3490 Macromolecules 1995, 28, 3490−3491

Novel Synthesis of Poly(cyclic orthoester)s by Cycloaddition Polymerization of Bis(trifluoroacetate)s with Bisepoxides Catalyzed by Quaternary Onium Salts

Atsushi Kameyama, Keiko Mochida, and Tadatomi Nishikubo*

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

Received December 19, 1994
Revised Manuscript Received February 24, 1995

Cyclopolymerization is a useful reaction to provide polymers having cyclic structures in the backbones. Concerning cyclopolymerization of epoxy monomers producing heterocyclic structures, Yokota et al. recently reported cyclopolymerization of a bisepoxy monomer[1] with Lewis acids or KOH as catalysts. Miyamoto reported the cyclopolymerization of glycidyl carboxylates[2] using a special aluminum complex as a Lewis acid proceeded selectively to give poly(cyclic orthoester)s. It has also been known that the reaction of epoxy compounds with certain nucleophiles using conventional Lewis acids such as BF_3OEt_2 or $ZnCl_2$ essentially includes a polymerization of the used epoxides as a side reaction.

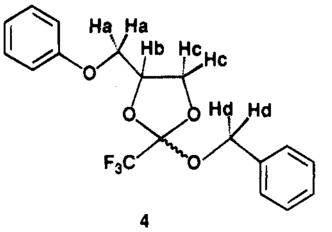
The authors recently reported selective transformations of epoxides with active carbonyl compounds into carboxylates[3] and cyclic carbonates[4] using quaternary onium salts or crown ether complexes as catalysts. We also found that a new cycloaddition reaction[5] of epoxides with alkyl trifluoroacetates in the presence of quaternary onium salts or crown ether complexes proceeds easily to afford five-membered cyclic orthoesters in good yield. An advantage of these reactions with the catalysts is the selective transformation of epoxides under neutral conditions, since quaternary onium salts and crown ether complexes do not catalyze a ring-opening polymerization of the used epoxides.

In this paper, we report a new synthesis under neutral conditions of poly(cyclic orthoester)s based on cycloaddition polymerization of bisepoxides with bis(trifluoroacetate)s using quaternary onium salts or crown ether complexes.

A new bifunctional monomer, bis[(trifluoroacetoxy)methyl]benzene (**1**; Scheme 1)[6] (bp 85−90 °C/0.45 mmHg), was synthesized in 70% yield by the esterification of trifluoroacetic acid with *p*-xylene-α,α′-diol in the presence of *p*-toluenesulfonic acid in tetrachloromethane at reflux temperature. Other bis(trifluoroacetate) monomers were also prepared under similar conditions.

The reaction of **1a** with Bisphenol A diglycidyl ether (**2a**) was carried out using 8 mol % of tetrabutylammonium bromide (TBAB) in *N*-methyl-2-pyrrolidone (NMP) at 90 °C for 48 h to afford a polymer (**3a**) with a number-average molecular weight (M_n) of 34 000, which was estimated by GPC based on polystyrene standards, in 97% yield. The structure[7] of the obtained polymer was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The IR spectrum showed peaks at 1247 and 1184 cm^{-1} due to the Ar−O−C stretching, at 1104 cm^{-1} due to cyclic C−O−C, and 1053 cm^{-1} due to C−O−C. Furthermore, the peaks based on carbonyl, oxirane ring, or hydroxyl groups were not observed at all. ^{1}H and ^{13}C NMR spectral data suggested that the polymer has cis and trans forms of the five-membered ring in the main chain. ^{1}H NMR signals due to the five-membered cyclic orthoester moiety of the polymer were identified based on the data of the model compound (**4**; Chart 1). In the ^{1}H NMR of the polymer, the signals of noncyclic and cyclic methylene protons were observed at 4.06−4.33 ppm and cyclic methine protons were shown at 4.50−4.60 ppm. The ^{13}C NMR showed two quartet signals due to the CF_3 of cis and trans isomers at 120.2 and 120.6 ppm. Therefore, it was proved that the cycloaddition polymerization of **1a** with **2a** using TBAB as the catalyst proceeded to afford the poly(cyclic orthoester) **3a** with the structure shown in Scheme 1.

Chart 1



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^{1}H NMR data δ (ppm):
3.92-4.40 (m, 4H, Ha and Hc)
4.42-4.82 (m, 1H, Hb)
4.77 and 4.86 (s, 2H, Hd)
6.86-7.40 (m, 10H, Ar)

The reaction of **1a** with **2a** also proceeded smoothly using tetrabutylammonium, phosphonium halides, and potassium halide/crown ether complexes as catalysts. The results are summarized in Table 1. The catalysts which contain bromide as the counteranion such as TBAB, tetrabutylphosphonium bromide (TBPB), and KBr/18-crown-6 ether (KBr/18-C-6) have higher catalytic activity than those including iodide and chloride. In particular, TBAB gave the polymer (**3a**) with the highest molecular weight (M_n = 34 000) under the same conditions. It means that the character of the counteranion of the neutral salt catalysts is a very important factor on the catalysis of the reaction of **1a** and **2a**.

On the other hand, when the reaction was conducted using 5 mol % of BF_3OEt_2 as a Lewis acid catalyst in toluene at −20 °C for 2 h, an insoluble polymer was obtained, which had an IR spectrum different from that of **3a**. Furthermore, GLC analysis of the methanol-soluble parts in precipitation showed that monomer **1** was scarcely consumed in the reaction. These results mean that a ring-opening polymerization of the epoxy group in **2a** predominantly proceeded to give the insoluble product in the reaction with BF_3OEt_2 as the catalyst. Thus, it was demonstrated that the quaternary onium salts and crown ether complexes selectively catalyzed the cycloaddition reaction of **1a** with **2a** to give the targeted polymer **3a** with five-membered cyclic orthoester in the backbone.

The reaction of **1a** with **2a** in the presence of 8 mol % of TBAB was carried out in various solvents at 90 °C for 48 h (Table 1). The corresponding poly(orthoester) **3a** with low molecular weights was obtained from the reaction in aromatic solvents such as anisole and chlorobenzene. On the other hand, the reaction in aprotic polar solvents such sulfolane, DMAc, and NMP gave the polymer having relatively high molecular weights. In particular, when the reaction was carried out in NMP, the targeted polymer with the highest molecular weight (M_n = 34 000) was afforded. This means that amide types of solvents having a high polarity are significantly effective solvents for the cycloaddition polymerization of the bisacetate with the bisepoxide using quaternary onium salts.

Cycloaddition polymerization of various bis(trifluoroacetate) monomers with **2a** using TBAB catalyst also

0024-9297/95/2228-3490$09.00/0

Scheme 1

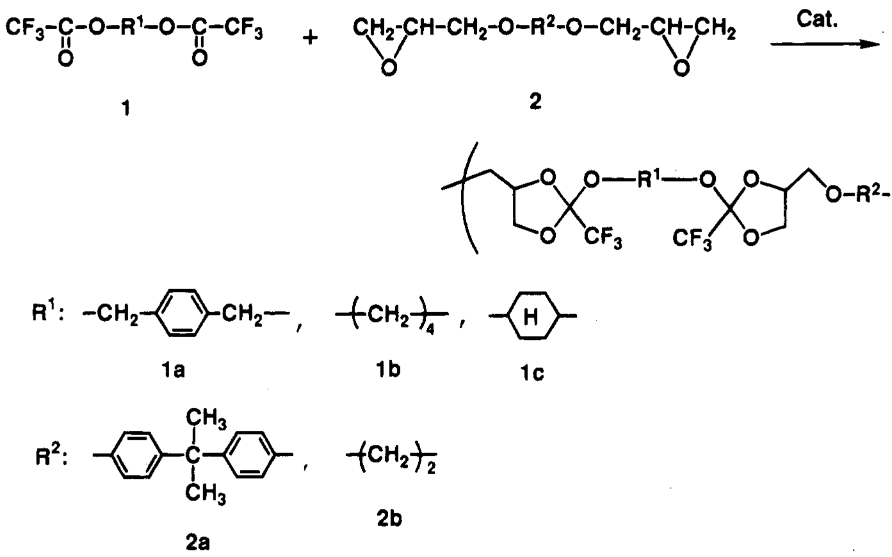

Table 1. Cycloaddition Polymerization of 1a with 2a[a]

run	catalyst	solvent	yield[b] (%)	M_n[c]	M_w/M_n[c]
1	TBAC[d]	NMP[h]	74	6 700	1.36
2	TBAB[e]	NMP	97	34 000	1.83
3	TBAI[f]	NMP	83	14 500	1.44
4	TBPB[g]	NMP	96	28 200	1.63
5	KBr/18-C-6	NMP	94	34 000	1.76
6	KI/18-C-6	NMP	78	15 000	1.46
7	TBAB	anisole	91	15 900	1.44
8	TBAB	chlorobenzene	89	18 000	1.43
9	TBAB	THF[i]	96	22 400	1.57
10	TBAB	sulfolane	96	28 600	1.58
11	TBAB	DMAc[j]	94	29 900	1.82

[a] The reaction was carried out with 1.2 mmol of **1** and **2** using 8 mol % of catalysts in 0.6 mL of solvents at 90 °C for 48 h. [b] Insoluble parts in methanol. [c] Estimated by GPC based on polystyrene standards. [d] TBAC: tetrabutylammonium chloride. [e] TBAB: tetrabutylammonium bromide. [f] TBAI: tetrabutylammonium iodide. [g] TBPB: tetrabutylphosphonium bromide. [h] NMP: *N*-methyl-2-pyrrolidone. [i] THF: tetrahydrofuran. [j] DMAc: *N,N'*-dimethylacetamide.

proceeded under mild conditions to give the corresponding poly(cyclic ether)s. The results are summarized in Table 2. In the case of the polymerization of bis(trifluoroacetoxy)butane (**1b**) with **2a**, a targeted poly(cyclic orthoester) **3b** with M_n of 32 000 was obtained. When bis(trifluoroacetoxy)cyclohexane (**1c**) was used as the monomer in the cycloaddition polymerization, the corresponding polymer **3c** was prepared, although the yields of methanol-insoluble fractions were low. These bisacetate monomers also reacted smoothly with an aliphatic bisepoxide (**2b**) in the presence of TBAB to afford the corresponding poly(cyclic orthoester)s with molecular weights of 8500–16 000 in moderate yields.

In summary, the present study demonstrates a successful synthesis of new poly(cyclic orthoester)s by the cycloaddition polymerization of bis(trifluoroacetate)s with certain bisepoxides catalyzed by quaternary onium salts or crown ether complexes.

Table 2. Cycloaddition Polymerization of Various Bisacetates with Bisepoxides[a]

	monomer			yield[b]		
run	bisacetate	bisepoxide	polymer	(%)	M_n[c]	M_w/M_n[c]
1	**1a**	**2a**	**3a**	97	33 900	1.83
2	**1b**	**2a**	**3b**	50	32 300	1.77
3	**1c**	**2a**	**3c**	44	15 900	1.27
4	**1a**	**2b**	**3d**	77[d]	8 800	1.20
5	**1b**	**2b**	**3e**	58[d]	15 700	1.70
6	**1c**	**2b**	**3f**	71[d]	8 500	1.21

[a] The reaction was carried out with 1.2 mmol of each monomer using 8 mol % of TBAB in 0.6 mL of NMP at 90 °C for 48 h. [b] Insoluble parts in methanol. [c] Estimated by GPC based on polystyrene standards. [d] Insoluble parts in *n*-hexane.

References and Notes

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(6) Identification. IR (KBr): 1785 ($\nu_{C=O}$), 1222, 1146 (ν_{C-O}). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 5.37 (s, 4 H, C*H*$_2$), 7.44 (s, 4 H, Ar–*H*). Anal. Calcd for $C_{12}H_8F_6O_4$: C, 43.65; H, 2.44. Found: C, 43.56, H, 2.37.
(7) Identification. IR (film): 1247, 1184, 1104, 1053 (ν_{C-O-C}). ^{1}H NMR (90 MHz, CDCl$_3$, TMS): δ 1.62 (s, 6 H, C*H*$_3$), 4.06–4.33 (m, 8 H, C*H*$_2$CHC*H*$_2$), 4.50–4.60 (m, 2 H, CH$_2$C*H*CH$_2$), 4.74–4.83 (m, 4 H, PhC*H*$_2$), 6.76–7.34 (m, 12 H, Ar–*H*).

MA9461254