated by SEC based on polystyrene standards.

Table II. The polyaddition of bis(oxetane) with certain active bis(ester)s in DMAc or NMP^a

Run no.	Condition			Temp. (°C)	Time (h)	Yield (%) ^b	M_n^c	M_w/M_n
	Bis(oxetane)	Bis(ester)	Solvent					
1	BEOB	BPAA	DMAc	160	48	0	—	—
2	BEOB	IBDPA	DMAc	160	48	90	7100	1.62
3	BEOB	IBDPB	DMAc	160	48	0	—	—
4	BEOB	IBDPD	DMAc	160	48	49	2500	1.04
5	4,4'-BEOBP	IBDPA	DMAc	160	96	95	17400	1.78
6	4,4'-BEOBP	IBDPB	DMAc	160	96	0	—	—
7	4,4'-BEOBP	IBDPD	DMAc	160	96	59	2700, 1800, 1100	multi. ^d
8	4,4'-BEOBP	IBDPB	NMP	180	96	38	2600, 1600, 1000	multi. ^d
9	4,4'-BEOBP	IBDPD	NMP	180	96	84	4500	1.85

^aThe reaction was carried out with bis(oxetane)s (1.0 mmol) and bis(ester)s (1.0 mmol) using TPPB (5 mol %) as a catalyst in the solvent (2 mol/L). ^bInsoluble materials in methanol. ^cEstimated by SEC based on polystyrene standards. ^dMultimodal.

conditions. This may be due to less solubility of the crown ether complexes into the reaction solvent.

Then, polyadditions of bis(oxetane) BEOB with such active bis(ester)s as IBDPA, IBDPB and BPAA were examined using 5 mol % of TPPB as the catalyst in DMAc at 160 °C for 48 h. As summarized in Table II, the reaction of BEOB with BPAA and IBDPB did not proceed under this reaction condition (runs 1 and 3 in Table II). On the other hand, the reaction of BEOB with IBDPD proceeded to give low molecular weight oligomer with $M_n = 2500$ in 49% yield (run 4 in Table I). The reaction of BEOB with IBDPA proceeded smoothly, and the polymer with $M_n = 7100$ was obtained in 90% yield (run 2 in Table I). These mean that the reactivity of active bis(ester) on the reaction with bis(oxetane) was strongly affected by the electrophilicity of the esters. That is, IBDPA and IBDPD composed from high nu-

cleophilic phenol unit such as IBDP and high nucleophilic carboxyl units such as acetyl and 2,4-dichlorobenzoyl ester groups have good reactivities (Scheme 1).

Polyadditions of 4,4'-BEOBP, which seems to be suitable structure to produce the polymer, with IBDPB and IBDPD were also examined under the same conditions applied for the polyaddition of 4,4'-BEOBP with IBDPA, using TPPB as the catalyst in DMAc at 160 °C for 96 h. Although the polyaddition of 4,4'-BEOBP with IBDPD gave the corresponding polymer in 59% yield, the molecular weight of the resulting polymer is not high enough. On the other hand, the polyaddition of 4,4'-BEOBP with IBDPB did not proceed at all.

Therefore, the polyadditions of 4,4'-BEOBP with IBDPB and IBDPD were taken place in NMP at higher temperature such as 180 °C. Upon this reaction

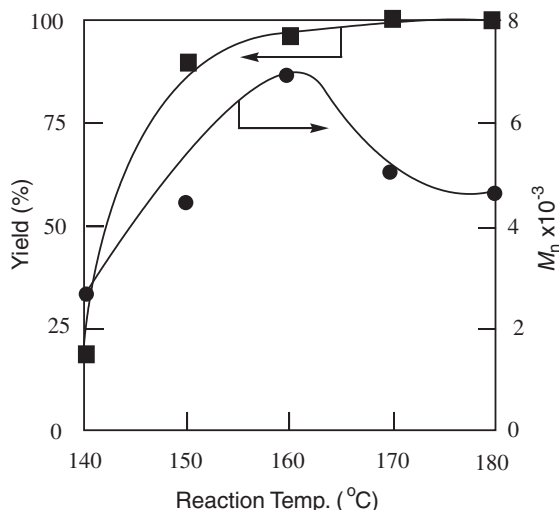


Figure 1. Effect of reaction temperature on the polyaddition of BEOB with IBDDPA. The reaction was carried out with BEOB (1.0 mmol) with IBDDPA (1.0 mmol) using TPPB (5 mol %) as the catalyst in DMAc (2 mol/L) for 48 h. (●): M_n , (■): Yield.

temperature, the polyaddition of 4,4'-BEOBP with IBDDPB proceeded partly, and low molecular weight oligomer was obtained in 38% yield. The polyaddition of 4,4'-BEOBP with IBDDPD was enhanced at 180 °C, and the corresponding polymer with $M_n = 4500$ was obtained in 84% yield (Table II).

The above results suggest that the yields and molecular weights of the polymers on the polyaddition of bis(oxetane)s with active bis(ester)s were also affected by the reaction time and temperature. Therefore, the effect of reaction temperature was examined on the polyaddition of BEOB with IBDDPA using 5 mol % of TPPB as a catalyst in DMAc for 48 h at several temperatures in the range between 140–180 °C. Figure 1 depicts the relationships of the yields, M_n s, and reaction temperatures. As shown in Figure 1, the yields of the polymers increased strongly with reaction temperature. The M_n s of the polymers also increased until 160 °C. However, at higher temperature than 160 °C, the M_n s of the resulting polymers decreased gradually. It may be suggested that some decomposition of ether linkages of the polymer chain occurred. This result seems that 160 °C is a suitable reaction temperature on the polyaddition of bis(oxetane) with active bis(ester).

The effect of reaction time on the polyadditions of BEOB or 4,4'-BEOBP with IBDDPA was examined using 5 mol % of TPPB as the catalyst in DMAc at 160 °C for various time. As shown in Figure 2, the yield of the polymer on the polyaddition of BEOB with IBDDPA was relatively good for 24 h, and we obtained the corresponding polymers quantitatively for more than 72 h. On the other hand, the M_n s of the polymers increased until 96 h of reaction. However,

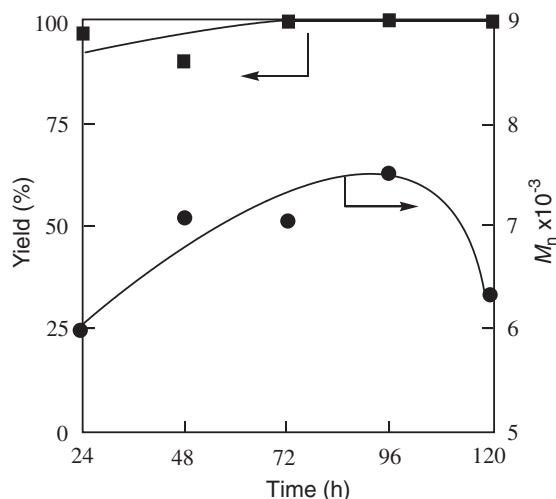


Figure 2. Effect of reaction time on the polyaddition of BEOB with IBDDPA. The reaction was carried out with BEOB (1.0 mmol) with IBDDPA (1.0 mmol) using TPPB (5 mol %) as the catalyst in DMAc (2 mol/L) at 160 °C. (●): M_n , (■): Yield.

after that, the M_n of the polymers decreased with reaction time. The same tendency was found on the polyaddition of 4,4'-BEOBP with IBDDPA under the same reaction conditions. From these results, it seems that the 96 h is suitable reaction time under this reaction condition, and some decomposition of the ether linkages in the polymer main chain might have occurred as a side reaction for longer time than 96 h.

Based on these results as mentioned above, the polyadditions of certain bis(oxetane)s (BEOB, 1,4-BEOMB, 4,4'-BEOBP, 2,2'-BEOBP, TM-BEOBP) with active bis(ester) IBDDPA were carried out in the presence of 5 mol % of TPPB in DMAc (2 mol/L) at 160 °C for 96 h as the optimum conditions, affording the corresponding polymers, poly(BEOB-IBDDPA), poly(1,4-BEOMB-IBDDPA), poly(4,4'-BEOBP-IBDDPA), poly(2,2'-BEOBP-IBDDPA), and poly(TM-BEOBP-IBDDPA) with M_n s in the range between 7200–17400 in 91–99% yields (Scheme 1). These results and conditions are summarized in Table III. These results show that poly(ether)s with high molecular weights were synthesized by the polyaddition of bis(oxetane) with active bis(ester).

The structures of all obtained polymers were confirmed by the IR, ^1H NMR and ^{13}C NMR spectroscopy, and the elemental analysis. This suggests that the polyaddition of bis(oxetane)s with active bis(ester)s proceeded selectively without any side reaction under appropriate reaction conditions.

All the obtained polymers could soluble in common organic solvents, such as DMSO, NMP, DMF, THF, and CHCl_3 , but insoluble in methanol, ethanol, and *n*-hexane.

Table III. The polyaddition of certain bis(oxetane)s with IBDPA^a

Run no.	Bis(oxetane)	Polymer	Yield (%) ^b	M_n^c	M_w/M_n
1	BEOB	Poly(BEOB-IPDPA)	94	7200	1.67
2	1,4-BEOMB	Poly(1,4-BEOMB-IPDPA)	99	11200	1.88
3	4,4'-BEOBP	Poly(4,4'-BEOBP-IPDPA)	95	17400	1.78
4	2,2'-BEOBP	Poly(2,2'-BEOBP-IPDPA)	90	11400	1.69
5	TM-BEOBP	Poly(TM-BEOBP-IPDPA)	91	12500	1.88

^aThe reaction was carried out with IPDPA (1.0 mmol) with bis(oxetane)s (1.0 mmol) using TPPC (5 mol %) in DMAc (2 mol/L) at 160 °C for 96 h. ^bInsoluble materials in methanol. ^cEstimated by SEC (THF) based on polystyrene standards.

CONCLUSIONS

We demonstrated the synthesis of the novel poly(ether)s by the polyaddition of bis(oxetane)s and active bis(ester)s. The reaction of bis(oxetane)s and active bis(ester)s was examined in the presence of the tetraphenylphosphonium halides as catalysts at 160 °C for 96 h in NMP, affording the corresponding poly(ether)s with high molecular weights in satisfactory yields. The obtained polymers could be soluble in common organic solvents. Furthermore, an approach to new oxetane resins as application of the reaction of bis(oxetane)s with active bis(ester)s is now under investigation.

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