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Note	

Metal-Free Living Cationic Polymerization Using Diaryliodonium Salts as Organic Lewis Acid Catalysts

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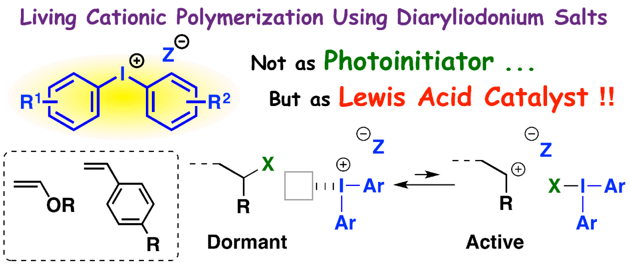


Abstract

A metal-free initiating system for the living cationic polymerization of alkyl vinyl ethers (VEs) and styrene derivatives was developed using diaryliodonium salts as an organic Lewis acid catalyst. Unlike many past examples of its use as a photoinitiator, diaryliodonium salts were demonstrated to function as a Lewis acid catalyst for cationic polymerization. The cationic polymerization of isobutyl VE smoothly proceeded using a diaryliodonium salt in conjunction with a cationogen that generates a carbon–halogen propagating end, yielding polymers with predictable molecular weights and very narrow molecular weight distributions. The central iodine atom of the diaryliodonium salt most likely exhibited Lewis acidity, thereby generating a dormant–active equilibrium through the reversible generation of a carbocation via the abstraction of the halogen anion from the propagating end. The role

of the diaryliodonium salts as Lewis acid catalysts was confirmed by a series of experiments that focused on the effects of concentrations, substituents on the aryl rings, and counteranions. Polymerizations of styrene derivatives and VEs with polar groups also proceeded using diaryliodonium salts in a controlled manner.

Introduction

Organocatalysts have attracted increasing attention as environmentally friendly catalysts due to growing awareness of the problems associated with metal catalysts in recent years.[1,2] Generally, metallic catalysts exhibit higher reactivities than organocatalysts and can catalyze various reactions; however, they have some drawbacks, such as possible depletion of some rare metals, contamination of products, and pollution of environments. In contrast, organocatalysts have advantages such as stability to air and moisture and no contamination of products by metallic residues. Moreover, some organocatalysts exhibit remarkable activities, such as high stereoselectivity and high activity, that are comparable to those of metal complex catalysts. Organocatalysts have also played an important role in polymer synthesis. For example, various organocatalysts, including phosphines, amines, thiourea derivatives, *N*-heterocyclic carbenes, and phosphazene bases, have been shown to function as highly active catalysts for ring-opening polymerizations of cyclic esters.[3–7] Photoredox organocatalysts have been employed for photoinduced controlled radical polymerization reactions.[8,9]

In cationic polymerizations, living polymerization of various monomers, including vinyl ethers (VEs) and styrene derivatives, have been enabled by the development of various Lewis acidic metal catalysts, which have allowed the precise synthesis of polymers with well-defined structures, such as block, graft, and star-shaped polymers and the polymerization under special conditions, such as in aqueous media.[10–19] Metal catalyst-free living cationic polymerizations were developed with initiating systems such as HI alone,[20] HI/nBu$_4$NX,[21,22] Me$_3$SiI/1,3-dioxolane,[23] CF$_3$SO$_3$H (TfOH)/dialkyl sulfide,[24] HCl/diethyl ether,[25,26] TfOH/nBu$_4$NI,[27] and cationic RAFT[28,29] systems. In many cases, however, catalyst-free systems are inferior to metal-catalyzed systems in terms of reaction rates and applicable monomers. Therefore, the development of Lewis acidic organocatalysts that exhibit activity comparable to metal catalysts in living cationic polymerization is desirable considering the drawbacks of the metal catalysts mentioned above. Recently, Takagi and coworkers reported the living cationic polymerization of isobutyl VE using an imidazolium salt as an organocatalyst.[30] Two iodine atoms of an imidazolium salt were considered to abstract a halogen anion from a carbon–halogen bond to generate the propagating carbocation.

We focused on diaryliodonium salts as potential candidates for Lewis acidic organocatalysts for living cationic polymerization. In cationic polymerizations, diaryliodonium salts have been exclusively used as photoinitiators.[31–33] The photodecomposition of the salts triggers the liberation of a proton or some carbocations, such as a phenyl cation, which initiates the cationic polymerization of a variety of monomers, including VEs and cyclic ethers. Our group also developed a controlled cationic polymerization of VEs with diaryliodonium salts as a photoinitiator by designing an initiating system that generates carbon–iodine bonds as spontaneously cleavable propagating ends.[34] Recently, diaryliodonium salts were reported to function as Lewis acid catalysts in organic reactions such as Mannich reactions.[35–36] Their ability to form halogen bonds is responsible for their Lewis acidity (Figure 1).[37–40] Specifically, the strong anisotropy of the electron distribution around the iodine atom bound to other atoms causes a large deviation in the positive charge (σ-hole) along the axis of the bond between the iodine and other atoms, which generates a strong interaction between the σ-hole and a Lewis base.

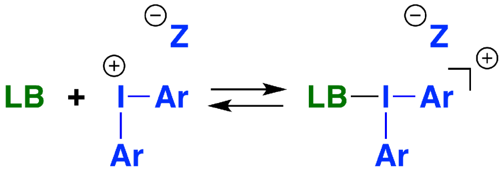
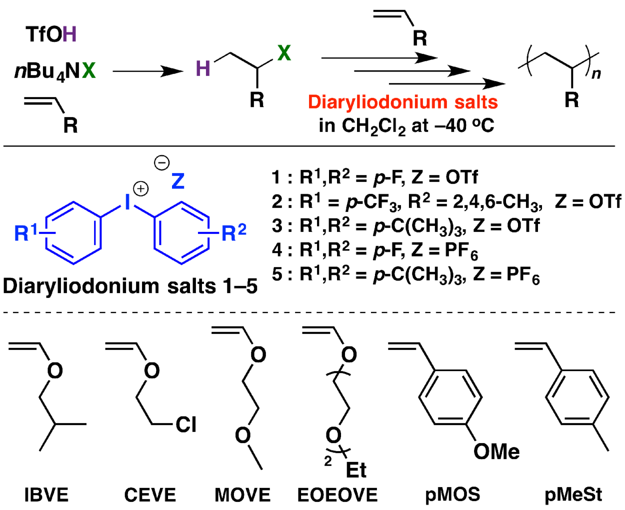


Figure 1. A diaryliodonium salt used as a halogen-bonding donor (e.g., references 37 and 39). LB: Lewis base.

In this study, we examined the potential of diaryliodonium salts as organic Lewis acidic catalysts for the cationic polymerization of VEs and styrene derivatives (Scheme 1). In particular, we aimed to construct a novel metal-free living cationic polymerization comparable to metal-based systems in terms of activity and monomer scope. First, we examined the suitability of diaryliodonium salts as catalysts for the living cationic polymerization of IBVE. Subsequently, the effects of the amounts and substituents of the diaryliodonium salts, the halogen atoms of the propagating ends, and the added salts were investigated to reveal the polymerization mechanism. Moreover, cationic polymerizations of other VEs and styrene derivatives were shown to proceed in controlled manners.



Scheme 1. Cationic polymerization of vinyl monomers using diaryliodonium salts as an organic Lewis acid catalyst.

Experimental Section

Materials. Isobutyl VE (IBVE; TCI, >99.0%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride. 2-Chloroethyl VE (CEVE; TCI, >97%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over sodium sulfate, and distilled twice under reduced pressure over calcium hydride. 2-Methoxyethyl VE (MOVE; kindly supplied by Maruzen Petrochemical) and 2-(2-ethoxy)ethoxyethyl VE (EOEOVE; kindly supplied by Maruzen

Petrochemical) were distilled over calcium hydride and then over metallic sodium. *p*-Methoxystyrene (pMOS; Wako, >97%) was dried overnight over sodium sulfate and distilled twice under reduced pressure over calcium hydride. *p*-Methylstyrene (pMeSt; Sigma-Aldrich; 96.0%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over sodium sulfate, and distilled twice over calcium hydride. nBu$_4$NI (Sigma-Aldrich; ≥99.0%), nBu$_4$NBr (Acros Organics; ≥99.0+%), nBu$_4$NCl (Fluka; ≥99.0%), and CF_3SO_3H (TfOH; Sigma-Aldrich; ≥99.0%) were used without further purification after preparing stock solutions in dichloromethane. Bis(4-fluorophenyl)iodonium triflate (**1**; TCI, >97.0%), [4-(trifluoromethyl)phenyl](2,4,6-trimethylphenyl)iodonium triflate (**2**; TCI, >98.0%), bis(4-*tert*-butylphenyl)iodonium triflate (**3**; Sigma-Aldrich, ≥99%), bis(4-fluorophenyl)iodonium hexafluorophosphate (**4**; TCI, >95%), and bis(4-*tert*-butylphenyl)iodonium hexafluorophosphate (**5**; Sigma-Aldrich, 98%) were used without further purification after preparing stock solutions in dichloromethane. The adduct of IBVE with HCl (IBVE–HCl) was prepared by the addition of HCl to IBVE.[41] HCl solution in diethyl ether (1.0 M; Sigma-Aldrich) was used as received. Dichloromethane (Wako, 99.0%) was dried by passage through solvent purification columns (Glass Contour).

Polymerization. The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the air temperature was approximately 450 °C) under dry nitrogen. Dichloromethane, dilute solutions of nBu$_4$NI and TfOH in dichloromethane, and IBVE were sequentially added into the tube using dry syringes. The polymerization was started by the addition of a diluted solution of **1** in dichloromethane at −40 °C. After 15 min, the reaction was terminated with prechilled methanol containing a small amount of aqueous ammonia. The quenched mixture was diluted with hexane and then washed with water. The volatiles were then removed under reduced pressure at 60 °C, and the residue was vacuum-dried under reduced pressure for more than 6 h at room temperature to yield a polymer. The monomer conversion was determined by gravimetry.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel

GMH_{HR}-M × 2 (exclusion limit molecular weight = 4×10^6; bead size = 5 μm; column size = 7.8 mm id × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; MW = 5.0×10^2 to 1.09×10^6, $M_w/M_n < 1.2$). NMR spectra were recorded on a JEOL JNM-ECA 500 (500.16 MHz for ^1H) spectrometer or a JEOL JNM-ECS 400 spectrometer (399.78 MHz for ^1H) spectrometer.

Results and Discussion

Cationic polymerization using diaryliodonium salts as organic Lewis acid catalysts

The cationic polymerization of IBVE was conducted using diaryliodonium salt **1**, which has two fluorine atoms on the aromatic rings as electron-withdrawing substituents, as a catalyst in dichloromethane at −40 °C (Scheme 1). An IBVE−hydrogen halide adduct generated in situ by the reaction of TfOH and $n\text{Bu}_4\text{NI}$, as reported in our previous study, was used as a cationogen.[27] As shown in Figure 2A (filled circles), the polymerization proceeded smoothly and reached over 95% conversion in 15 min (entry 1 in Table 1). The polymerization was much faster than the polymerization in the absence of the diaryliodonium salt (entry 2 in Table 1; a square symbol in Figure 2A).[27] Additionally, the use of $n\text{Bu}_4\text{NOTf}$ instead of a diaryliodonium salt accelerated the polymerization (entry 3) as in the case of the polymerization with salts such as $n\text{Bu}_4\text{N(ClO}_4)$[21] and $n\text{Bu}_4\text{NI}$[22]; however, the polymerization using **1** was much faster than that using $n\text{Bu}_4\text{NOTf}$. These results indicate that the diaryliodonium salt catalyzed the polymerization. The $\ln([M]_0/[M])$−time plots gave a straight line from the origin, indicating that the concentration of the propagating species was constant during the reaction (open circles in Figure 2A). Furthermore, the product polymers had M_n values that agreed well with the theoretical values and increased in proportion to the monomer conversion (Figure 2B). The

MWD curves of the product polymers had unimodal and narrow MWDs ($M_w/M_n < 1.1$; Figure 2B and 2C). Polymers with M_n values consistent with the theoretical values and narrow MWDs were also produced when IBVE–HCl or HCl/Et_2O were used as the cationogen with $n$$Bu_4NCl$ (entries 3 and 5 in Table S1). In the ^{1}H NMR spectra of the product polymer, the integral ratio of the α-end (methyl group) and the ω-end (acetal methine group) derived from the methanol quencher was approximately 3/1 (Figure S1), suggesting that the initiation and propagation reactions proceeded in a controlled manner. In addition, peaks assignable to structures resulting from side reactions such as β-proton elimination or side-chain abstraction reactions were not observed. These results suggested that polymerization using the diaryliodonium salt as a catalyst proceeded in a highly controlled manner.

Table 1. Cationic polymerization of vinyl monomers using various diaryliodonium salts[a]

Entry	Monomer	Diaryliodonium salt	Time	Conv (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ (GPC)[b]	M_w/M_n (GPC)[b]
1	IBVE	**1**	15 min	97	11.2	11.7	1.05
2[c]	IBVE	–	600 h	96	18.2	9.5	1.39
3[c]	IBVE	$n$$Bu_4NOTf$[d]	196 h	98	18.6	13.6	1.17
4	IBVE	**2**	18 min	100	11.5	12.8	1.11
5	IBVE	**3**	4 h	93	8.8	10.5	1.10
6	IBVE	**5**	30 min	76	8.7	9.6	1.05
7	CEVE	**1**	30 h	94	14.8	11.4	1.10
8	MOVE	**1**	25 min	96	11.0	10.4	1.28
9	EOEOVE	**1**	45 min	94	14.3	8.3	1.22
10	pMOS	**1**	48 h	90	13.6	10.8	1.40
11	pMOS	**4**	20 min	96	14.5	14.2	1.35
12[e]	pMeSt	**1**	672 h	14	1.9	2.7	2.26
13[e]	pMeSt	**4**	110 min	95	12.6	18.6	1.69

[a] $[\text{monomer}]_0$ = 5 vol% (entry 5, $[\text{IBVE}]_0$ = 0.38 M), 6 vol% (entries 1, 4, and 6–13, $[\text{IBVE}]_0$ = 0.46 M, $[\text{CEVE}]_0$ = 0.59 M, $[\text{MOVE}]_0$ = 0.53 M, $[\text{EOEOVE}]_0$ = 0.38 M, $[\text{pMOS}]_0$ = 0.45 M, $[\text{pMeSt}]_0$ = 0.45 M), or 10 vol% (entries 2 and 3, $[\text{IBVE}]_0$ = 0.76 M), $[\text{TfOH}]_0$ = 4.0 mM (except for entries 12 and 13), $[n\text{Bu}_4\text{NI}]_0$ = 4.2 mM (except for entries 12 and 13), $[\text{diaryliodonium salt}]_0$ = 0 (entries 2 and 3), 2.0 (for entries 1, 4–9, and 12), 4.0 (for entries 10 and 13), or 8.0 (for entry 11) mM, in dichloromethane at –40

°C. [b] By GPC using polystyrene standards. [c] From reference 27. [d] $n\text{Bu}_4\text{NOTf}$ (8.0 mM) was used instead of a diaryliodonium salt. [e] $[n\text{Bu}_4\text{NI}]_0$ = 0.2 (entry 12) or 0.6 (entry 13) mM, $[\text{TfOH}]_0$ = 0 mM, $[\text{IBVE–HCl}]_0$ = 4.0 mM, $[\mathbf{1}]_0$ = 2.0 mM (entry 13).

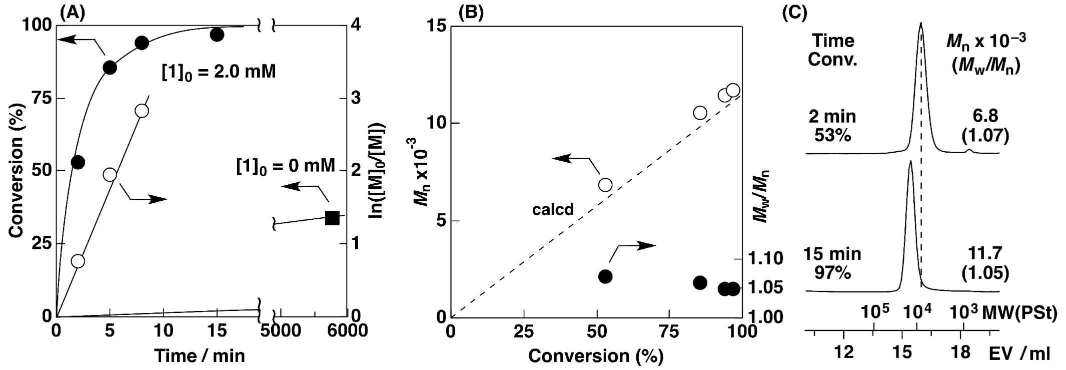


Figure 2. (A) Time–conversion curves and first order plot of the polymerization of IBVE, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[\text{IBVE}]_0$ = 0.46 (circle) or 0.76 (square) M, $[\text{TfOH}]_0$ = 4.0 mM, $[n\text{Bu}_4\text{NI}]_0$ = 4.2 mM, $[\mathbf{1}]_0$ = 2.0 (circle) or 0 (square) mM, in dichloromethane at –40 °C. The data in the absence of **1** are cited from reference 27.

To confirm the livingness of the polymerization reaction using **1**, a monomer-addition experiment and polymerization at different monomer/cationogen ratios were conducted. When a fresh portion of IBVE was added later in the reaction,[42] the polymerization continued to proceed smoothly (Figure 3A). The obtained polymers had very narrow MWDs, and the M_n values agreed with the theoretical values (Figure 3B and 3C). The polymerizations with different amounts of cationogen also proceeded in a controlled manner, giving polymers with M_n values close to the theoretical values, which were calculated from the ratios of $[\text{IBVE}]_0$ to $[\text{TfOH}]_0$ (Figure 4). In other words, all the cationogens derived from TfOH (a VE−hydrogen iodide adduct) could initiate the controlled polymerization. These results indicate that metal-free living cationic polymerization of IBVE proceeded using **1** as an organocatalyst.

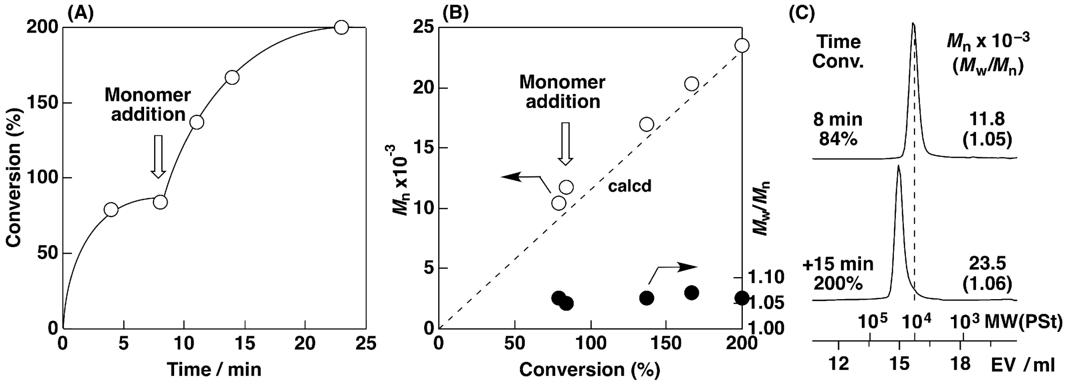


Figure 3. (A) Time–conversion curves of the polymerization of IBVE, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[\text{IBVE}]_0$ = 0.46 M, $[\text{IBVE}]_{\text{added}}$ = 0.46 M, $[\text{TfOH}]_0$ = 4.0 mM, $[n\text{Bu}_4\text{NI}]_0$ = 4.2 mM, $[\mathbf{1}]_0$ = 2.0 mM in dichloromethane at –40 ºC.

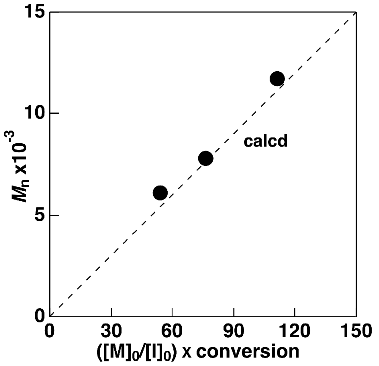


Figure 4. M_n–$[\text{M}]_0/[\text{I}]_0$ plot of the polymerization of IBVE. Polymerization conditions: $[\text{IBVE}]_0$ = 0.46 M, $[\text{TfOH}]_0$ = 4.0, 6.0, or 8.0 mM, $[n\text{Bu}_4\text{NI}]_0$ = 4.2, 6,3 or 8.4 mM mM, $[\mathbf{1}]_0$ = 2.0 mM in dichloromethane at –40 ºC. See Figure S2 for the M_n–conversion plots.

The role of the diaryliodonium salt as a catalyst was further confirmed by polymerizations at different concentrations of **1**. As shown in Figure 5, the polymerization of IBVE proceeded at 1.0–4.0 mM of **1** in a controlled manner, while the polymerization rates were higher at higher concentrations of **1** (Figure 5A). Moreover, the M_n values of the products did not depend on the amount of **1** and agreed with the theoretical values (Figure 5B). These results indicate that the diaryliodonium salt functioned as a catalyst in this polymerization.

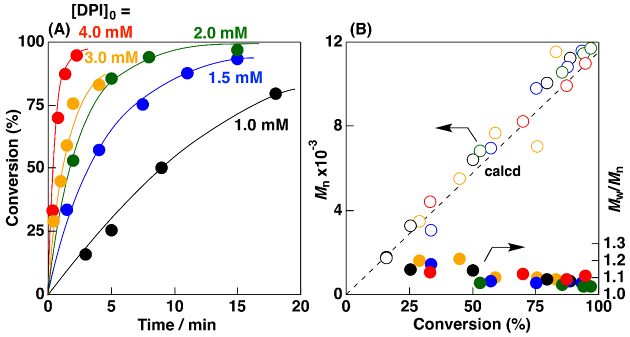
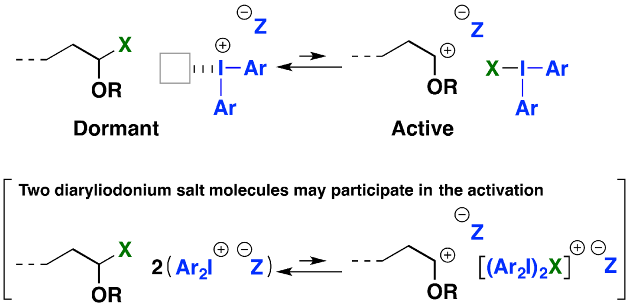


Figure 5. (A) Time–conversion curves of the polymerization of IBVE and (B) M_n and M_w/M_n values of the obtained polymers. Polymerization conditions: [IBVE]$_0$ = 0.46 M, [TfOH]$_0$ = 4.0 mM, [nBu$_4$NI]$_0$ = 4.2 mM, [**1**]$_0$ = 1.0 (black), 1.5 (blue), 2.0 (green; the same data to those shown in Figure 2), 3.0 (orange), and 4.0 (red) mM in dichloromethane at –40 ºC.

Based on the results demonstrated above, we propose the following mechanism for the polymerization. The central iodine atom of a diaryliodonium salt most likely functions as a Lewis acidic site, as suggested in previous studies using diaryliodonium salts as Lewis acid catalysts.[35–40] The central iodine atom abstracts the halogen from the carbon–halogen bond of the cationogen or propagating end through a Lewis acid-base interaction, thereby generating an initiating or a propagating carbocation (Scheme 2). The dormant–active equilibrium is probably generated through the reversible abstraction and liberation of a halogen anion by the diaryliodonium salt, as in the case of living cationic polymerizations using Lewis acidic metal catalysts.[10–17] The role of a diaryliodonium salt as a Lewis acid was also confirmed by the generation of a trityl cation[43] from trityl chloride via the abstraction of the chloride anion (Figure S3). In addition, when UV light was irradiated soon after the initiation of the polymerization, polymers containing uncontrolled portions with broad MWDs were produced (Figure S4) probably because of the degradation of the diaryliodonium salt as in the case of the photoinitiated cationic polymerization.[31–34] In other words, the diaryliodonium salt most likely functioned solely as a Lewis acid catalyst in the absence of UV irradiation.



Scheme 2. The plausible mechanism of metal-free cationic polymerization of vinyl monomers using a diaryliodonium salt as an organic Lewis acid catalyst.

The effects of substituents and counteranions

The effects of the substituents on the aryl rings were examined using diaryliodonium salts **1**–**3** (entries 1, 4 and 5 in Table 1). The polymerization proceeded in a living manner regardless of the diaryliodonium used (Figure 6B), and polymers with narrow MWDs and M_n values that agreed with the theoretical values were obtained (Figure 6B). However, the polymerizations using **1** and **2** were obviously faster than that using **3** as the catalyst (Figure 6A; the apparent rate constants (k_{app}) were determined based on the equation $-d[\text{IBVE}]/dt = k_{app}[\text{IBVE}]$ as follows: 5.9×10^{-3} s^{-1} for **1**, 5.3×10^{-3} s^{-1} for **2**, and 1.9×10^{-4} s^{-1} for **3**). This result indicates that the Lewis acidity of the iodine atom of the diaryliodonium salt was affected by the substituents. Specifically, **1** and **2**, which have two fluorine atoms and a trifluoromethyl group, respectively, as electron-withdrawing substituents, exhibited stronger Lewis acidity than **3**, which does not have electron-withdrawing moieties.[44,45]

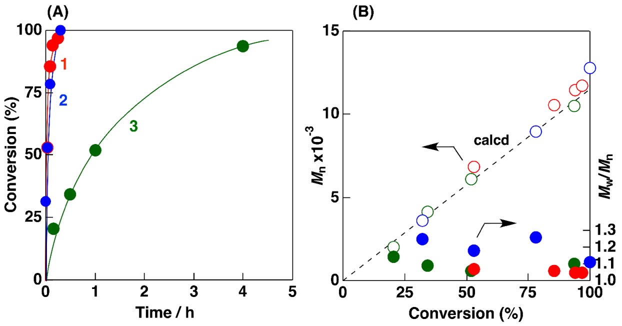


Figure 6. (A) Time–conversion curves of the polymerization of IBVE using diaryliodonium salts **1**–**3** and (B) M_n and M_w/M_n values of the obtained polymers. Polymerization conditions: $[\mathrm{IBVE}]_0 = 0.46$ M, $[\mathrm{TfOH}]_0 = 4.0$ mM, $[n\mathrm{Bu_4NI}]_0 = 4.2$ mM, $[\mathbf{1–3}]_0 = 2.0$ mM in dichloromethane at –40 ºC.

The counteranions of the ammonium salts, which were used for generating the cationogens in conjunction with TfOH, also affected the polymerization rate. The halogen atom of the carbon–halogen bond at the propagating end is derived from the tetrabutylammonium halide used; hence, carbon–iodine, carbon–bromine, and carbon–chlorine bonds are generated when $n\mathrm{Bu_4NI}$, $n\mathrm{Bu_4NBr}$, and $n\mathrm{Bu_4NCl}$ are used, respectively. When the polymerization was conducted with these tetrabutylammonium salts, the polymerization rates changed in the order of I > Br > Cl (Figures S5 and S6; entry 1 in Table 1 and entry 1 in Table S1). This order corresponds to the strength of the carbon–halogen bonds during heterolytic cleavage. The apparent rate constant of the iodide case ($k_{\mathrm{app}} = 5.9 \times 10^{-3}$ s^{-1}; entry 1 in Table 1; vide supra) was over 10^3 times larger than the chloride case (1.2×10^{-6} s^{-1}; entry 1 in Table S1).

The role of diaryliodonium salts as catalysts

To examine the number of active sites on the diaryliodonium salts, the polymerization was conducted with different concentrations of the tetrabutylammonium salt.[46,47] Halogen anions derived from the excess $n\mathrm{Bu_4NI}$ relative to the amount consumed by the reaction with TfOH are considered to interact with a diaryliodonium salt as a Lewis basic species, which will retard polymerization. We defined the value "Ratio A" as the ratio of the amount of $n\mathrm{Bu_4NI}$ molecules not consumed in the reaction with TfOH to the amount of a diaryliodonium salt. When Ratio A is smaller than 1.0, the polymerization proceeded smoothly, whereas the polymerization was obviously slow when Ratio A was greater than 1.0 (Figure 7). This result suggests that a diaryliodonium salt has one Lewis acidic site. Specifically, diaryliodonium molecules that were not capped by a halogen anion derived from the tetrabutylammonium salts existed and abstracted the iodide anion from the propagating end at Ratio A values smaller than 1.0, while all the diaryliodonium molecules were deactivated by capping by a halogen anion at Ratio A values larger than 1.0.

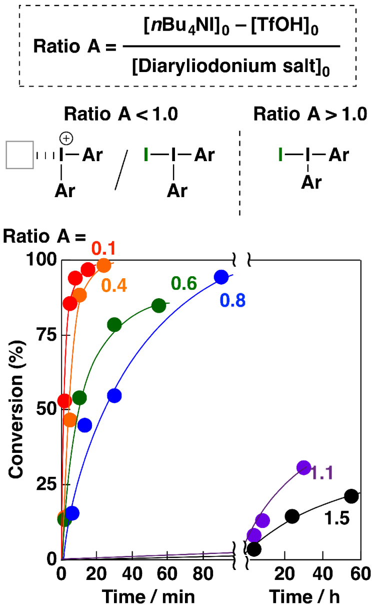


Figure 7. Time–conversion curves of the polymerization of IBVE at different concentrations of nBu$_4$NI. Polymerization conditions: [IBVE]$_0$ = 0.46 M, [TfOH]$_0$ = 4.0 mM, [nBu$_4$NI]$_0$ = 4.2–7.0 mM, [**1**]$_0$ = 2.0 mM in dichloromethane at –40 ºC.

The effect of the concentration of diaryliodonium salts on the polymerization kinetics was also examined through the analysis of the apparent rate constants. From the first-order plots of the polymerizations using **1**, the apparent rate constants were determined at various concentrations of diaryliodonium salts. The reaction order was estimated to be approximately 2 (1.94) from the plots of the apparent rate constant versus the concentration of diaryliodonium salts (Figure S7). This result suggests that two diaryliodonium molecules participate in the rate-determining step of the polymerization under these conditions in a manner similar to the living cationic polymerization using Lewis acids such as $EtAlCl_2$ and $TiCl_4$.[48,49] Two diaryliodonium molecules may form a halogen-bridged dimer in the activation of the carbon–halogen end (Scheme 2) like a $Ti_2Cl_9^-$ species. Indeed, diaryliodonium salts are known to form an anion-bridged dimer in a crystal.[40,50]

Polymerization of vinyl ethers with functional side chains and styrene derivatives

The polymerizations of VEs with polar groups such as a chloroalkyl group (CEVE; this VE is less reactive than IBVE due to the electron-withdrawing effect of the chlorine atom) and an oxyethylene chain (MOVE and EOEOVE; these VEs exhibit comparable reactivities to IBVE) were also feasible with diaryliodonium salts as organocatalysts (entries 7–9 in Table 1; Figures S8 and S9). The M_n values of the polymers obtained with **1** increased with increasing monomer conversion, which suggests that the polymerization was mediated by long-lived species. The results indicate that such polar groups do not suppress the catalytic activity of the diaryliodonium salts as Lewis acids.

Styrene derivatives were also polymerized using diaryliodonium salts as catalysts. The polymerization of *p*-methoxystyrene (pMOS) using **1** proceeded smoothly and reached 90% conversion in 48 h under conditions similar to those used for the polymerization of IBVE (entry 10 in Table 1; Figure S10). However, the product polymers obtained in the later stage of polymerization had smaller M_n values than the theoretical values. Based on the results of the polymerizations using various diaryliodonium salts, the counteranion OTf^- was likely responsible for the small M_n values, probably due to side reactions such as β-proton elimination.[51–53] Thus, instead of **1** having OTf^-, by using **4**, which has PF_6^- as a counteranion, the polymerization of pMOS proceeded in a controlled manner and afforded products with M_n values close to the theoretical values (entry 11 in Table 1, Figure 8). In addition, the polymerization using **4** was much faster than that using **1**, which indicates that OTf^- may react with the pMOS-derived propagating carbocation and generate a reversibly cleavable covalent bond.[54] The polymerization of IBVE using a diaryliodonium salt with PF_6^- (**5**; entry 6 in Table 1) also proceeded faster than that using the OTf^- counterpart (**3**; entry 5). The effects of the anionic species present in the reaction solution need to be examined in more detail. The controlled polymerization of *p*-methylstyrene (pMeSt), which is a less reactive styrene derivative than pMOS, was also feasible when appropriate reaction conditions were selected (entries 12 and 13 in Table 1; Figure S12) based on the pMOS polymerization results. Less reactive styrene derivatives, such as styrene and *p*-chlorostyrene, than pMeSt can also be potentially polymerized using diaryliodonium salts when reaction conditions are suitably designed.

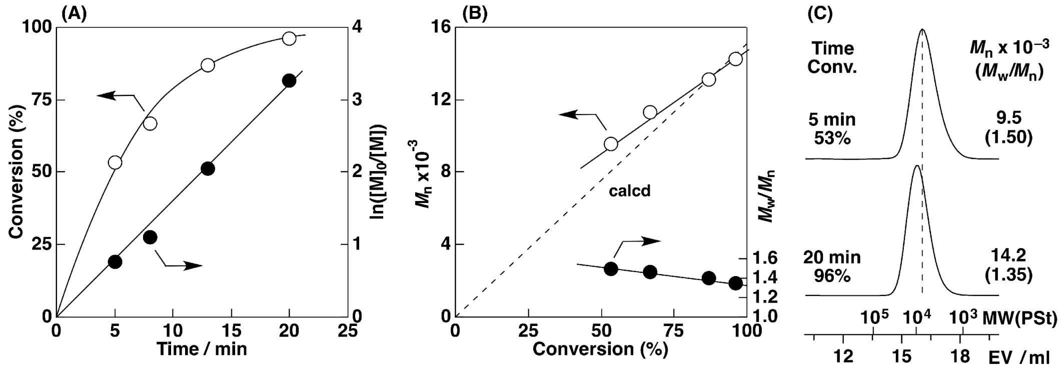


Figure 8. (A) Time–conversion curves of the polymerization of pMOS, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[pMOS]_0$ = 0.45 M, $[TfOH]_0$ = 4.0 mM, $[n\text{Bu}_4\text{NI}]_0$ = 4.2 mM, $[\mathbf{4}]_0$ = 8.0 mM in dichloromethane at –40 ºC.

Conclusion

In conclusion, we developed a metal-free living cationic polymerization using diaryliodonium salts as organic Lewis acid catalysts. The central iodine atom of the diaryliodonium salt most likely abstracts a halogen from the carbon–halogen bond of the propagating end to generate a propagating carbocation. The presence of electron-withdrawing substituents on the aryl rings of the diaryliodonium salt obviously increased the polymerization rate, which also indicated the Lewis acidity of the diaryliodonium salt. A dormant–active equilibrium appeared to be formed as in the case of the living cationic polymerization using metal catalysts, resulting in well-defined poly(VE)s and poly(styrene derivative)s with controllable molecular weights and very narrow MWDs. The results obtained in this study will further the development of both metal-free living cationic polymerizations using organocatalysts that exhibit reactivities comparable to conventional Lewis acidic metal catalysts and the precise syntheses of well-defined polymers via environmentally benign processes.

Associated Content

Supporting Information

^{1}H NMR spectrum of the obtained polymer and polymerization data.

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Notes

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