Synthesis of Polythiourethane-Based Macro Chain Transfer Agents and Their Block Copolymers with Vinyl Monomers via Controlled Multimode Polymerization

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Living polymerization[1−7] is the most advanced synthetic methods in the field of polymer synthesis, and one of the leading methods to design block copolymers through the sequential monomer addition technique. Although this technique for formation of block copolymers can be achieved easily in a one-pot synthesis, this method is restricted by relative monomer reactivity. Multimode polymerization proves to be promising due to limitations on synthesizing different block copolymers by using a single type of propagating species. The polymerization involving macro chain transfer agents (maroCTAs), classified on the basis of interconversion between various propagating mechanisms.[7,8] Thang et al. have reported that poly(ethylene oxide)-*block*-polystyrene was synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization with commercially available hydroxyl end-functional poly(ethylene oxide) as a macroCTA.[7] Using similar strategies, synthesis of various block copolymers has been also achieved, e.g., poly(ethylene-*co*-butylene)-*block*-poly(styrene-*co*-maleic anhydride),[9] poly(lactic acid)-*block*-poly(methyl methacrylate),[10] poly(lactic acid)-*block*-poly(*N*-isopropylacrylamide),[11] and so on. These techniques are promising methods for the design of various other copolymers, which were prepared by radical or anionic to RAFT transformation. On the contrary, the synthesis of block copolymers by the combination of cationic, especially cationic ring-opening, and RAFT polymerization have not yet been reported. A candidate approach is the end-capping reaction of a living polymer with an appropriate terminating reagent, because this strategy has been widely applied to construction of various copolymers, i.e., transformation of a propagating end for block copolymerization.[12] Previously, we have been successful in quantitative end-capping reaction of the growing end in the obtained polythiourethane with dithiocarbamates as terminating reagents after controlled cationic ring-opening polymerization of cyclic thiourethane.[13] In this communication, we investigate the synthesis of well-defined macro chain transfer agents (macroCTA) based on polythiourethane obtained by controlled cationic ring-opening polymerization and end-capping reaction of the growing end with dithiocarbamates, and the synthesis of block copolymers via reversible addition−fragmentation chain transfer (RAFT) process.

For the synthesis of macroCTAs, we employed 3-methyl-5-phenyloxazolidine-2-thione (MPOT) as a cyclic monomer, which was prepared by the reaction of α-(4-methylaminomethyl)benzyl alcohol and thiophosgene in the presence of triethylamine in dry tetrahydrofuran (THF) at 60 °C. With methyl trifluoromethanesulfonate (TfOMe) ($[\mathrm{MPOT}]/[\mathrm{TfOMe}] = 10$) as an initiator, the cationic ring-opening polymerization of MPOT was conducted in CH_2Cl_2 at 30 °C under nitrogen atmosphere for 17 h, and was quenched by the addition of dithiocarbamates, sodium 1-pyrrolecarbodithioate and diethylammonium *N*,*N*-diethyldithiocarbamate,[14,15] to afford the corresponding macroCTAs in quantitative yields (Scheme 1). The size-exclusion chromatography (SEC) analysis of the obtained macroCTA1 and macroCTA2 showed unimodal peaks (number-average molecular weights (M_n) of macroCTA1 and macroCTA2 were estimated to be 2200 and 2100 whose distributions ($M_w/M_n = 1.10$ and 1.11) were narrow enough. These M_ns were in excellent agreement with the theoretical values (macroCTA1: 2090 and macroCTA2: 2096) based on the feed ratio.[16] By conducting the ^{1}H NMR spectroscopy on the obtained polymers, we confirmed that the terminal ends in the obtained polymers have the structure of CTAs, i.e., (a) α-methylbenzyl 1-pyrrolecarbodithioate (h, i, j, and k) and (b) diethyldithiocarbamate structures (h, i, j, and k) (see Supporting Information Figure 1S). To check the controlled nature on cationic ring-opening polymerization of MPOT with TfOMe as an initiator, we investigated the correlation between the feed ratio of monomer MPOT to TfOMe and the molecular weight of the obtained polymer. The molecular weight increased linearly in proportion to the feed ratio, and molecular weight was controlled by the amount of TfOMe (see Supporting Information Figure 2S). Further, narrow unimodal SEC peaks ($M_w/M_n = 1.05-1.10$) are observed for the polymers obtained at quantitative conversion (>99%), clearly indicating that the cationic polymerization of MPOT proceeded through a controlled nature similar to a previously reported study.[17,18]

Prior to RAFT polymerization with macroCTAs, we examined the RAFT polymerization of vinyl monomers with modelCTAs to establish the optimum conditions and select applicable vinyl monomers for the polymerization with maroCTAs. ModelCTAs were synthesized by the addition of sodium 1-pyrrolecarbodithioate or diethylammonium *N*,*N*-diethyldithiocarbamate and stable cyclic *endo*-iminothiocarbonate triflate salt (ITCB)[14] obtained from MPOT with TfOMe (Scheme 2). The modelCTAs of pyrrole- and diethyl-types, CTA1 and CTA2, were obtained in 62 and 73% yields, respectively. Vinyl monomers such as styrene (St), methyl methacrylate (MMA), and *N*,*N*-dimethylacrylamide (DMAm) was radically polymerized using CTA1 and CTA2 with AIBN as an initiator in various concentrations. The results are summarized in Table 1. When the polymerization of St were carried out using CTA1 with AIBN at $[M]_0/[CTA]_0/[I]_0 = 100/2/1$ in chlorobenzene (2 M) at 60 °C for 20 h, the molecular weight ($M_n = 2200$) of the crude polymer were good agreement with the theoretical value ($M_n = 2000$) calculated from monomer/CTA molar ratio and the monomer conversion (run 1). The molecular weight distribution showed unimodal peaks without shoulders and tailings, and it was narrow enough ($M_w/M_n = 1.16$). When DMAm was employed for the polymerization, the molecular weight was

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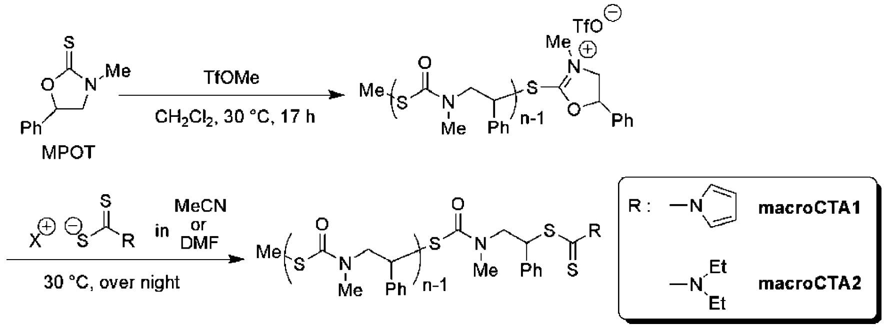
Scheme 1. Synthesis of Macro Chain Transfer Agents (macroCTAs)



Scheme 2. Synthesis of Macro Chain Transfer Agents (macroCTAs) and Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization of Vinyl Monomers

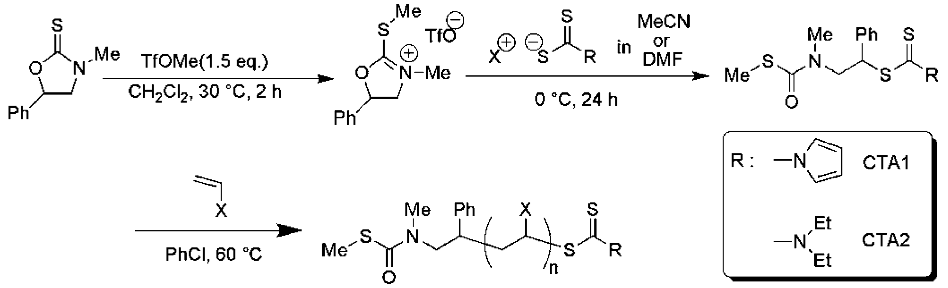


Table 1. Polymerization of Vinyl Monomers Using 2,2′-Azobis(isobutyronitrile) (AIBN) in Chlorobenzene at 60 °C[a]

run	monomer[b]	CTA	concn (mol/L)	time (h)	convn[c] (%)	M_n[d](theory)	M_n[e](SEC)	M_w/M_n[e](SEC)
1	St	CTA1	2	20	43	2000	2200	1.16
2	St	CTA2	2	20	69	3600	16 000	2.83
3	MMA	CTA1	2	3	65	3300	30 400	1.48
4	MMA	CTA2	2	20	93	4600	12 000	1.56
5	DMAm	CTA1	1	3.5	71	3500	1900	1.12
6	DMAm	CTA2	1	20	99	4900	23 000	2.02

[a] $[M]_0/[CTA]_0/[I]_0 = 100/2/1$. [b] Abbreviations (monomers): St = styrene, MMA = methyl methacrylate, and DMAm = *N*,*N*-dimethylacrylamide. [c] Determined by ^{1}H NMR spectroscopy. [d] M_n(theory) = ([monomer]/[CTA]) × conversion × MWt of monomer. The above expression does not include the small number of chains formed from the initiator. It also assumes complete consumption of the chain transfer agent. [e] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*′-dimethylformamide (DMF, 50 mM LiBr).

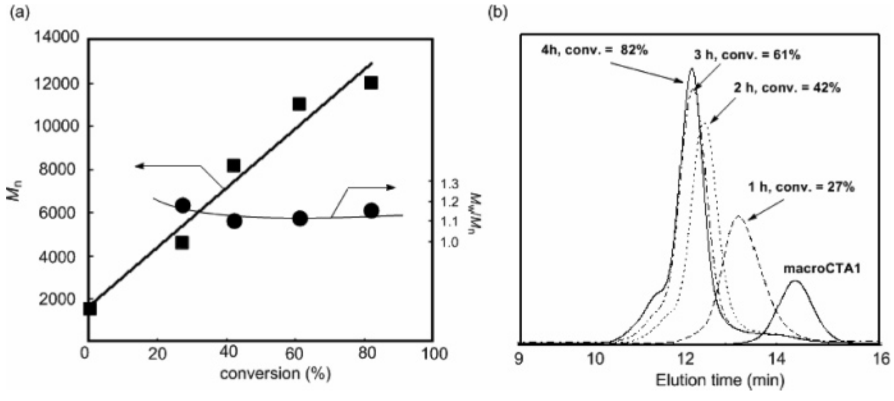


Figure 1. (a) Number-average molecular weight and molecular weight distribution as a function, and (b) evolution of SEC traces with conversion for the polymerization of DMAm with AIBN in the presence of macroCTA1 in PhCl at 60 °C. $[\text{maroCTA1}]_0/[\text{AIBN}]_0 = 2$.

lower than the theoretical value (run 5). However, the distribution of polyDMAm was narrower than that of polySt, and the conversion was higher after a short reaction time. The polymerization of MMA provided a polymer with higher molecular weight ($M_n = 30\,400$) and broader distribution ($M_w/M_n = 1.48$). In the cases using CTA2 (runs 2, 4, and 6), the molecular weights of all polymers could not be controlled, and the distributions were also very wide. As a reason, we consider that the chain transfer constant (C_{tr}) of the CTA2 analogous structure to *N*,*N*-diethyl *S*-benzyl dithiocarbamate is lower than that of CTA1 to benzyl 1-pyyrolecarbodithioate.[19] These results indicate that CTA1 is suitable for the RFAT polymerization of vinyl monomers, except for MMA.

Under the same experimental conditions as used for the modelCTAs, St and DMAm were polymerized in PhCl (2 M) at 60 °C to afford the corresponding block copolymers, in the presence of AIBN and macroCTA1 ($M_n = 1500$, $M_w/M_n = 1.13$, $[\text{MPOT}]_0/[\text{TfOMe}]_0 = 7.0$). The polymerization with St at a ratio of $[M]_0/[\text{macroCTA1}]_0/[\text{AIBN}]_0 = 200/2/1$ was very slow, as evidenced by a very gradual increase in conversion, i.e., only

44% and 74% conversions even after 24 and 48 h, respectively. Although no significant shoulder peaks at high molecular weight regions were observed in SEC curves, tiny tailings can be seen, suggesting that a small amount of residual low molecular weights dead chains remains in the final produce. Nevertheless, polydispersity index remained below 1.5 (see Supporting Information Figure 3S). When DMAm was employed for the polymerization at a same constant value, relatively high conversion (82%) was reached after 4 h. The polymerization is relatively fast with conversions of 27, 42, 61, and 82% at reaction times of 1, 2, 3, and 4 h. Figure 1a shows the evolutions of M_n and M_w/M_n with conversion for DMAm during the polymerizations at a constant value similar to St. The molecular weights increase linearly with conversion. The experimental molecular weights were higher than the calculated ones. The SEC traces obtained at different polymerization times clearly illustrate the increase in molar mass with time (Figure 1b), having unimodal peaks with a tiny shoulder between 61 and 82% conversion. The formation of a high molecular weight shoulder was observed due to dead chains, which are formed for every mole of initiator decomposed in high initiator concentration.[16] Regardless of the SEC peaks having a shoulder, its molecular weight distributions remained below 1.2. These results indicate that macroCTA1 acted effectively as chain transfer agent for the RAFT polymerization of St and DMAm.

In summary, we could demonstrate the first example of well-defined AB block copolymers based on polythiourethane by RAFT polymerization of vinyl monomers using macroCTAs. MacroCTAs were prepared by efficiently end-capping reaction of the growing end after controlled cationic ring-opening polymerization of cyclic thiourethane (MPOT). MacroCTA1 having α-methylbenzyl 1-pyrrolecarbodithioate structure in the terminal end proved to be effective chain transfer type in RFAT polymerization of St and DMAm to afford the AB block copolymers with narrow molecular weight distributions after RAFT polymerization conditions of vinyl monomers were investigated by employing modelCTAs, which were synthesized by the addition of dithiocarbamates and a stable cyclic *endo*-iminothiocarbonate triflate salt obtained from MPOT and TfOMe.

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Supporting Information Available: Text giving typical experimental procedures and figures showing the ^{1}H NMR of macroCTAs, controlled nature of cationic polymerization of MPOT, and evolution of SEC traces with conversion for the polymerization of St. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The theoretical values of macroCTAs was calculated as follows. MacroCTA1: M_n (theoretical) = (formula weight of MPOT; 193.27) × ([MPOT]/[TfOMe]; 10) + [formula weight of end groups; the initiating group (15.03) and MPOT at the terminal group (148.27)]. MacroCTA2: M_n (theoretical) = (formula weight of MPOT; 193.27) × ([MPOT]/[TfOMe]; 10) + [formula weight of end groups; the initiating group (15.03) and MPOT at the terminal group (142.22)].

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