

SHORT COMMUNICATIONS

Synthesis of Poly(cyclic orthoester)s by the One-Pot Reaction of Potassium Perfluoroalkylcarboxylates with Epibromohydrin Using Two-Step Catalysis of Quaternary Onium Salts

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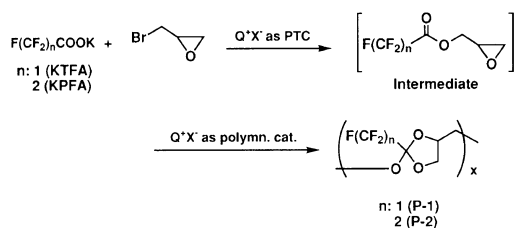
Quaternary onium salts and crown ethers are extremely useful as phase transfer catalysts (PTC) in synthetic organic chemistry and polymer synthesis. Our research group has studied in detail chemical modifications¹ of polymers such as poly(chloromethylstyrene) using PTC. Moreover, photosensitive polymers² and photoresponsive polymers³ for solar energy storage were successfully synthesized by the chemical modifications using PTC.

Meanwhile, the authors reported new catalytic activity of quaternary onium salts or crown ether complexes on the addition reactions of cyclic ethers or sulfides with carboxylic acid derivatives.⁴ For example, the addition reaction of oxiranes⁵ or thiiranes⁶ with *S*-phenyl carboxylates using the aforementioned catalysts proceeded smoothly and regioselectively to give the corresponding products. As an application, new acyl group transfer polymerization⁷ of thiiranes was successfully achieved using carboxylic acid derivatives as initiators and quaternary onium salts or crown ether complexes as catalysts.

More recently, we reported a unique cycloaddition reaction⁸ of oxiranes with alkyl

perfluoroalkylcarboxylates using the catalysts, which provide five-membered cyclic orthoesters. It was also found that although the reaction of oxiranes with alkyl carboxylates such as ethyl acetate or ethyl benzoate did not proceed at all, the reaction with alkyl perfluoroalkylcarboxylates proceeded very smoothly in the presence of the catalysts. This means that perfluoroalkyl groups activate the adjacent carbonyl group to react the oxiranes. Furthermore, the cycloaddition reaction was successfully applied for the synthesis of poly(cyclic orthoester)s⁹ by the cycloaddition polymerization of bis(oxirane)s with bifunctional trifluorocarboxylates. It was also suggested that those cycloaddition reactions using conventional Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$ did not proceed because of the acid-induced ring-opening polymerization of the used oxiranes, even though synthesis of orthoesters by the acid-catalyzed reaction of oxiranes with certain carbonyl compounds has been known. Thus, it should be emphasized that an advantage of the reactions using quaternary onium salts or crown ether complexes is the selective transformation of cyclic ethers under neutral condi-

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Scheme 1.

tions.

From this background, we designed a one-pot synthesis of poly(cyclic orthoester)s by the reaction of perfluoroalkylcarboxylate derivatives with a oxirane based on a two-step catalysis of quaternary onium salts or crown ether complexes. In the reaction, glycidyl ester derivatives as intermediates were initially produced by phase transfer catalysis of those catalysts. Then, the cycloaddition polymerization of the formed glycidyl ester derivatives proceeds to give the corresponding poly(cyclic orthoester)s.

In this paper, we wish to report new synthesis of poly(cyclic orthoester)s by one-pot reaction of potassium perfluoroalkylcarboxylates with epibromohydrin using quaternary onium salts as phase transfer catalysts and polymerization catalysts.

The reaction of potassium trifluoroacetate (KTFA) with EBH was conducted using 8 mol% of tetrabutylammonium bromide (TBAB) as a catalyst in various solvents at 90°C for 24 h. The results are summarized in Table I. When the reaction was carried out in low polar solvents such as anisole or chlorobenzene, the corresponding polymer was not obtained. This means that the first nucleophilic substitution reaction of KTFA with EBH catalyzed by TBAB as PTC scarcely proceeded in the low polar solvents. On the other hand, the reaction proceeded smoothly in *N*-methyl-2-pyrrolidone (NMP) to afford the targeted polymer with number-average molecular weight (\bar{M}_n) of about 9000 in 73% yield. The reaction was efficiently enhanced in *N,N*-dimethylacetamide or tetrahydrofuran

Table I. Synthesis of P-1 by one-pot reaction of KTFA with EBH using TBAB in various solvents^a

Solvent ^b	Yield/% ^c	\bar{M}_n ^d	\bar{M}_w/\bar{M}_n
Anisole	0	—	—
Chlorobenzene	0	—	—
THF	77	11600	1.44
NMP	73	8600	1.27
DMAc	64	11000	1.31
DMSO	40	11000	1.58

^a The reaction was carried out with KTFA (3 mmol) and EBH (3 mmol) using TBAB in solvent (1 ml) at 90°C for 24 h. ^b THF, tetrahydrofuran; NMP, *N*-methyl-2-pyrrolidone, DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide. ^c Insoluble parts in *n*-hexane. ^d Estimated by GPC based on polystyrene standards.

Table II. Effect of catalysts on the reaction of KTFA with EBH using TBAB^a

Catalyst ^b	Yield/% ^c	\bar{M}_n ^d	\bar{M}_w/\bar{M}_n
None	56	6700	1.37
TBAC	60	11900	1.32
TBAB	73	8600	1.27
15-C-5	54	10400	1.29
18-C-6	59	10100	1.32

^a The reaction was carried out with KTFA (3 mmol) and EBH (3 mmol) using catalyst in NMP (1 ml) at 90°C for 24 h. ^b TBAC, tetrabutylammonium chloride; TBAB, tetrabutylammonium bromide; 15-C-5, 15-crown-5; 18-C-6, 18-crown-6. ^c Insoluble parts in *n*-hexane. ^d Estimated by GPC based on polystyrene standards.

to give the polymer with \bar{M}_n of 11000 in moderate yields. Therefore, it was suggested that the phase transfer catalysis of the substitution reaction of KTFA with EBH is the important process on the one-pot reaction.

The effect of the catalysts on the reaction of KTFA with EBH was examined in NMP at 90°C for 24 h (Table II). When the reaction was carried out without catalysts, the polymer with \bar{M}_n of 6700 was obtained in 56% yield. It seems that the substitution reaction of KTFA with EBH proceeds gradually in the high-polar solvent to form the corresponding intermediate, glycidyl trifluoroacetate, eliminating KBr in the first step, and then the produced KBr

catalyzed¹⁰ the following cycloaddition polymerization of the intermediate.

The reaction was enhanced by the addition of quaternary onium salts or crown ethers under the same conditions. When the reaction was carried out using 18-crown-6 (18-C-6), the corresponding polymer with \bar{M}_n of 10000 was obtained. The increase of the molecular weight might be ascribed to the incorporation of the produced KBr by 18-C-6 to form the corresponding crown ether complex. Tetrabutylammonium chloride (TBAC) and TBAB also enhanced the reaction, in particular, the reaction using TBAC gave the polymer with the highest \bar{M}_n of 12000. This means that quaternary onium salts efficiently catalyze the substitution reaction in the first step as PTC followed by polymerization in the second step during the reaction of KTFA with EBH.

The structure of the resulting polymer (P-1) was ascertained by IR and ¹H NMR spectroscopies. The IR spectrum showed peaks at 2962 cm⁻¹ due to C-H stretching, at 1280 cm⁻¹ due to C-F stretching, and at 1184 and 1116 cm⁻¹ due to the C-O-C stretching. Furthermore, no peaks due to carbonyl group and oxirane ring were observed in the corresponding regions. As shown in Scheme 2., ¹H NMR spectral data was identified with reference to the spectral data of a poly(cyclic orthoester) previously reported by Hall.¹¹ Thus, it was proved that the targeted polymer with five-membered cyclic orthoester in the main chain was obtained by the one-pot

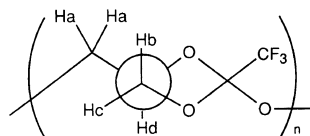
reaction of KTFA with EBH.

The one-pot reactions of other potassium perfluoroalkylcarboxylates with EBH using TBAB were also carried out in NMP under the similar conditions. The reaction of EBH with potassium pentafluoropropionate (KPFA) proceeded to give the corresponding polymer (P-2) with \bar{M}_n of 8000.

In summary, it was demonstrated that the one-pot reaction of potassium perfluoroalkylcarboxylates with epibromohydrin proceeded successfully using quaternary onium salts to give new polymers with five-membered cyclic orthoester structures in the backbones. The quaternary onium salts act as phase transfer catalysts in the first step and polymerization catalysts during the one-pot reaction.

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¹H-NMR data
(ppm, CDCl₃, TMS)

3.62-3.94	(m, 2H, Ha)
3.94-4.09	(m, 1H, Hb)
4.09-4.30	(m, 1H, Hc)
4.30-4.81	(m, 1H, Hd)

Scheme 2.