

Regio-controlled ring-opening polymerization of perfluoroalkyl-substituted epoxides†

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Highly fluorinated epoxides were polymerized under mild conditions regioregularly, which gave easy access to isotactic polymers by using optically pure epoxides.

Organofluorine compounds have been paid much attention because of their unique features, especially in materials science.^{1,2} Since the properties of polymers depend strongly on their molecular weight, molecular weight distribution, and structure of the main chain, their precise control is a challenging theme. Intensive efforts have been devoted to controlled polymerization of fluorinated olefins in coordination polymerization,^{3–5} ring-opening metathesis polymerization,⁶ atom-transfer radical polymerization,⁷ and anionic polymerization.^{8–10} However, no examples have been reported for controlled polymers derived from fluorinated epoxides. Only one report has appeared on regioregular polyether formation from 3,3,3-trifluoropropylene oxide.^{11,12} Generally, standard synthetic strategies for non-fluorinated compounds cannot be directly applied to the reaction of organofluorine compounds because of their unusual properties. For example, highly fluorine-substituted molecules or fragments display a low affinity with general organic or aqueous solvents. Hence, development of a new catalyst–initiator system is essential to obtain polymers starting from fluorine-rich epoxides. Here we report the polymerization of highly fluorinated epoxides to give regioregular polyethers. Isotactic polyethers were also synthesized by using enantiopure epoxides. The structures of the polymers were characterized by ¹³C NMR spectroscopy and MALDI-TOF mass spectrometry.

First, we referred to the catalyst–initiator system previously employed for the ring-opening polymerization of propylene oxide. Among the examples of efficient production of regioregular polyethers,^{13–15} we examined the system reported by Deffieux using ^tPrONa as an initiator and AlⁱBu₃ as a catalyst.¹⁴ When fluorinated epoxide **1** was subjected to the conventional reaction conditions, that is treatment of **1** with ^tPrONa–AlⁱBu₃ in cyclohexane, a trace amount of oligomer precipitated before full consumption of epoxide **1** (Table 1, run 1). Since the polymer of **1** is insoluble in general organic solvents, the use of fluorous solvents seems to be indispensable for the polymerization of **1**. Accordingly, epoxide **1** was next treated with ^tPrONa–AlⁱBu₃ in a fluorous solvent, C₆F₆. In this case, however, again no polymerization can

Table 1 Optimization of ring-opening polymerization of epoxide **1**^a

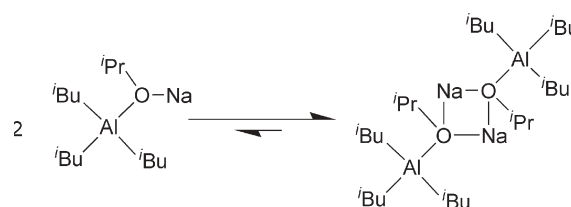
1 : Rf = $\frac{5}{n}$ C₄F₉

Run	Initiator	AlR ₃	T/°C	t/h	Yield (%)	M _n /g mol ⁻¹	M _w /M _n
1 ^b	^t PrONa	ⁱ Bu	rt	6	3.8	—	—
2	^t PrONa	ⁱ Bu	rt	12	0	—	—
3	[ⁿ Bu ₄ N] ⁺ Cl ⁻	ⁱ Bu	rt	12	0	—	—
4	[PPN] ⁺ Cl ⁻	ⁱ Bu	0	2	29	17000	1.8
5	[MePPh ₃] ⁺ Cl ⁻	ⁱ Bu	0	2	33	11000	1.9
6	[MePPh ₃] ⁺ Br ⁻	ⁱ Bu	0	1	95	14000	2.1
7	[MePPh ₃] ⁺ Br ⁻	Et	rt	12	0	—	—
8	[MePPh ₃] ⁺ Br ⁻	—	rt	12	0	—	—
9	—	ⁱ Bu	rt	12	0	—	—

^a Epoxide **1** (2.8 mmol), C₆F₆ (2.0 mL), initiator (0.025 mmol), AlR₃ (0.25 mmol in 1 M toluene solution). ^b Cyclohexane was used as a solvent instead of C₆F₆.

be seen at all (Table 1, run 2). It should be noted that even propylene oxide gave no product in C₆F₆. Given that Li[R₃AlCl] (R = alkyl) was reported to form a dimeric aggregate which contains a Li–Cl–Li–Cl four-membered ring,¹⁶ aggregation of ^tPrONa–AlⁱBu₃ as described in Scheme 1 or its related structure might be responsible for the catalyst deactivation in C₆F₆.¹⁷

Thus, as an initiator, we next examined the use of organic salts which contain non-coordinating cations such as ammonium and phosphonium. These non-coordinating cations were expected to prevent aggregation.^{20,21} No activity was seen using [ⁿBu₄N]⁺Cl⁻ (run 3) but the use of [Ph₃P=N=PPh₃]⁺Cl⁻ ([PPN]⁺Cl⁻) as initiator gave polymeric material as a viscous oil in 29% yield (run 4). A phosphonium salt [MePPh₃]⁺Cl⁻ also brought polymerization (run 5). Initiator with bromide [MePPh₃]⁺Br⁻ was proven to have much higher activity giving the polymer in 95% yield (run 6).²² The use of AlEt₃ as a catalyst resulted in no polymerization (run 7). In the absence of either Lewis acid catalyst or initiator, no polymerization occurred (runs 8 and 9).

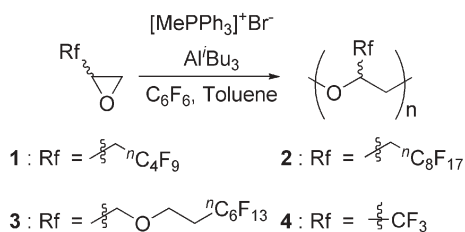


Scheme 1 Assumed aggregation structure of ^tPrONa–AlⁱBu₃.

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† Electronic supplementary information (ESI) available: Experimental details, MALDI-TOF mass spectrometry data and ¹³C NMR spectra of polymers. See DOI: 10.1039/b606693c

Table 2 Ring-opening polymerization of various perfluorinated epoxides^a



Run	Monomer	$T/^\circ\text{C}$	t/h	Yield (%)	$M_n/\text{g mol}^{-1}$	M_w/M_n
1	(+)- 1	0	1	81	15000	1.7
2 ^b	(±)- 2	0	1	—	—	—
3	(±)- 3	0	1	96	28000	1.9
4	(+)- 3	0	1	99	31000	1.8
5 ^c	(±)- 4	r.t.	40	45	2200	1.2

^a Conditions as those in Table 1. ^b Obtained polymer was not purified due to the low solubility. ^c Measurement of M_n employed a different method from other polyethers (see ESI†).

The scope and generality of this reaction were further explored under the reaction conditions of Table 1, run 6, and the results are summarized in Table 2. A polymer was efficiently produced from enantiopure (+)-**1** (run 1) in a similar manner to racemic **1**.²³ Epoxide **2** bearing a longer perfluoroalkyl chain was also polymerized (run 2), but full characterization of the product was impossible because of its low solubility in any solvents including fluorinated ones. Epoxide **3**, having a perfluoroalkyl chain through an ether linkage, was polymerized to give a polyether as a viscous oil (run 3). The product was highly soluble in most organic solvents. The polymer of optically pure (+)-**3** was also successfully obtained (run 4).²³ The reaction of epoxide **4** which has a trifluoromethyl group directly attached to the epoxide ring resulted in low activity (run 5).

The production of regioregular polymers from **1** and **3** was demonstrated by ¹³C NMR spectra of the obtained polymers in C₆F₆. Polymers prepared from (±)-**1** in runs 4–6 of Table 1 showed four peaks of the methylene carbon in the main chain reflecting the tacticity. For the polymer in run 6 of Table 1, the area ratio was 22 : 25 : 25 : 28 from lower magnetic field to higher (Fig. 1a). In contrast, the ¹³C NMR spectrum of the polymer made from (+)-**1** (Table 2, run 1) gave only one methylene carbon peak

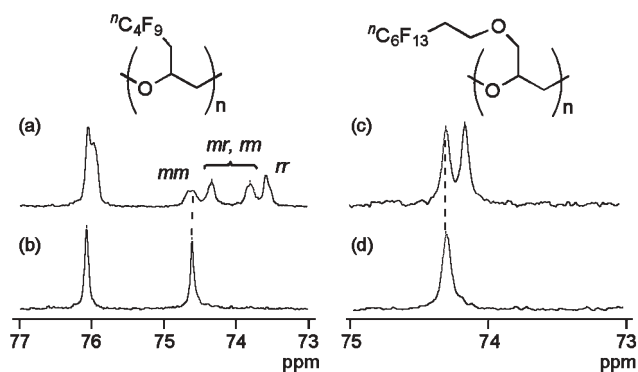
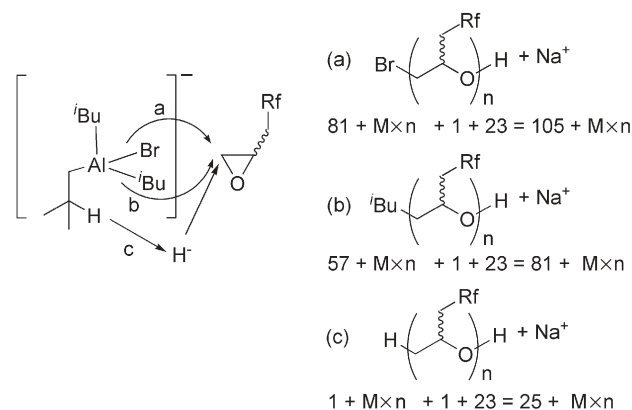


Fig. 1 ¹³C NMR spectra of polymers from (a) (±)-**1** (Table 1, run 6), (b) (+)-**1** (Table 2, run 1), (c) (±)-**3** (Table 2, run 3), and (d) (+)-**3** (Table 2, run 4).



Scheme 2 Three series of mass numbers initiated by (a) bromide, (b) isobutyl group, and (c) hydride (M = molecular weight of monomer).

in the lowest magnetic field of the four peaks (Fig. 1b). Generally regioregular ring-opening polymerization of propylene oxide proceeds through successive nucleophilic attacks on the less hindered methylene carbon rather than the methine carbon.^{11,24} Accordingly, it is reasonable to assume that the methine carbon retains its configuration and that isotactic polyethers are obtained by using enantiopure epoxide. As a result, the methylene peak at the lowest field of the four should be regarded as a *mm*-triad. By comparing the two charts, four peaks can be assigned as triad [*mm*, *mr* (or *rm*), *mm* (or *mr*), *rr* from lower magnetic field to higher, $P_m = 0.47$].

The polymer obtained from (±)-**3** (Table 2, run 3) also had a regioregular structure. The peak split at 74.2 and 74.3 ppm with an area ratio of 1 : 1 was assigned to a methylene carbon although it is not clear whether it is the one in the main chain or in the side chain (Fig. 1c). Polyether from (+)-**3** (Table 2, run 4) gave only one peak at 74.3 ppm (Fig. 1d). Judging from the above, the two peaks correspond to a diad (*m* and *r* from lower to higher) and $P_m = 0.5$. In contrast to the polymers from **1** and **3**, the polymer obtained from **4** had a regiorregular structure.^{11,12}

It was disclosed that not only bromide but also the isobutyl group and hydride attacked epoxides in the initiation step (Scheme 2a–c). Oligomers from **1** and **3** (monomer/initiator ratio of 11.2) and the polymer from **4** in run 5 of Table 2 were analyzed by MALDI-TOF mass spectrometry. In each case, three series of polymers (a)–(c) were detected corresponding to bromide, isobutyl, and hydride end groups in good accordance with the previous report that Al'iBu₃ could work as both a hydride and an isobutyl anion source in the ring-opening reaction of various epoxides.^{25,26}

In conclusion, fluorinated epoxides were easily polymerized under mild conditions. The obtained polymers had an exclusive regioregular structure. When optically pure epoxides were used, isotactic polymers were obtained. Further application of the product as a new material is now in progress.

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