SHORT COMMUNICATIONS

Center-Propagating Type Polymerization of Thiirane
Using an Acyl-Group Transfer PolymerizationSusumu KAWAKAMI, Atsushi KAMEYAMA, Mitsuhiro MIYATA,
and Tadatomi NISHIKUBO[†]Department of Applied Chemistry, Kanagawa University, Rokkakubashi,
Kanagawa-ku, Yokohama 221, Japan

(Received August 21, 1996)

KEY WORDS Center-Propagating Type Polymerization / Group Transfer Polymerization / Thiirane /
S-Thioesters /

Recently, great attention has been paid to living polymerization aiming at synthesis of polymer with controlled architecture. Living polymerization allows the preparation of block copolymers having a desired sequence and size of blocks. In the case of usual living polymerization using outside-type bifunctional initiators (type I), telechelic polymers can be prepared as shown in Scheme 1.

Scheme 1.

On the other hand, in the case of living polymerization using center-type bifunctional initiators (type II), center-propagating type polymerization proceeds to produce the polymer with reactive groups in the center of the main chain as shown in Scheme 2. Although Kricheldorf *et al.*¹ reported center-propagating type polymerization of lactones induced by $\text{Bu}_2\text{Sn}(\text{OMe})_2$ initiator, this reaction is not a living polymerization. However, there is no report on the synthesis of polymers with bifunctional groups in the center of the main chain, with well-controlled molecular weight, and with sufficiently narrow molecular weight distribution.

Scheme 2.

We reported² recently a new acyl-group transfer polymerization of thiiranes using carboxylic acid derivatives as initiators and quaternary onium salts as catalysts (Scheme 3). That is, this polymerization system involves transfer of terminal-acyl groups in the polymer chain. In this paper, we describe a new example of center-propagating type polymerization using acyl-group transfer polymerization of thiirane initiated by a center-type bifunctional initiator.

A center-type bifunctional initiator, 2,2'-bis-[4-(4-chlorothiophenoxy carbonyl)phenyl]hexafluoropropane (BTTP) (mp 230°C), was prepared in 57% yield by esteri-

Scheme 3.

fication reaction of 2,2'-bis-(4-chloroformyl phenyl)hexafluoropropane with 4-chlorothiophenol using triethylamine as HCl acceptor in THF.

Bulk polymerization of 3-phenoxypropylene sulfide (PPS) was carried out³ using BTTP as initiator and tetrabutylammonium bromide (TBAB) as catalyst at 90°C for 24 h. The polymerization proceeded smoothly to give the corresponding polymer with number-average molecular weight (M_n) of 4500 and molecular weight distribution (M_w/M_n) of 1.20, as estimated by GPC based on the polystyrene standards, in quantitative yield. The structure of the obtained polymer was identified⁴ by IR and ^1H NMR spectra. The IR spectrum showed a characteristic weak absorption due to $\text{C}=\text{O}$ stretching of S-thioester group at 1663 cm^{-1} . The ^1H NMR data supported that the β -cleavage of the thiirane ring of PPS occurred selectively to give the poly(sulfide). Furthermore, a small signal due to aromatic protons of the 4-chlorobenzoyl group was observed at 7.85–7.92 ppm. These results indicate that the resulting polymer has S-acyl groups, which came from the center-type bifunctional initiator BTTP, in the polymer main chain. That is, PPS was polymerized by the initiator BTTP in the presence of TBAB catalyst involving an acyl group transfer in each propagation step (Scheme 4).

Scheme 4.

When the bulk polymerization of PPS using BTTP in the presence of TBAB was carried out at various feed ratios of PPS to the initiator ($[\text{Monomer}]_0/[\text{Initiator}]_0$)

[†] To whom all correspondence should be addressed.

Figure 1. Effect of the feed ratio of monomer and initiator on the bulk polymerization of PPS (10 mmol) using BTTP (x mmol) and TBAB ($2 \times x$ mmol).

Table I. Effect of concentration of monomer on the polymerization^a

Run	Amount of solvent	Time/h	Yield/% ^b	$M_n \times 10^{-3}$ ^c	M_w/M_n ^c
1	0 mL	24	94	4.5	1.20
2	1 mL/ 3.8 mol L^{-1}	72	94	4.8	1.15
3	2 mL/ 1.9 mol L^{-1}	72	89	4.2	1.14

^a The reaction was carried out with PPS (3.77 mmol) and the initiator (0.15 mmol) using TBAB (0.30 mmol) in NMP at 90°C. ^b Insoluble parts in MeOH. ^c Estimated by GPC based on polystyrene standards.

in the range from 25 to 100, polymers were obtained in quantitative yield in every case. As shown in Figure 1, the molecular weight increased linearly with increasing the initial feed ratio ($[\text{Monomer}]_0/[\text{Initiator}]_0$) of PPS. In each feed ratio, M_n of the polymer which estimated by ^1H NMR (Obsd) agreed reasonably with the calculated value from the initial feed ratio (Calcd). This means that the molecular weight of the polymer can be controlled by the initial feed ratio. However, M_w/M_n values ($M_w/M_n = 1.2\text{--}1.3$) of the obtained polymers were larger than that of typical living polymer ($M_w/M_n \approx 1.1$). It seems that the reaction system does not become a real living system due to the low solubility of the initiator. In fact, a white precipitate was observed at the beginning of the polymerization.

To solve this problem, the solution polymerization of PPS was performed in *N*-methyl-2-pyrrolidone (NMP). The solution polymerization was carried out with various concentrations at 90°C for 72 h (Table I). In all cases of solution polymerization, the reaction proceeded homogeneously. When the reaction was carried out with concentration of PPS of 3.8 mol L^{-1} , a polymer with M_n of 4800 and considerably narrow M_w/M_n (1.15) was obtained in 94% yield (Run 2). The M_n value estimated by ^1H NMR (4600) agreed with the theoretical one (4800) calculated from the initial feed ratio. This means that the reaction proceeded in living nature.

To investigate the living nature of this polymerization system, the solution polymerization of PPS with BTTP in the presence of TBAB in NMP was carried out at various feed ratios of PPS to the initiator in the range from 16 to 100, and these results are shown in Figure 2. At each feed ratio, the reaction proceeded smoothly to give a polymer in quantitative yield. The M_n of the polymers at 100% monomer conversion, increased linearly with the initial feed ratio. Moreover, in each feed

Figure 2. Effect of the feed ratio of monomer and initiator on the solution polymerization of PPS (10 mmol) using BTTP (x mmol) and TBAB ($2 \times x$ mmol) in NMP (1 mL).

Figure 3. Change of GPC curve of the post-polymer from the pre-polymer.

ratio, M_n of the polymer which estimated by ^1H NMR agreed reasonably with the calculated value from initial feed ratio. Figure 2 also showed correlation between M_w/M_n and initial feed ratio. The M_w/M_n values of the resulting polymers were fairly small ($M_w/M_n < 1.24$).

Post-polymerization of PPS was carried out using reprecipitated poly(PPS) with M_n of 3700 and M_w/M_n of 1.13 as macro-initiator and TBAB as catalyst in NMP at 90°C for 72 h. As shown in Figure 3, the reaction proceeded successfully from the pre-polymer to the post-polymer with M_n of 8700 and M_w/M_n of 1.28 in 98% yield. The M_n of the post-polymer was also calculated at 9300 by ^1H NMR analysis based on the signals at 7.85–7.92 ppm, which agreed reasonably with the theoretical one (8800) calculated from the initial feed ratio. This means that poly(PPS) with center *S*-thioester groups act efficiently as initiator for the post-polymerization of PPS.

In conclusion, center propagating type acyl-group transfer polymerization of thiirane was successfully achieved using the center-type bifunctional initiator BTTP. Moreover, this solution polymerization system has a high degree of living nature. We believe that this new living polymer has potential importance as a starting polymer for synthesis of various polymers with novel structures.

REFERENCES AND NOTES

1. H. R. Kricheldorf, S. R. Lee, and N. Scharnagl, *Macromolecules*, **27**, 3139 (1994).
2. a) A. Kameyama, K. Shimotsuma, and T. Nishikubo, *Macromol. Rapid Commun.*, **15**, 335 (1994). b) A. Kameyama, K. Shimotsuma, and T. Nishikubo, *Polym. J.*, **28**, 66 (1996).
3. The experimental procedure was as follows. TBAB (0.096 g, 0.30 mmol) was placed in an ampule under dry atmosphere, and dried under reduced pressure at 60°C for 5 h. PPS (0.623 g, 3.75 mmol) and the initiator (0.097 g, 0.15 mmol) was added into the tube, then the tube was sealed followed by heating at 90°C for 24 h. The reaction mixture was diluted with a small amount of chloroform then poured into methanol. The recovered polymer was reprecipitated in CHCl₃/methanol and then collected by decantation and dried under reduced pressure to give final product. Yield = 0.767 g (94%). The polymer yield was calculated by the following equation, Yield (%) = $[W/(I + T)] \times 100$, in which *W* is weight of the obtained polymer, *I* and *T* are weights of the initiator and the used thiirane monomer, respectively.
4. IR (neat): 2926 (ν_{C-H}), 1663 ($\nu_{C=O}$), 1598 ($\nu_{C=C}$ of Ar), 1239 cm⁻¹ (ν_{C-O-C}). ¹H NMR (CDCl₃): δ 2.95–3.11 (m, 3.0H, S-CH(CH₂)CH₂O), 3.95–4.23 (m, 2.0H, CH₂-OPh), 6.82–7.19 (m, 5.4H, aromatic H), 7.85–7.92 (m, 0.2H, aromatic H).