Highly Tolerant Living/Controlled Anionic Polymerization of Dialkyl Acrylamides Enabled by Zinc Triflate/Phosphine Lewis Pair
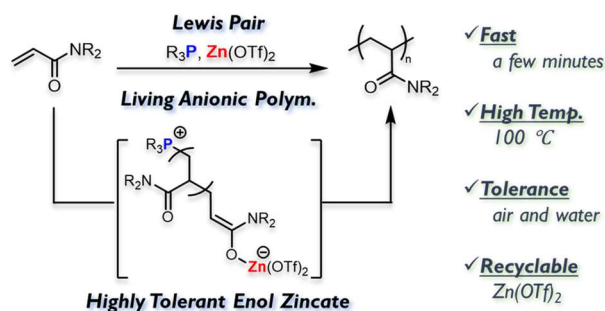
Riki Akita and Shin-ichi Matsuoka*

Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466-8555, Japan

Corresponding Author: Shin-ichi Matsuoka

http://orcid.org/0000-0001-7488-9971; E-mail: matsuoka.shinichi@nitech.ac.jp, Tel: +81-52-735-7254

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ABSTRACT

Living polymerizations of polar vinyl monomers have been successful for decades. However, they still suffer the following challenges: fast propagation, air/moisture tolerance, and negligible side reactions even at elevated temperatures. Here, we developed an unprecedented polymerization that overcomes these limitations using a Lewis pair catalyst. The anionic polymerization of dialkyl acrylamides proceeded in a living/controlled matter using $Zn(OTf)_2/PPh_3$ within a wide temperature range of 25–100 °C for short times (1–10 min) even under open-air conditions. The recovery and reuse of $Zn(OTf)_2$ without loss of polymerization activity were observed to be possible. The polymerization was retarded by excess $Zn(OTf)_2$, additive methanol, and water, indicating equilibriums of the propagating species with them. The putative propagating zinc triflate-ate complex was tolerant to the protic additives and significantly selective for the propagation.

Keywords

Lewis pair, living anionic polymerization, acrylamides, zincate

Living/controlled polymerization is an essential technique for producing well-defined polymers, which enables an understanding of the polymer structure–property relationship and the material application thereof. Reversible-deactivation radical polymerization (living radical polymerization) has been widely employed for this purpose owing to its tolerance for a wide range of functional groups and operational simplicity. However, the propagation must be slowly conducted under inert or specific conditions to circumvent the undesired bimolecular termination and oxygen deactivation.[1–7] Oppositely, living anionic polymerization (including organometallic-mediated polymerization) can proceed faster and achieve a relatively higher control of the polymer structure (molecular weight, distribution, tacticity, and chain-end functionalization).[8–10] However, the initiator and propagating metal enolate are inherently highly reactive toward various polar functions, e.g., acidic hydrogen and carbonyls.[11–14] Therefore, the polymerization must be conducted under stringently purified conditions at moderate or low temperatures by adding additives as needed to obtain reproducible polymerization outcomes. In this context, the development of reliable and universal procedures for highly tolerant living/controlled anionic polymerization is an important and challenging issue to overcome.[15]

Frustrated Lewis pairs have received considerable interest in the fields of catalysis, polymers, and material sciences.[16,17] The Lewis pair (LP) polymerizations[18–20] of polar vinyl monomers catalyzed by aluminum-,[21–32] borane-,[33–37] rare-earth[38–40] and late transition metal-based LPs[41–43] have been performed. Notable features of LP polymerization are that (1) propagating enolates, derived from Lewis acids (LAs), i.e., enolaluminates and enolborates, are well-defined. In addition, (2) highly active propagating enolates can be generated via the cooperative activation of monomers even using relatively low reactive (e.g., air/moisture stable) LAs and Lewis bases (LBs).[37]. Rieger[23] and Zhang[25] et al. reported the living/controlled polymerization of dialkyl acrylamides using triphenyl aluminum-based LPs to rapidly produce high molecular weight polymers. Hon et al. reported an air-tolerant borane/phosphine LP for the acrylate polymerizations even at high temperatures and under open-air conditions (exposing the air for 3

min and then sealing)[35]. We have harnessed water-tolerant metal triflate-based LPs for polymerizations in organic solvents and on-water,[41–43] where the metallic elements (Sc, Y, Fe, Cu, Zn, Ga, In, and Sn) and solvents affect the propagating mechanisms (anionic or radical polymerization).[43] LP polymerization is a rapidly growing area of research because LA-derived propagating enolates, showing distinctive reactivity from alkaline metal enolates, enable precise polymer synthesis that cannot be achieved by conventional anionic polymerization.

Compared with ring-opening polymerization,[44–46] the polymerization of polar vinyl monomers using zinc catalysts or zinc counterions remains considerably less explored. Several notable examples include an isolated cationic zinc enolate,[47] a higher-order zincate complex of tBu$_4$ZnLi$_2$,[48–51] and dialkylzincs.[9,13,52–54] The polymerization using tBu$_4$ZnLi$_2$ proceeds even in the presence of protic reagents.[48–51] An anionic propagation via enol zincates has been proposed; however, the possibilities of free-radical generation in water-accelerated polymerization have not been debated. Living anionic polymerization via alkali metal enolates has been achieved by adding excess dialkylzincs.[9,13,52–54] The lowered polymerization rate[52] suggests that intermediary enol zincates would be formed during the polymerization. Although these previous studies suggest that enol zincates seem to be promising propagating species, mechanistic considerations using well-defined enol zincates are required to explore their potential.

Herein, we report the living/controlled anionic polymerization of acrylamides catalyzed by LPs comprising Zn(OTf)$_2$ and phosphines (PPh$_3$ or PCy$_3$). The polymerizations were completed within minutes at high temperatures and were tolerant to MeOH, water, and open-air conditions. A highly tolerant anionic polymerization mechanism involving enol zincates is explained based on various polymerization studies: molecular-weight control, kinetics, additive effects, and the recyclability of Zn(OTf)$_2$.

We initially investigated the solvent effects on the polymerization of N,N-diethyl acrylamide (DEAA) using $Zn(OTf)_2/PCy_3$ ($[M]_0:[LA]_0:[LB]_0 = 80:2:1$) at 25 °C for 4 h (entries 1–8, Table S1). The polymerization was initiated by adding DEAA to the $Zn(OTf)_2/PCy_3$ mixture. The polymerization quantitatively proceeded in dichloromethane (DCM), toluene, and PhCl to afford poly(DEAA) with narrow molecular weight distributions (M_w/M_n, $Đ$) of less than 1.2. The polymerization in tetrahydrofuran (THF) and chloroform afforded good yields and relatively high $Đ$ values (1.39, THF; 11.0, chloroform). No polymer was obtained in N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and methanol presumably because of their coordination to the Zn center (Table S1). The use of PPh_3, instead of PCy_3, yielded similar polymerization results (entries 1 and 9, Table S1). The polymerization using $Zn(OTf)_2/P^tBu_3$ afforded the polymer with a slightly broad $Đ$ value (>1.3) with 88% conversion (entries 10, Table S1). The use of $Zn(OTf)_2/PMes_3$, $Zn(OAc)_2/PR_3$, and $Zn(NTf_2)_2/PR_3$ in DCM were ineffective for the polymerization (entries 11–16, Table S1). Additionally, no polymers were obtained using either PCy_3 or $Zn(OTf)_2$ alone.

Table 1 summarizes the polymerization results using $Zn(OTf)_2/PCy_3$. The $Đ$ values slightly broadened with a decrease in $[LA]_0/[LB]_0$ ratio from 2 to 0.2 (entries 1–4, Table 1). The M_n values obtained at the ratios of 2 and 1 were practically equal and close to the theoretical values, assuming that one polymer chain was formed from one LB (entries 1 and 2, Table 1). However, M_n values exceeding the theoretical values were obtained at the ratios of 0.4 and 0.2 but were dependent on the $[M]_0/[LA]_0$ ratio (entries 3 and 4, Table 1). These results showed that one molecule of each PCy_3 and $Zn(OTf)_2$ was required to initiate and propagate one polymer chain. Higher-molecular-weight polymers with narrow $Đ$ values were synthesized at the $[M]_0:[LA]_0:[LB]_0$ ratios of 200:2:1 and 400:2:1 at 25 °C for 4 h and 17 h, respectively (entries 5 and 6, Table 1; size exclusion chromatography (SEC) and proton nuclear magnetic resonance (^{1}H NMR) results in Figure S1(a) and S2(a), respectively). The M_n values linearly increased with the conversion maintaining narrow $Đ$ values with monomodal SEC chromatograms (Figures 1(A)

and S1(b)). The active chain end of the polymer (M_n = 9,500, $Đ$ = 1.25) synthesized using $Zn(OTf)_2$/PCy$_3$ ([M]$_0$:[LA]$_0$:[LB]$_0$ = 80:2:1, in PhCl, for 45 min, 90% conv.) was extended by the addition of equimolar DEAA without a deactivated polymer chain to yield twice the M_n of 17,500 and a narrow $Đ$ of 1.34 (Figure S1(c)). The matrix-assisted laser desorption ionization–time-of-flight mass spectrometry (MALDI-TOF-MS) spectrum indicated the initiating $^+$PCy$_3$ and hydrogen termini (Figure S3). The M_n (obtained at [M]$_0$:[LA]$_0$:[LB]$_0$ = 40:1:1) estimated by the ^{1}H NMR integral ratio was consistent with that estimated by SEC and the theoretical value ($M_{n,SEC}$ = 5,700, $M_{n,NMR}$ = 6,020, $M_{n,theor.}$ = 5,340) (Figure S4). Overall, these experiments showed that the polymerization proceeded in a living manner. In addition to the DEAA polymerization, N,N-dimethyl acrylamide (DMAA) and 4-acryloylmorpholine (AMO) were polymerized under similar conditions to afford polymers with narrow $Đ$ values (entries 12 and 13, Figures S2(b)(c)). The copolymerization of DEAA and AMO afforded the corresponding poly(DEAA-ran-AMO), wherein the random sequence was supported by comparing the monomer consumption rates (Figure S5). The block copolymer, poly(DEAA-b-DMAA), was synthesized by the sequential addition of DEAA followed by DMAA under conditions similar to those of entry 1, as confirmed by the clear shift of the SEC curve toward the high-molecular-weight side (Figure S1(d)). In contrast to the excellent control and activity of the polymerization of dialkyl acrylamides, no polymerizations of α,β-unsaturated esters, such as n-butyl acrylate, 2-methoxyethyl acrylate, methyl methacrylate, methyl crotonate, and ethyl sorbate, occurred under similar conditions of entry 1. Additionally, the living poly(DEAA) synthesized under similar conditions of entries 1 and 2 did not initiate the polymerization of n-butyl acrylate at 25 °C in DCM. These preliminary results showed the specific catalytic activity of $Zn(OTf)_2$/LB for the polymerization of dialkyl acrylamides.

Table 1. Polymerization of acrylamides using $Zn(OTf)_2/PCy_3$.

entry	monomer[a] type	mmol	$[M]_0:[Zn(OTf)_2]_0:[PCy_3]_0$	solv. (mL)		time (min) 25 °C	60 °C	100 °C	conv.[b] %	$10^{-3}M_n{}^{c}$	$10^{-3}M_{theor.}{}^{d}$	$Đ{}^{c}$	I^{*d} %
1	DEAA	4	80:2:1	DCM	1.0	240	-	-	>99	11.2	10.4	1.13	92
2	DEAA	4	80:1:1	DCM	1.0	240	-	-	100	10.2	10.5	1.26	103
3	DEAA	2	40:0.4:1	DCM	1.0	60	-	-	96	19.5	5.2	1.30	26
4	DEAA	4	40:0.2:1	DCM	2.0	20	-	-	100	23.2	5.4	1.33	23
5	DEAA	10	200:2:1	DCM	1.5	240	-	-	98	25.4	25.2	1.26	99
6	DEAA	20	400:2:1	DCM	2.5	1020	-	-	93	45.0	47.6	1.26	106
7	DEAA	4	80:2:1	PhCl	1.0	-	3	-	>99	9.4	10.4	1.13	110
8	DEAA	10	200:2:1	PhCl	1.5	2	3	-	>99	25.2	25.5	1.19	101
9	DEAA	20	400:2:1	PhCl	3.5	5	10	-	95	64.1	48.6	1.27	76
10	DEAA	10	200:2:1	PhCl	1.5	2	-	1	100	21.0	25.7	1.15	122
11	DEAA	20	400:2:1	PhCl	3.5	5	-	2	100	52.0	51.2	1.27	98
12	AMO	4	80:2:1	DCM	2.0	240	-	-	93	18.4	10.8	1.22	58
13	DMAA	5	100:1:1	DCM	1.0	240	-	-	100	15.2	10.2	1.17	67

[a]DEAA, *N,N*-diethyl acrylamide; AMO,4-acryloylmorpholine; DMAA: *N,N*-dimethyl acrylamide. [b]1H NMR. [c]SEC (DMF/LiBr, PMMA standards). [d][M]_0/[PCy_3]_0×MW(M)×conv+MW(PCy_3). [d]Initiation efficiency, $M_{theo}/M_n×100$.
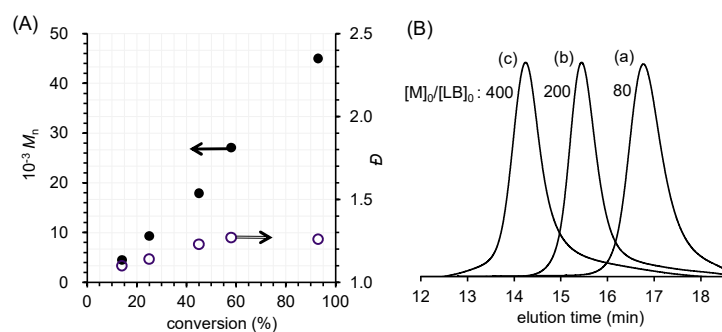

Figure 1. (A) Plots of M_n and $Đ$ versus conversion during the DEAA polymerization using $Zn(OTf)_2/PCy_3$ (entry 6 in Table 1). (B) SEC chromatograms of poly(DEAA) synthesized in PhCl at 60 °C at various $[M]_0/[LB]_0$ ratios ((a) entries 7, (b) 8, and (c) 9 in Table 1).

High-temperature polymerizations were conducted to shorten the reaction time. The DEAA polymerization mixture was stirred at 25 °C for several minutes and subsequently at 60 °C for 3 or 10 min, resulting in practically quantitative conversions. When the reaction temperature was directly increased to 60 °C without stirring at 25 °C, the polymerization results were not reproducible with a decrease in the initiator efficiency in some cases. The molecular weights could be controlled with narrow $Đ$ values depending on the $[M]_0/[LB]_0$ ratios (80, 200, and 400) (entries 7–9) (Figure 1(B)). Furthermore, the polymerization at 100 °C for just 1 or 2 min at $[M]_0/[LB]_0$ ratios of 200 and 400 achieved a quantitative conversion, controlled M_n, and low $Đ$ (entries 10 and 11, Figure S1(e)). Thus, the propagating terminal is significantly selective for the Michael addition to the monomer within a wide temperature range (25 °C –100 °C). To the best of our knowledge, there is no previous report on controlled anionic polymerizations at such high temperatures.

The excellent selectivity of the propagation and air/moisture stability of $Zn(OTf)_2$ and PPh_3 prompted us to operate the polymerizations under open-air conditions (Table 2). The $Zn(OTf)_2/PPh_3$ solution was stirred in the open-air for 5 min before polymerization, and the addition of DEAA and subsequent polymerizations were also conducted in the open-air. The initial polymerization of DEAA in DCM at 25 °C for 4 h afforded the polymer with 65% conversion (entry 1, Table S2). The SEC chromatogram indicated the formation of the narrow-$Đ$ polymer, accompanied by a small fraction of a significantly high-molecular-weight polymer ($M_n = 1.0 \times 10^5$) (Figure S1(f)). We previously reported that phenothiazine (PTZ; 1.0 mol%) completely inhibited the LP radical polymerization.[41,43] It (0.17 mol%) was then added to the open-air polymerization system, completely suppressing the formation of the high-M_n polymer formed via free-radical propagation (entry 2, Table S2, Figure S1(g)). Thus, all subsequent polymerizations were conducted in the presence of PTZ. The polymerization in PhCl at 25 °C for 20 min in the open-air afforded poly(DEAA) with an excellent controlled M_n and a narrow $Đ$ value in a 97% conversion (entry 1, Table 2). Furthermore, the chain extension of the resulting polymer was completely

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successful as the SEC chromatogram shifted to the high-molecular-wight side without dead polymer chains (Figure 2(A)(a)). In addition, the chain extension in the polymerization at 60 °C for 3 min was almost completely achieved (entry 2, Table 2, Figure 2(A)(b)).

Table 2. Polymerization of DEAA using $Zn(OTf)_2$/PPh_3 in the open-air or in presence of water/MeOH.

entry[a]	$[M]_0:[LA]_0:[LB]_0$	additive		atmosphere[c]	time (min)		conv.[d]	$10^{-3}M_n$[e]	$10^{-3}M_{theor.}$[f]	$Đ$[e]
		type	eq.[b]		25 °C	60 °C	%			
1	80:2:1	-	-	air	20	-	97	11.1	10.1	1.26
	+80:0:0	-	-	air	240	-	100	18.3	20.6	1.27
2	80:2:1	-	-	air	2	3	98	14.9	10.2	1.22
	+80:0:0	-	-	air	-	3	>99	24.4	20.4	1.29
3	80:2:1	H_2O	0.13	N_2	120	-	81	15.9	8.5	1.89
4	80:2:1	H_2O	0.13	N_2	-	120	99	16.6	10.3	1.50
5	80:2:1	MeOH	1.0	N_2	120	-	97	14.7	10.1	1.27
6	80:2:1	MeOH	1.0	N_2	-	120	90	18.7	9.4	1.48
7	80:2:1	MeOH	10.0	N_2	-	120	4	-	0.4	-

[a]entries 1 and 3; DEAA: 12 mmol, PhCl: 3.0 mL, entries 2 and 4; DEAA (12 mmol) was added to the polymerization mixtures of entries 1 and 3, respectively. entries 5-9; DEAA: 4 mmol, PhCl: 1.0 mL. [b]relative to PPh_3. [c]humidity value of 30–35 %. [d]1H NMR. [e]SEC (DMF/LiBr, PMMA standards). [f]$[M]_0/[LB]_0 \times$ MW(M) $\times$ conv + MW(LB).
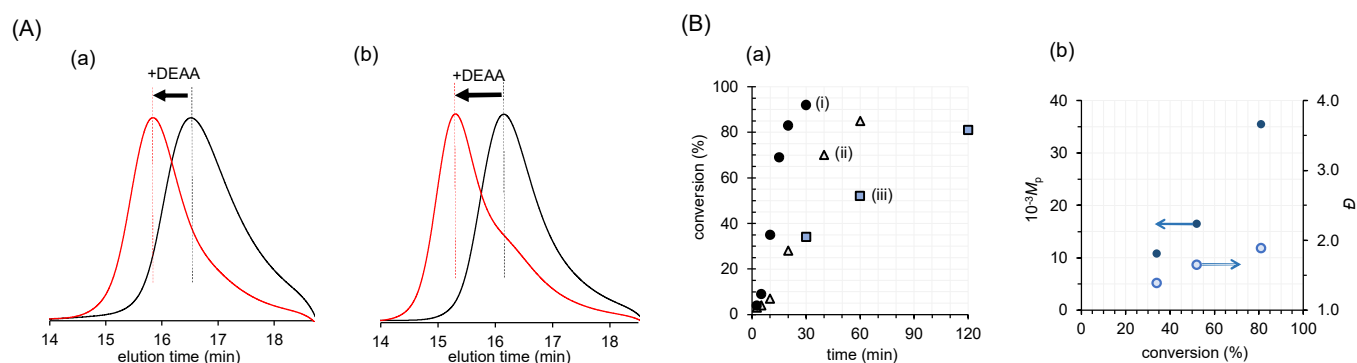
Figure 2. (A) SEC chromatograms of poly(DEAA) obtained via chain-extension experiments under open-air conditions ((a) entries 1 and (b) 2 in Table 2). (B)(a) Effects of protic additives on the DEAA polymerization rate under nitrogen (i) in dry PhCl (entry 1, Table 1), (ii) MeOH–PhCl (entry 5, Table 2), and (iii) water–PhCl (entry 3, Table 2). (B)(b) Plots of M_p (molecular weight of SEC peak top) and $Đ$ versus conversion in the water–PhCl (entry 3, Table 2).

To analyze the effects of protic additives, the polymerizations under nitrogen were examined in water-saturated PhCl (water, 0.14 equivalent to PPh$_3$) and MeOH-containing PhCl (MeOH, 1.0 equivalent to PPh$_3$) (entries 3–7, Table 2). Despite their presence, the polymerizations proceeded with high to quantitative conversions. A controlled M_n and narrow $Đ$ (1.27) were obtained in the MeOH–PhCl at 25 °C (entry 5, Table 2, Figure S1(h)). Comparing the rate of the polymerizations in PhCl (entry 1, Table 1), the water–PhCl (entry 3, Table 2), and the MeOH–PhCl (entry 5, Table 2), it was observed that the additive MeOH and water retarded the polymerization but slowly achieved high conversions (Figure 2(B)(a)). The molecular weight of the polymers obtained in the water–PhCl increased against conversion maintaining a monomodal SEC distribution (Figures 2(B)(b) and S1(i)). This polymerization behavior can also exclude the possibilities of a free radical polymerization, which generally produces a high molecular weight polymer at low conversions.

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We kinetically studied the DEAA polymerization under nitrogen. The linear relationship between $\ln([M]_0/[M])$ and time indicated a first-order dependence on $[M]_0$ (Figure 3(A), time–conversion plot; see Figure S6). Thus, unactivated free DEAA is kinetically involved in the propagation. This is contrary to the zero-order kinetics in the DEAA polymerization using $Sc(OTf)_3/PPh_3$,[43] wherein the propagating reaction with the Sc-activated DEAA is kinetically relevant. This difference can be attributed to the Lewis acidities of $Sc(OTf)_3$ and $Zn(OTf)_2$ toward the DEAA carbonyl group.

Next, the polymerization rates (R_p) at various $[LA]_0/[LB]_0$ ratios were estimated. The highest R_p was obtained at a $[LA]_0/[LB]_0$ of 1, and increasing the ratio from 1 to 2 decreased the R_p values (Figure 3(B); the corresponding kinetic data is shown in Figure S7). Excess $Zn(OTf)_2$ did not accelerate the polymerization via monomer activation, which is consistent with the first-order kinetic results. It retarded the propagation and consequently narrowed the $Đ$ (vide supra). Thus, we assume that the excess $Zn(OTf)_2$ or $Zn(OTf)_2$-activated monomer may interact and/or exchange with the propagating Zn species, but the underlying mechanism is not clear. A similar retardation was observed in the anionic polymerization of methacrylates in the presence of diethylzinc as the additive.[52]
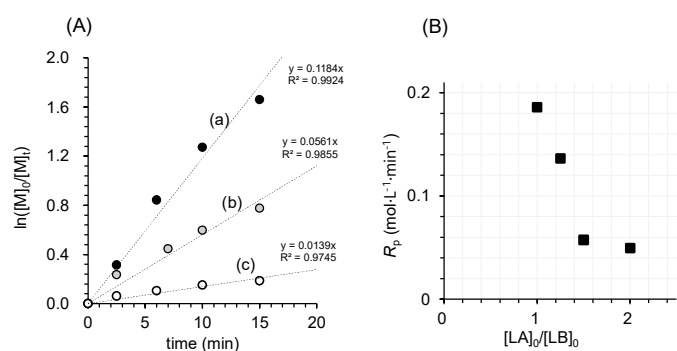
Figure 3. Kinetic studies of DEAA polymerization ($Zn(OTf)_2$/PCy_3, DCM, 25 °C). (A) Pseudo-first order kinetic plots at various LP concentrations: ($[M]_0$:$[LA]_0$:$[LB]_0$ = 40:1:1 (a), 53:1:1 (b), and 80:1:1 (c)). (B) Effects of $Zn(OTf)_2$ concentration on polymerization rate (R_p) ($[M]_0$:$[LA]_0$:$[LB]_0$ = 40:1–2:1).

To gain mechanistic insight and demonstrate sustainability, we examined the recyclability of $Zn(OTf)_2$ (Table S3, Figures S8 and S9). After the mixture of the DEAA polymerization (DCM, 25 °C, 4 h, $[M]_0$:$[LA]_0$:$[LB]_0$ = 80:2:1 and 80:1:1) was extracted with water and washed with DCM, $Zn(OTf)_2$ was recovered as a white powder in a moderate yield. The ^{13}C NMR spectrum of the recovered $Zn(OTf)_2$ was identical to that of the original $Zn(OTf)_2$. The DEAA polymerizations using the recovered $Zn(OTf)_2$ occurred under identical conditions. There was no apparent difference from the original polymerization in the conversion (quantitative) and M_n and $Đ$ values of the polymer even after repeating the polymerization-recovery cycle twice.

Finally, the mechanistic insights are as follows (Scheme 1). The monomer activation by $Zn(OTf)_2$ was supported by the ^1H NMR downfield shifts of β–proton signals in the monomer–$Zn(OTf)_2$ mixtures, whereas no chemical shift changes were observed in the α,β-unsaturated esters–$Zn(OTf)_2$ mixtures (Figure S10). The lack of polymerization activity using either $Zn(OTf)_2$ or PCy_3 also supported the cooperative initiation by the LP. Thus, the initiation involves the conjugate addition of phosphines to $Zn(OTf)_2$-activated monomer (I), which proceeds faster than the subsequent propagation because the controlled M_n and narrow $Đ$ values were obtained. Although the isolation of enol zincate II has not been

successful to date, the generation of II as the intermediate via the conjugate addition initiation is considered reasonable; analogues of enolaluminates,[21,22,24,28,55,30,32] enolborates,[36] and others[38,40] have been isolated in the LP cooperative conjugate additions. The first-order dependence of $[M]_0$ (Figure 3(A)) indicates the unactivated monomers react with zincate II. The high tolerance of the propagating species to MeOH and water suggests that free enolates were not generated via an elimination of $Zn(OTf)_2$ from the terminals. One polymer chain was formed from one molecule of each PCy_3 and $Zn(OTf)_2$ (vide supra, entries 1–4, Table 1), which also supported that the initiating and propagating terminals are the phosphonium and enol zincate, respectively. Based on the lack of the polymerizability and low coordination ability of various α,β-unsaturated esters and the lack of the *n*-butyl acrylate reactivity to the propagating poly(DEAA) terminal, it is tempting to suggest that the efficient Michael addition propagation of the acrylamides is presumably because the monomer can be activated via the coordination of the more Lewis basic monomer carbonyl oxygens to the propagating zinc center. The retardation by stoichiometric protic additives suggests their equilibrium coordination to the propagating Zn centers (between III and IV) via a higher-order zincate (IV)[56]. Excess MeOH terminated the polymerization through the equilibrium coordination (IV) and protonation (V). No exchanges of the triflate occurred during the propagation and termination because the recycling of $Zn(OTf)_2$ was possible. This equilibrium termination may be comparably discussed with the well-known equilibrium coordination of water to metal triflates,[57] which is distinct from the significantly rapid and possibly diffusion-controlled protonation of alkaline-metal enolates during conventional anionic polymerization.
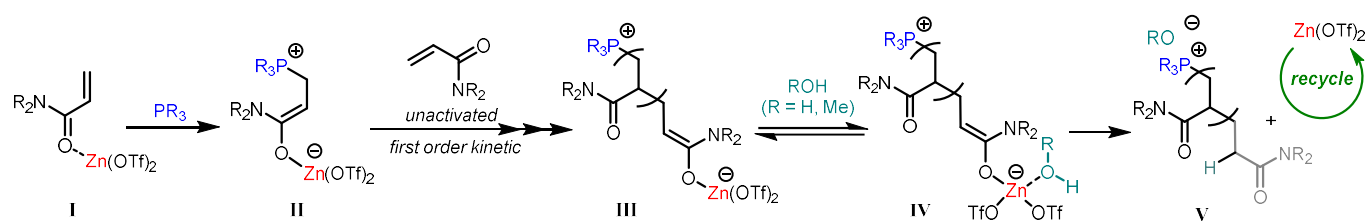
Scheme 1. Proposed polymerization mechanism via propagating enol zincates (II–IV) and equilibrium termination (III–V) under the condition of $[PR_3]_0 = [Zn(OTf)_2]_0$.

In conclusion, we report that the anionic polymerization of acrylamides proceeded in a living/controlled manner at high temperatures under open-air conditions catalyzed by the commercially available and recyclable $Zn(OTf)_2$-based LP. This was successful because $Zn(OTf)_2/PPh_3$ and the propagating enol zincate are tolerant to air/moisture and protic reagents but are significantly selective for propagation. We successfully demonstrated user-friendly and practically applicable catalysts that overcome scientific and technical difficulties in current living/controlled anionic and radical polymerizations.

Supporting Information

Instrumentation, materials, experimental procedures, supplementary tables, NMR and MALDI-TOF-MS spectra, SEC chromatograms, and kinetic data.

Author Contribution

Riki Akita: investigation, visualization, and writing-original draft. Shin-ichi Matsuoka: conceptualization, project administration, visualization, funding acquisition, writing original draft, review and editing. The authors have read and approved the final version of the manuscript.

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