The First Synthesis of Alternating Copolymers of Oxetanes with Cyclic Carboxylic Anhydrides Using Quaternary Onium Salts

Atsushi Kameyama,[†] **Kensuke Ueda, Hiroto Kudo, and Tadatomi Nishikubo***

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

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Oxetanes have been known to polymerize with cationic initiators[1] to provide the corresponding poly(ether)s. Recently, Lewis acid-promoted anionic polymerizations of oxetane[2,3] were studied, and the polyether with controlled molecular weights and molecular weight distributions was successfully synthesized. Copolymerization of oxetanes has also been studied: the copolymerization of oxetane with carbon dioxide using a Lewis acid[4] gave a copolymer, though not the corresponding alternating copolymer. The alternating copolymer of oxetane with carbon dioxide, that is polycarbonate, was synthesized using organotin halide−Lewis base systems.[5] Recently, the copolymerization of oxetane with cyclic carboxylic anhydrides using bulky titanium bisphenolates was investigated to find that the copolymers containing both alternating sequence and homopolymer moieties of oxetane were obtained.[6] Except this study, the copolymerization of oxetane with cyclic carboxylic anhydrides has not been reported. This is the exact opposite of well-known alternating copolymerization of oxiranes with cyclic carboxylic anhydrides using anionic initiators.[7]

Meanwhile, we found that oxetanes have a similar reactivity to oxiranes, which react with several reagents using suitable catalysts. For instance, the reactions of oxetanes with carboxylic acids,[8] phenols,[9] and thiophenols[10] proceeded successfully in the presence of quaternary onium halides or crown ether complexes. These new reactions were applied to the synthesis of some polymers such as poly(ester)s, poly(ether)s, and poly(sulfide)s by the polyadditions of bis(oxetane)s with dicarboxylic acids,[8] bis(phenol)s,[9] and bis(thiophenol)s.[10] Furthermore, the authors also reported that oxetanes could react with *S*-phenyl carboxylates[11] and acyl chlorides[12] using the aforementioned catalysts under mild reaction conditions. These mean that oxetanes are potentially reactive to some carbonyl compounds such as active carboxylic esters under neutral conditions. In a series of studies on the new reactions of oxetanes with carbonyl compounds, the authors found unexpectedly an alternating polymerization of oxetanes with cyclic carboxylic anhydrides. We now report the first synthesis of alternating copolymers of oxetanes and cyclic carboxylic anhydrides using quaternary onium salts.The reaction of 3-(benzyloxymethyl)-3-ethyloxetane (BMEO) with equimolar phthalic anhydride (PAn) using 5 mol % of tetrabutylphosphonium bromide (TBPB) without solvent was carried out in a sealed tube at 130 °C for 24 h. After precipitation of the reaction mixture into ethanol/*n*-hexane [1:1 (v/v)] and drying, a product was obtained in 78% yield (Table 1). The obtained polymer was well characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopies, elemental analysis, and GPC. The IR spectrum[13] of the product showed characteristic absorption peaks due to C=O stretching of ester groups and due to C−O stretching of ether group respectively at 1726 and 1271 cm^{-1}. The ^{1}H NMR[14] exhibited proton signals assignable to methylene groups due to the ring-opened structure of BMEO and due to aromatic rings of each monomer with reasonable intensity ratios, which were assumed the same composition of BMEO and PAn.The ^{13}C NMR[15] showed carbon-13 signals corresponding to the structure of the alternating copolymer of BMEO and PAn; in particular, the signal due to C=O of the ester groups was observed at 167.1 ppm. The elemental analysis[16] of the product reasonably agreed with the calculated values assuming that the product was composed of equimolar BMEO and PAn. Furthermore, the GPC measurement showed a unimodal profile suggesting the product was a polymer with M_n of 11 100 and M_w/M_n of 1.28. All of these data proved that the obtained product was the polyester, that is, alternating copolymer of BMEO and PAn.

Scheme 1

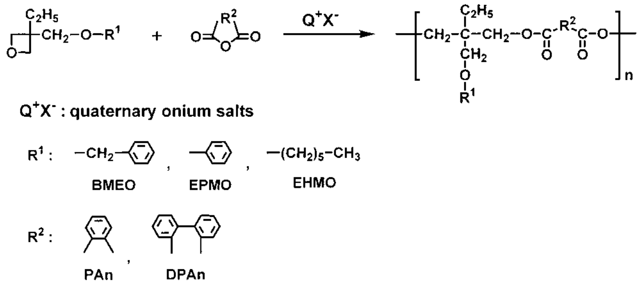

Table 1. Synthesis of Polyesters by the Copolymerization of Oxetanes with Cyclic Carboxylic Anhydrides[a]

monomer				composition[c]		
oxetane	anhydride	cat.	yield (%)[b]	oxetane: anhydride	M_n[d]	M_w/M_n[d]
BMEO	PAn	TBAC	35	1:1	4700	1.13
BMEO	PAn	TBAB	38	1:1	5400	1.22
BMEO	PAn	TBPC	68	1:1	9500	1.37
BMEO	PAn	TBPB	78	1:1	11100	1.28
BMEO	PAn	TPPB	81	1:1	7300	1.28
EPMO	PAn	TBPB	51	1:1	6500	1.32
EHMO	PAn	TBPB	27	1:1	4100	1.31
BMEO	DPAn	TBPB	71	1:1	2900	1.43

[a] The reaction was carried out with oxetanes (1 mmol) and cyclic carboxylic anhydrides (1 mmol) using 5 mol % of catalysts in bulk at 130 °C for 24 h. [b] Insoluble parts in ethanol/*n*-hexane [1:1 (v/v)]. [c] Measured by ^{1}H NMR. [d] Estimated by GPC (THF) based on polystyrene standards.

Quaternary phosphonium halides were effective for the synthesis of the alternating copolymers of BMEO and PAn. When tetrabutylphosphonium chloride (TBPC) or tetraphenylphosphonium bromide (TPPB) was used for the copolymerization, the corresponding alternating copolymer with M_n of 9500 (M_w/M_n: 1.37) and M_n of 7300 (M_w/M_n: 1.28) were obtained. On the other hand, the reaction using tetrabutylammonium chloride (TBAC) or

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[†] Present address: Department of Chemistry, Faculty of Engineering, Kanagawa University.

* To whom all correspondence should be addressed.

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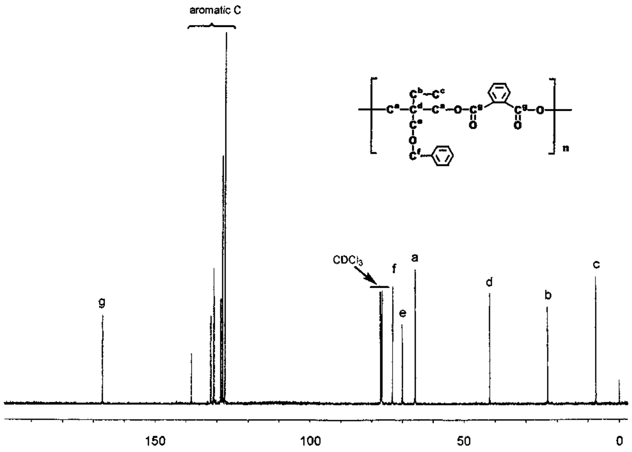

Figure 1. ^{13}C NMR spectrum of the alternating copolymer of BMEO and PAn.

bromide (TBAB) afforded the alternating copolymer with moderate M_n of about 5000 in low yields. The higher catalytic activity of quaternary phosphonium halides would be attributed to their good thermal stability at relatively high temperature as 130 °C.

The presence of halogen atoms in the obtained polymers was investigated by the Beilstein test. The Beilstein test of the polymer (M_n: 11 100) proved that the polymer contained halogen atoms. To clear an initiation reaction of the copolymerization of BMEO with PAn, the structure of a terminal of the polymers was examined with an oligomer (M_n: 3400) obtained by the copolymerization using 15 mol % of TBPB in bulk at 130 °C for 24 h. The ^{13}C NMR spectrum of the oligomers showed the carbon-13 signal assignable to $BrCH_2^-$ group at 36.5 ppm. This means that the polymer has bromide at the initiating terminal. Therefore, it is considered that the alternating copolymerization is initiated by nuclephilic addition of bromide to the oxetane group of BMEO. The present alternating copolymerization is an unusual copolymerization of oxetanes, because it is known that common anionic initiators cannot polymerize oxetane monomers.

The copolymerizations of several oxetanes with cyclic carboxylic anhydrides using 5 mol % of TBPB were conducted under the same conditions. The copolymerization of BMEO with diphenic anhydride (DPAn) provided the alternating copolymer with M_n of 3000. The copolymerization of 3-ethyl-3-phenoxymethyloxetane (EPMO) and 3-ethyl-3-hexyloxymethyloxetane (EHMO) with PAn also afforded the alternating copolymers with M_n of 6500 and 4100, respectively. The structures of the resulted polymers were confirmed as the corresponding alternating copolymers by their spectral data.

Figure 2 shows the relationship between monomer feed ratios and polymer yields and molecular weights. The copolymerization in the feed ratio of BMEO:PAn = 2:1 produced the copolymer with M_n of 3600 (M_w/M_n: 1.29) in 69% yield. The copolymerization with the feed ratio of BMEO:PAn = 1:2 also produced the copolymer with M_n of 4500 (M_w/M_n: 1.3) in 51% yield. The spectral data of all resulted polymers suggested that the alternating copolymer of BMEO and PAn was obtained irrespective of the monomer feed ratios. It was confirmed that residues in the soluble parts after the reprecipitation were oligomers with alternating sequences of BMEO and PAn and unreacted monomers. It was also found that the yields and molecular weights became maximum values in the feed ratio 1:1. This is the characteristic behavior of conventional alternating copolymerization. Thus, it was reasonably proved that the copolymerization of BMEO and PAn proceeded in an alternating copolymerization manner irrespective of the monomer feed ratios.

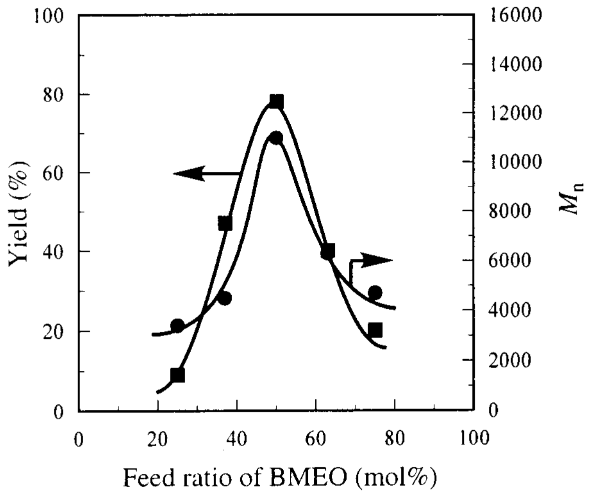

Figure 2. Effect of feed ratio of monomers on the copolymerization. The reaction was carried out with BMEO and PAn (total 2.0 mmol) using TBPB (5 mol %) in bulk at 130 °C for 24 h. (■) Yield of polymers insoluble parts in ethanol/*n*-hexane [1:1(v/v)]. (●) M_n.

In summary, the synthesis of the alternating copolymers of oxetanes with cyclic carboxylic anhydrides using quaternary onium salts was demonstrated. The alternating copolymerization of oxetanes with cyclic carboxylic anhydrides was initiated by halide anions of quaternary onium salts used and was a quite unique copolymerization of oxetanes. The mechanistic studies on the alternating copolymerization of oxetanes with cyclic carboxylic anhydrides using quaternary onium salts are now in progress.

References and Notes

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(13) Identification. IR (film, cm^{-1}): 1726 (νC=O of ester), 1579 (νC=C), 1271 (νC−O−C of ester), 1122, 1074 (νC−O−C).
(14) Identification. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 0.84 (t, J = 8.0 Hz, 3 H, CH$_3$), 1.56 (q, J = 8.0 Hz, 2 H, CH$_2$), 3.39 (s, 2 H, CH$_2$), 4.15−4.63 (m, 6 H, CH$_2$), 7.22−7.57 (m, 9 H, aromatic H).

(15) Identification. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 7.4 (CH_3), 23.1 (CH_2), 41.8 ($C_{quat.}$), 65.8 (CH_2), 70.0 (CH_2), 73.3 (CH_2-Ph), 127.4, 128.2, 128.8, 131.0, 132.0, 138.2, (aromatic C), 167.1 ($C=O$).

(16) Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.19; H, 6.30. Found: C, 70.60; H, 6.48.

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