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Sequential Cationic and Anionic Polymerizations by Triflate Complexes of Bulky Titanium Bisphenolates: One-Pot Synthesis of Polyoxetane−Poly(ϵ-caprolactone) Block Copolymer

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In general, electrophilic species hardly coexist with nucleophilic reagent, since they are highly subject to degradative neutralization with each other. On the other hand, when they are sterically hindered, such a degradative reaction can be suppressed. We have shown that bulky nucleophiles such as aluminum porphyrin complexes of enolates and alkoxides can coexist with sterically hindered Lewis acids such as aluminum 2,6-disubstituted phenolates.[1] This has enabled high-speed living anionic polymerization, where the bulky Lewis acids enhance the nucleophilic reactivity of monomers through coordination and accelerate the anionic chain growth in a controlled fashion.[2] As a conceptual extension of this methodology, we herein report sequential one-pot cationic and anionic polymerizations of oxetane (OX) and ϵ-caprolactone (CL) using triflate complexes of sterically hindered titanium bisphenolates.

When silver triflate (1.1 equiv) was added at 25 °C under Ar to a CH_2Cl_2 solution of bulky dichlorotitanium bisphenolate **2a**, the solution immediately turned from dark red to dull red. After stirring for 1 h, the reaction mixture was filtered and evaporated, and the residue was recrystallized from THF/hexane (1/1) under Ar, affording a monochloro−monotriflate complex **2b**·$(thf)_2$ as dark-red cubic crystals. X-ray crystal structure analysis gave an ORTEP view of the complex, in which the triflate group is attached in a monodentate fashion to the octahedral titanium center at a distance of 2.06 Å.[3]

ϵ-Caprolactone (CL) can be polymerized both anionically and cationically, while oxetane (OX) is polymerizable mostly cationically with a few exceptions.[4] We previously investigated titanium alkoxide (**1c**, **2c**) and dichloride (**1a**, **2a**) complexes of bulky bisphenolates as initiators for the ring-opening polymerization of these two monomers and reported that CL can be polymerized with the titanium alkoxides (**1c**, **2c**) in a controlled fashion, whereas OX is not polymerized by either of the above two initiators.[5] In contrast, we found that titanium triflate complexes of bulky bisphenolates (**1b**, **2b**) polymerized both CL and OX. For example, when 50 equiv of OX was added under Ar to a CH_2Cl_2 solution (3 mL) of **1b** (1 mmol), the solution turned bright red, characteristic of titanium alkoxide complexes of bisphenolates,[5] and the polymerization took place at 25 °C to reach 100% monomer conversion in 54 h, affording a polyether with M_n and M_w/M_n of 2900 and 1.25, respectively.[6] The degree of polymerization (DP_n) of the polymer (50) agreed well with the monomer-to-initiator (**1b**) mole ratio. On the other hand, the polymerization of CL by **1b** (0.1 mmol, $[CL]_0/[\mathbf{1b}]_0 = 100$) under similar conditions was also controlled, to give at 85% monomer conversion (24 h) a polyester with M_n and M_w/M_n of 8200 and 1.24, respectively.

We also found that the titanium triflate complexes can copolymerize OX and CL. For example, when an equimolar mixture of OX and CL was added at 25 °C to a CH_2Cl_2 solution of **2b** at a mole ratio $[OX]_0/[CL]_0/[\mathbf{2b}]_0$ of 100/100/1, both monomers were consumed (■ and ●, Figure 1) to give a copolymer with M_n of 11 000 and M_w/M_n of 1.60 (100 and 49% conversions for OX and CL, respectively) in 20 h. ^{1}H NMR analysis of the copolymer showed the presence of both cross and homo sequences,[7] in which the contents of the cross sequences [OX → CL]/

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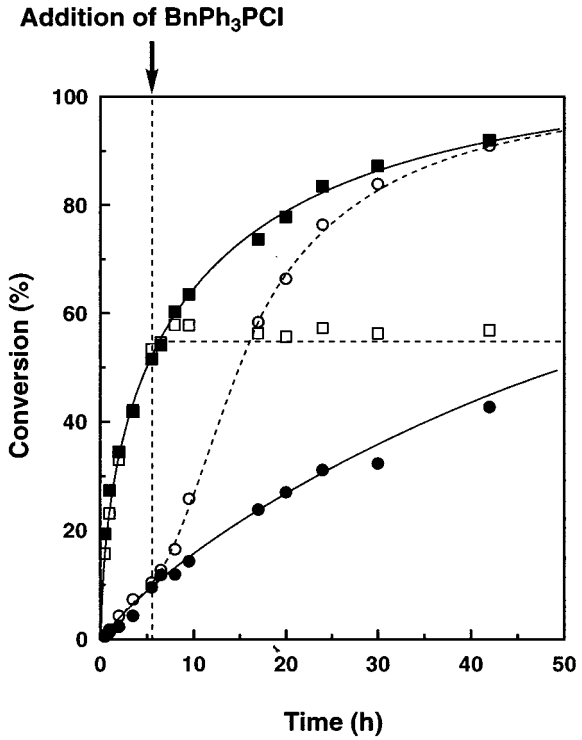


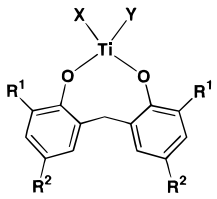
Figure 1. Copolymerization of oxetane (OX, ■) and ϵ-caprolactone (CL, ●) initiated with titanium triflate **2b** ($[OX]_0/[CL]_0/[\mathbf{2b}]_0 = 100/100/1$) in CH_2Cl_2 at 25 °C. Plots □ (OX) and ○ (CL) represent the time course of the copolymerization when $BnPh_3PCl$ (1.5 equiv with respect to Ti) was added in 5.5 h after the initiation.

([OX → OX] + [OX → CL]) and [CL → OX]/([CL → CL] + [CL → OX]) were 13 and 8%, respectively. In contrast, use of titanium alkoxide **2c**, in place of **2b**, for the copolymerization generated a homopolymer of CL without consumption of OX.[5]

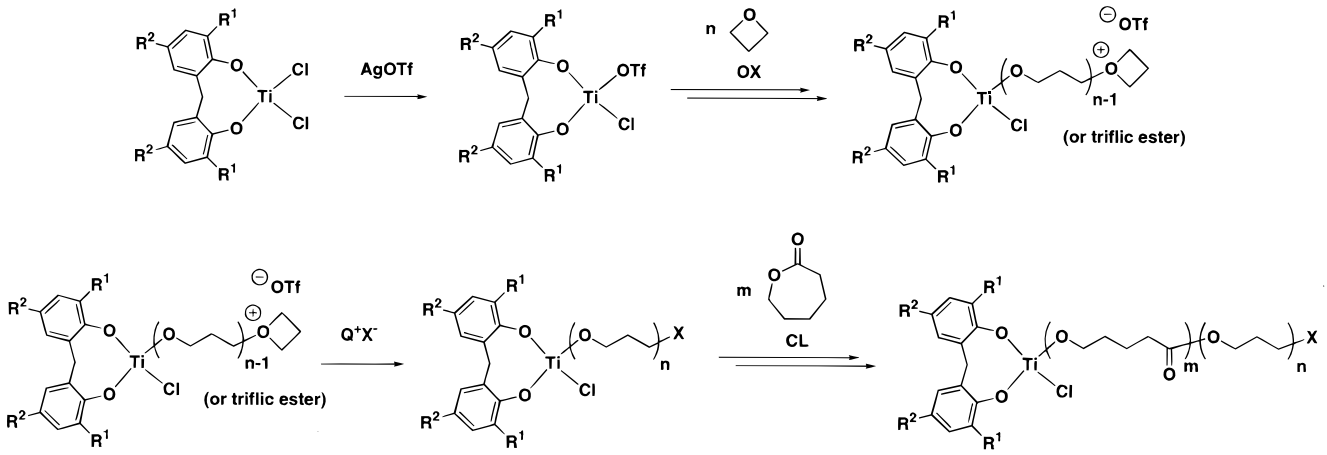
The polymerization of OX most likely proceeds cationically according to Scheme 1, in which the growing polymer has an oxonium triflate (or triflic ester) reactive end with a titanium alkoxide, inert for the polymerization of OX,[5] at the other chain end. In fact, the polymerization of OX was terminated by onium halides such as benzyltriphenylphosphonium chloride ($BnPh_3PCl$) and ethyltriphenylphosphonium bromide ($EtPh_3PBr$) or a protic reagent such as MeOH. Furthermore, addition of $BnPh_3PCl$ (1.5 equiv with respect to **2b**) to the copolymerization system completely inhibited OX polymerization (Figure 1, □), whereas that of CL continued with some acceleration[8] (Figure 1, ○). In relation to these results, a CH_2Cl_2 solution of $EtPh_3PBr$ (1.1 equiv with respect to Ti) was added to the polymerization mixture of OX with **1b** ($[OX]_0/[\mathbf{1b}]_0 = 20$, 100% monomer conversion), and the polymer was isolated by column chromatography on silica gel. The ^{13}C NMR spectrum in $CDCl_3$ of the polymer (δ 67.7 [OCH_2], 30.0 [CH_2]) showed relatively weak signals due to a bromopropyl end group (δ 32.7 [$BrCH_2$], 31.0 [CH_2], 67.5 [CH_2O])[9] originating from the reaction of the electrophilic growing end with Br^- and those due to a hydroxypropyl end group (δ 62.2 [$HOCH_2$], 32.3 [CH_2], 70.4 [CH_2O]) resulting from protonation of the titanium alkoxide ω-end. The relative intensity of these two signals was close to unity. Although **1b** also bears a potential reactive Cl−Ti bond,[5] no chlorinated end group was observed for the polymer. On the other hand, when MeOH was added instead of $EtPh_3PBr$ to the polymerization system, a polyether with methoxypropyl (δ 58.8 [MeO], 70.0 [$MeOCH_2$], 30.3 [CH_2], 67.9 [CH_2O])[10] and hydroxypropyl end groups was isolated.

These observations also suggest that titanium alkoxide remains intact at the ω-end of poly(OX), and the cationic polymerization proceeds cleanly without backbiting and chain-coupling reactions between the electrophilic and nucleophilic end groups. Since the titanium alkoxide is nucleophilic enough to initiate polymerization of CL,[5] we investigated the possibility of a one-pot block copolymerization of OX and CL (Scheme 1).

Scheme 1



1a: $R^1 = {}^{tert}Bu$, $R^2 = Me$, X = Y = Cl
1b: $R^1 = {}^{tert}Bu$, $R^2 = Me$, X = Cl, Y = OSO_2CF_3
1c: $R^1 = {}^{tert}Bu$, $R^2 = Me$, X = Y = $OCH(CH_3)_2$
2a: $R^1 = Ph$, $R^2 = H$, X = Y = Cl
2b: $R^1 = Ph$, $R^2 = H$, X = Cl, Y = OSO_2CF_3
2c: $R^1 = Ph$, $R^2 = H$, X = Y = $OCH(CH_3)_2$
3: $R^1 = H$, $R^2 = Me$, X = Cl, Y = OSO_2CF_3



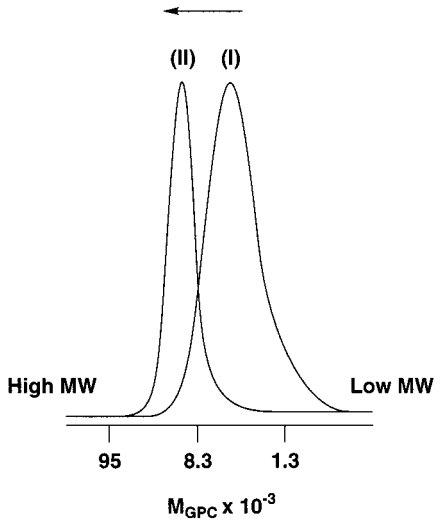


Figure 2. Block copolymerization of oxetane (OX) and ϵ-caprolactone (CL) initiated with **1b** ($[OX]_0/[CL]_0/[\mathbf{1b}]_0 = 50/100/1$) in CH_2Cl_2 at 25 °C: $EtPh_3PBr$ (1.5 equiv with respect to Ti) was added to the system before addition of CL. GPC chromatograms of the prepolymer of OX (I: $M_n = 2700$, $M_w/M_n = 1.29$; 100% OX conversion) and the block copolymer of OX and CL (II: $M_n = 11\,000$, $M_w/M_n = 1.15$; 100% CL conversion).

Thus, OX was polymerized with **1b** ($[OX]_0/[\mathbf{1b}]_0 = 5$ mmol/0.1 mmol) in the first stage up to 100% monomer conversion ($M_n = 2700$, $M_w/M_n = 1.29$; Figure 2 (I)), and after quenching the electrophilic growing end with $EtPh_3PBr$ (0.15 mmol), CL (10 mmol) was added to the system. As expected, CL polymerized to attain 54 and 100% monomer conversion in 6 and 18 h, respectively. GPC analysis of the polymer showed a unimodal sharp elution peak ($M_n = 11\,000$, $M_w/M_n = 1.15$; Figure 2 (II)) at a higher molecular weight region than that of the prepolymer of OX (Figure 2 (I)), indicating the controlled formation of a polyoxetane−poly(ϵ-caprolactone) block copolymer. The contents of OX and CL in the block copolymer, as determined by ^{1}H NMR, were 36 and 64%, respectively. Second-stage polymerization of CL without quenching the electrophilic growing terminal with Br^- generated a block copolymer with a little broader molecular weight distribution ($M_n = 16\,000$, $M_w/M_n = 1.30$). Coexistence of the electrophilic and nucleophilic species in the polymerization with **1b** is most likely due to steric hindrance of the titanium alkoxide terminal by the bulky *tert*-butyl groups on the bisphenolate ligand, since use of a triflate complex (**3**) with a less bulky bisphenolate ligand resulted in a poorly controlled polymerization of OX ($M_n = 2800$, $M_w/M_n = 1.53$ at 100% monomer conversion). Furthermore, upon addition of CL to the above polymerization mixture, CL was not polymerized irrespective of whether or not the system was pretreated with onium halide.

In conclusion, we have demonstrated for the first time the one-pot synthesis of a novel block copolymer of oxetane and ϵ-caprolactone by sequential cationic and anionic polymerizations with titanium triflate complexes (**1b** and **2b**), in which the bulky bisphenolate ligands allow the cationic (oxonium triflate or triflic ester) and anionic species (titanium alkoxide) to coexist for a sufficiently long time without degradative neutralization.

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Supporting Information Available: Polymerization of CL by a titanium monoalkoxide complex in the presence of $BnPh_3PCl$, ^{1}H NMR chart of poly(OX-*co*-CL), and ^{1}H NMR, UV/vis, and crystal data of **2b**·$(thf)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Molecular weights (M_n and M_w), estimated by GPC calibrated with polystyrene standards, were multiplied by a factor of 0.6 for all polymer samples. See refs 4 and 5.
(7) ^{1}H NMR ($CDCl_3$): OX → OX, δ 3.49 ($-(CH_2)_2CH_2O(CH_2)_3O-$); OX → CL, 4.16 ($-(CH_2)_2CH_2OC(O)(CH_2)_5O-$); CL → CL, 4.07 ($-C(O)(CH_2)_4CH_2OC(O)(CH_2)_5O-$); CL → OX, 3.40 ($-C(O)(CH_2)_4CH_2O(CH_2)_3O-$).
(8) A similar acceleration effect of $BnPh_3PCl$ was observed for the polymerization of CL by a titanium monoalcoholate complex of bulky bisphenolate.[5] See Supporting Information.
(9) On reference to $BrCH_2CH_2CH_2CH_3$. ^{13}C NMR ($CDCl_3$): δ 34.7 ($BrCH_2$), 33.6 ($BrCH_2CH_2$), 21.2 (CH_2CH_3), and 13.1 (CH_3).
(10) On reference to $CH_3OCH_2CH_2CH_2OH$. ^{13}C NMR ($CDCl_3$): δ 59.0 (CH_3), δ 59.0 (CH_3), 71.8 (OCH_2), 32.2 (CH_2), and 61.7 (CH_2OH).

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