



Title	Photoinduced Superacceleration of Metal-Free Living Cationic Polymerization Using Diaryliodonium Salts as Organic Lewis Acid Catalysts
Author(s)	Mishima, Yuji; Kanazawa, Arihiro; Aoshima, Sadahito
Citation	Macromolecules. 2023, 56(17), p. 6941-6950
Version Type	AM
URL	<a href="https://hdl.handle.net/11094/103821">https://hdl.handle.net/11094/103821</a>
rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Macromolecules, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <a href="https://doi.org/10.1021/acs.macromol.3c01177">https://doi.org/10.1021/acs.macromol.3c01177</a> .
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

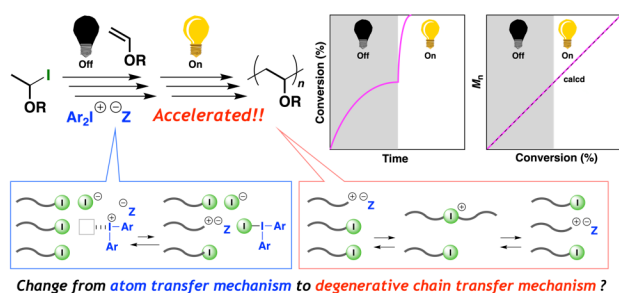
The University of Osaka

# Photoinduced Superacceleration of Metal-Free Living Cationic Polymerization Using Diaryliodonium Salts as Organic Lewis Acid Catalysts

Yuji Mishima, Arihiro Kanazawa, and Sadahito Aoshima\*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

## For TOC Use Only



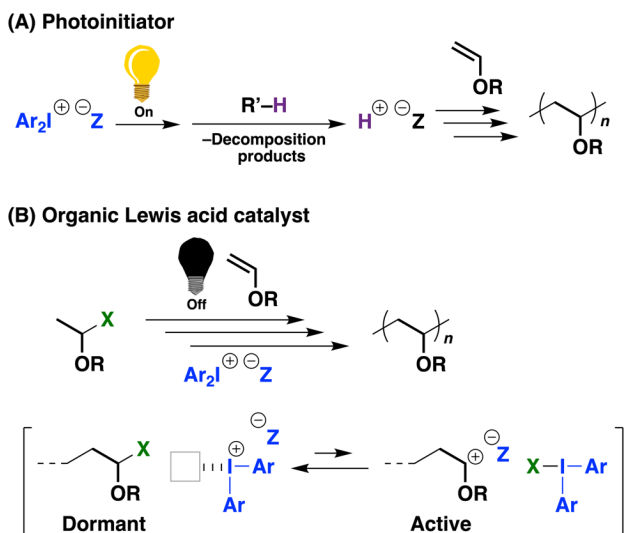
## Abstract

Living cationic polymerization of vinyl ethers (VEs) using diaryliodonium (DAI) salts as organic Lewis acid catalysts was accelerated without loss of livingness via UV light irradiation during polymerization. Before UV irradiation, the polymerization proceeded via carbocation generation from the carbon–iodine bonds at the propagating ends through the abstraction of the iodide anion by the DAI salts. Our initial expectation regarding the effect of UV irradiation during the polymerization was the stop of polymerization or the loss of polymerization control due to the decomposition of the DAI salts; however, accelerated living polymerization occurred. Based on our thorough investigation, the acceleration associated with livingness likely occurred by the change in the polymerization mechanism from atom transfer mechanisms to degenerative chain transfer mechanisms. Specifically, iodide anions were consumed in the DAI salt decomposition, which led to gradual generation of carbocations that did not contain iodide counteranions and resulted in an iodine transfer-type degenerative chain transfer polymerization. Acceleration was also observed in cationic

polymerizations of functional group-containing VEs and styrenes.

## Introduction

Photoinitiated and/or photocontrolled polymerization reactions have been extensively studied and developed due to both academic interests and considerable potential for applications in various fields. In particular, tremendous research efforts have been recently devoted to the development of photocontrolled radical polymerizations, such as photocontrolled reversible addition-fragmentation chain transfer (RAFT).<sup>1-5</sup> In cationic polymerization, some onium compounds, such as diaryliodonium (DAI) salts and triarylsulfonium salts, were reported to function as photoinitiators in the cationic polymerizations of vinyl monomers and cyclic monomers.<sup>6-8</sup> For example, DAI salts were found to generate cationic species such as protons via decomposition triggered by UV irradiation (Scheme 1A).<sup>9-11</sup> In addition, photoinitiated or photocontrolled living cationic polymerization has been achieved via the design of suitable initiating systems and conditions. Our group also reported that photoinitiated cationic polymerization of vinyl ethers (VEs) proceeded in a living manner when *n*Bu<sub>4</sub>NI was used in conjunction with the DAI salts due to the generation of propagating species with a carbon-iodine bond and the spontaneous cleavage of the bond.<sup>12</sup> Unlike this example, many photocontrolled living cationic polymerizations use the degenerative chain transfer mechanism, which is shown by cationic RAFT polymerizations,<sup>13,14</sup> to yield polymers with controlled molecular weights (MWs) and narrow molecular weight distributions (MWDs).<sup>15-20</sup>

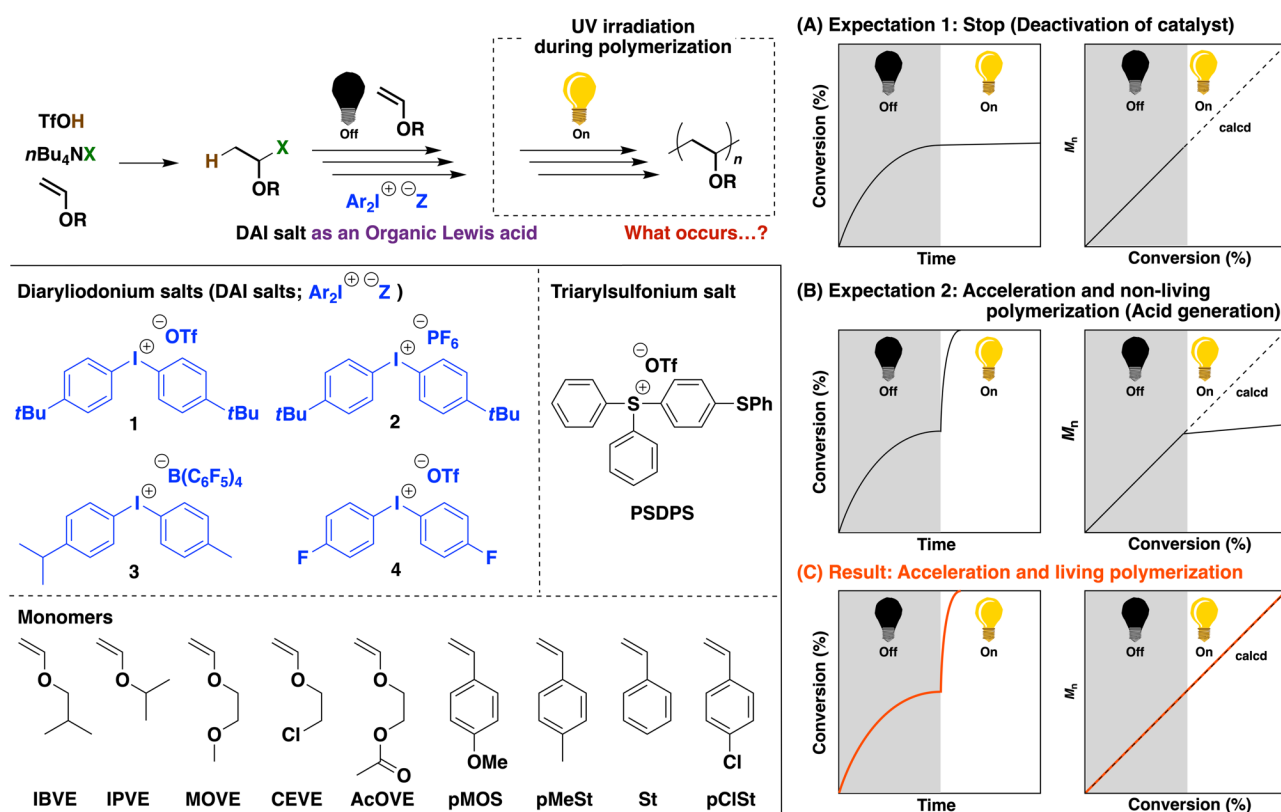


**Scheme 1.** DAI salts used as (A) photoacid generator and (B) organic Lewis acid in cationic polymerization.

Unlike its role as a photoinitiator, the role of DAI as a Lewis acid catalyst was examined in studies of Lewis acid-catalyzed reactions of low-MW compounds.<sup>21,22</sup> The positively charged iodine atom of DAI salts exerted Lewis acidity via a halogen-bonding interaction with a Lewis basic species.<sup>23–26</sup> Focusing on this aspect of DAI salts, our group developed metal-free living cationic polymerization of VEs and styrenes using DAI salts as Lewis acid catalysts.<sup>27</sup> The polymerization proceeded via the reversible generation of carbocations from the carbon–iodine bonds at the propagating ends through the abstraction of the iodide anion by DAI salts (Scheme 1B). The substituents of DAI salts affected the Lewis acidity; hence, faster polymerization occurred when DAI salts with electron-withdrawing substituents were used. Iodine-containing compounds other than DAI salts were also reported to catalyze living cationic polymerization via halogen-bonding interactions.<sup>28,29</sup> However, the catalytic activity of DAI salts and related compounds is lower than that of many metal-based Lewis acid catalysts. It is of great significance to develop metal-free systems that allow for living cationic polymerization of low reactive monomers, such as styrene derivatives with electron-withdrawing substituents.

In a series of our studies on living cationic polymerization using DAI salts as Lewis acid

catalysts, we used UV light irradiation during polymerization. Our initial expectation was the stop of polymerization or the loss of livingness via the DAI salt decomposition after UV irradiation (Scheme 2A and 2B). However, surprisingly, polymerization was drastically accelerated while maintaining the livingness even after UV irradiation (Scheme 2C). Such a drastic acceleration is highly attractive when considering the development of metal-free systems for polymerizations of low reactive monomers. Therefore, in this study, we examined the UV irradiation-triggered acceleration of the cationic polymerization of VEs using DAI salts as Lewis acid catalysts. In particular, a detailed investigation was conducted to elucidate the acceleration mechanism. Moreover, the UV irradiation-triggered acceleration system was applied to cationic polymerizations of functional group-containing VEs and styrenes.



**Scheme 2.** Cationic Polymerization of Vinyl Monomers Using DAI Salts as Organic Lewis Acid Catalysts and UV irradiation in the middle stage of polymerization.

## Experimental Section

See the Supporting Information for the Materials and Characterization subsections.

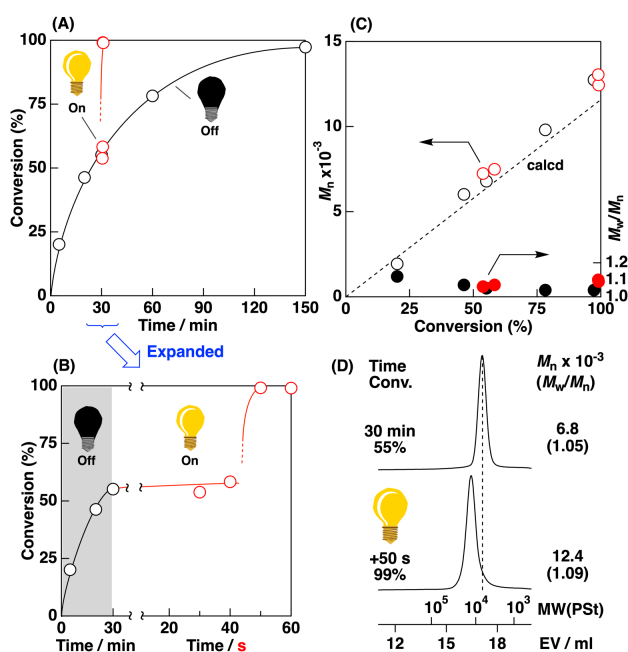
**Polymerization.** The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the air temperature was approximately 450 °C) under dry nitrogen. Dichloromethane, solutions of *n*Bu<sub>4</sub>NI and TfOH in dichloromethane, and isobutyl VE (IBVE) were sequentially added into the tube using dry syringes. The polymerization was initiated by the addition of a solution of **1** in dichloromethane at –40 °C. After 30 min, the solution was irradiated using a 250 W high-pressure mercury lamp (Ushio, SP-9) for a certain time period. 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 aqueous sodium hydroxide solution and water. The volatiles were evaporated under reduced pressure at 50 °C. The monomer conversion was determined by gas chromatography (GC), gravimetry, or <sup>1</sup>H NMR spectroscopy of the quenched reaction mixture.

## Results and Discussion

### UV Irradiation during the Cationic Polymerization Using DAI Salts as Organic Lewis Acid Catalysts

Cationic polymerization of IBVE was conducted using **1** as a Lewis acid catalyst in conjunction with trifluoromethanesulfonic acid (TfOH)/*n*Bu<sub>4</sub>NI<sup>30</sup> in dichloromethane at –40 °C. As reported in our previous study,<sup>27</sup> the polymerization proceeded smoothly in a living manner, resulting in polymers with *M<sub>n</sub>* values that increased in accordance with the theoretical values based on the charged amount of TfOH and the consumed amounts of IBVE (Figure 1A and 1C, black circles). During this polymerization reaction, UV light was irradiated with a high-pressure Hg lamp. Notably,

the polymerization was drastically accelerated after UV irradiation (Figure 1A and 1B, red circles; entry 1 in Table 1). 55% monomer conversion was reached in 30 min before UV irradiation, while 99% conversion was attained in 50 s after UV irradiation. More surprisingly, polymers with controlled MWs and narrow MWDs were obtained after UV irradiation. As shown in Figure 1C (red circles), the  $M_n$  values increased in accordance with the theoretical values, as in the case of polymerization without UV irradiation. The MWD curve shifted to the high-MW region while maintaining a unimodal distribution (Figure 1D). From the  $^1\text{H}$  NMR analysis of the product polymer (Figure S1), the peaks assignable to structures derived from side reactions, such as  $\beta$ -proton elimination, were almost undetected. These results indicated that the polymerization using **1** as a catalyst proceeded in a living manner even after acceleration via UV irradiation. The difference of stereoregularity (tacticity) was not observed between the polymers obtained before and after UV irradiation (Figure S2).



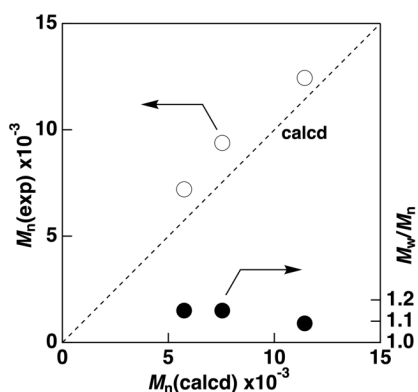
**Figure 1.** (A), (B) Time–conversion curves of the polymerization of IBVE (black: UV off, red: UV on), (C)  $M_n$  and  $M_w/M_n$  values, and (D) MWD curves of the obtained polymers. Polymerization conditions:  $[\text{IBVE}]_0 = 0.46$  M,  $[\text{TfOH}]_0 = 4.0$  mM,  $[\text{nBu}_4\text{NI}]_0 = 4.2$  mM,  $[\mathbf{1}]_0 = 2.0$  mM, in dichloromethane at  $-40$  °C.

**Table 1. Cationic Polymerization of IBVE Using Diaryliodonium Salts or PSDPS<sup>a</sup>**

entry	onium salt	added salt	temp. (°C)	time before irradiation	irradiation time	conv. (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ (GPC) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
1	1	<i>n</i> Bu <sub>4</sub> NI	−40 °C	30 min	–	55	6.4	6.8	1.05
				30 min	50 s	99	11.4	12.4	1.09
2	2	<i>n</i> Bu <sub>4</sub> NI	−40 °C	20 min	–	43	4.9	6.8	1.05
				20 min	45 s	>99	11.6	13.3	1.10
3	3	<i>n</i> Bu <sub>4</sub> NI	−40 °C	10 min	–	35	4.1	4.6	1.07
				10 min	40 s	97	11.2	13.3	1.13
4	4	<i>n</i> Bu <sub>4</sub> NI	−40 °C	2 min	–	32	3.7	4.4	1.08
				2 min	30 s	97	11.2	12.8	1.18
5	4	<i>n</i> Bu <sub>4</sub> NBr	−40 °C	40 min	–	65	7.6	9.1	1.11
				40 min	5 min	>99	11.5	12.3	1.22
6	4	<i>n</i> Bu <sub>4</sub> NCl	−40 °C	165 h	–	49	5.6	6.2	1.08
				165 h	10 min	99	11.5	10.9	3.56
7	1	<i>n</i> Bu <sub>4</sub> NI	0 °C	5 min	–	34	3.9	4.6	1.12
				5 min	30 s	>99	11.6	4.9	1.79
8	1	<i>n</i> Bu <sub>4</sub> NI	−78 °C	40 min	–	9	1.0	1.1	1.15
				40 min	3 min	>99	11.5	14.9	1.41
9	1	<i>n</i> Bu <sub>4</sub> NI	−40 °C	5 min	–	20	2.4	1.9	1.12
				5 min	60 s	99	11.5	12.9	1.17
10	1	<i>n</i> Bu <sub>4</sub> NI	−40 °C	10 s	–	12	1.4	1.0	1.45
				10 s	20 s	82	9.5	11.5	1.23
11	PSDP <sub>c</sub>	<i>n</i> Bu <sub>4</sub> NI	−40 °C	69 h	–	53	6.2	6.9	1.04
				69 h	2 min	>99	11.6	9.8	1.19

<sup>a</sup> [IBVE]<sub>0</sub> = 0.46 M, [TfOH]<sub>0</sub> = 4.0 mM, [added salt]<sub>0</sub> = 4.2 mM, [onium salt]<sub>0</sub> = 2.0 mM, in dichloromethane at −40 °C. <sup>b</sup> By GPC (polystyrene calibration).

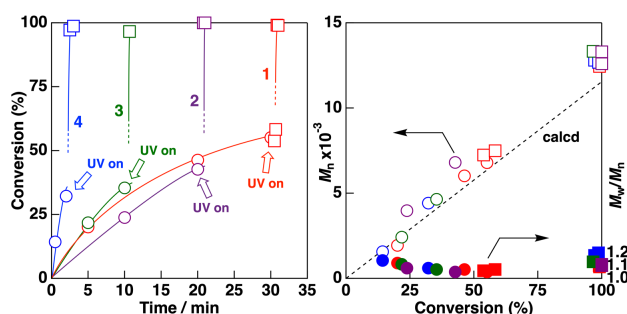
To examine the amounts of propagating chains during polymerization, UV irradiation was applied to the cationic polymerizations at different concentrations of the TfOH (Figures 2 and S3). The polymerizations were accelerated without loss of livingness after UV irradiation in each case. The  $M_n$  values of the obtained polymers obviously depended on the amount of TfOH (open circles in Figure 2). Therefore, acceleration of the polymerization most likely occurred without the generation of new propagating chains. In other words, the propagating chains that already existed before UV irradiation underwent accelerated propagation reactions.



**Figure 2.**  $M_n$  values of the IBVE polymers obtained at different concentrations of TfOH (after UV irradiation). The  $M_n(\text{calcd})$  values were calculated from  $[\text{IBVE}]_0/[\text{TfOH}]_0 \times \text{conversion}$ . Polymerization conditions:  $[\text{IBVE}]_0 = 0.46 \text{ M}$ ,  $[\text{TfOH}]_0 = 4.0, 6.0, \text{ or } 8.0 \text{ mM}$ ,  $[\text{nBu}_4\text{NI}]_0 = 4.2, 6.3, \text{ or } 8.4 \text{ mM}$ ,  $[\mathbf{1}]_0 = 2.0 \text{ mM}$ , in dichloromethane at  $-40 \text{ }^\circ\text{C}$ . See Figure S3 for the  $M_n$ -conversion plots.

### Effects of Various DAI Salts, Tetrabutylammonium Halides, Temperature, and Timing of UV Irradiation.

DAI salts with different substituents and counteranions were used as Lewis acid catalysts in the cationic polymerization. Polymerizations with DAI salts **2–4** were faster than those with **1**, while all the reactions proceeded in a living manner (Figure 3, circle symbols). When UV light irradiation was irradiated at the middle stage, polymerizations were clearly accelerated in all cases (entries 2–4 in Table 1; Figure 3, square symbols). Moreover, polymers with controlled  $M_n$ s and narrow MWDs were obtained, as in the case of the polymerization with **1**. The results indicated that the acceleration of living polymerization via UV irradiation did not depend on the kinds of DAI salts.



**Figure 3.** (A) Time-conversion curves of the polymerization of IBVE and (B)  $M_n$  and  $M_w/M_n$  values of the obtained polymers [before (circles) and after (squares) UV irradiation]. Polymerization conditions:  $[\text{IBVE}]_0 = 0.46 \text{ M}$ ,  $[\text{TfOH}]_0 = 4.0 \text{ mM}$ ,  $[\text{nBu}_4\text{NI}]_0 = 4.2 \text{ mM}$ ,  $[\text{DAI salt}]_0 = 2.0 \text{ mM}$ , in dichloromethane at  $-40 \text{ }^\circ\text{C}$ . The data using **1** are the same as those in Figure 1. Entries 1–4 in Table

1.

Unlike comparable results with different DAI salts, the kinds of tetraalkylammonium salts affected the controllability of polymerization. In the cationic polymerization of VEs with the TfOH/*n*Bu<sub>4</sub>NX (X = I, Br, or Cl) system, carbon–halogen bonds were generated at the propagating ends.<sup>30</sup> For example, carbon–iodine bonds were generated when *n*Bu<sub>4</sub>NI was used in the above experiments. When *n*Bu<sub>4</sub>NBr was used instead of *n*Bu<sub>4</sub>NI, the polymerization was accelerated after UV irradiation, and a polymer with a controlled  $M_n$  and relatively narrow MWD was obtained (entry 5 in Table 1; Figure S4; see Figure S1 for the <sup>1</sup>H NMR spectrum). The polymerization was even accelerated when *n*Bu<sub>4</sub>NCl was used (entry 6 in Table 1; Figure S4). However, different from the *n*Bu<sub>4</sub>NI and *n*Bu<sub>4</sub>NBr cases, a polymer with a bimodal MWD was obtained. The lower-MW peak of the bimodal MWD was very similar to the unimodal peak of the polymer obtained before UV irradiation. Therefore, the higher-MW portion was most likely generated after UV irradiation.

Acceleration via UV irradiation was also observed in polymerizations at 0 and –78 °C (entries 7 and 8 in Table 1; Figure S5). The MWD curves of the obtained polymers shifted to the higher-MW region compared to those of the products obtained before UV irradiation. However, a product obtained at 0 °C had a tailing in the lower-MW region of the MWD curve (entry 7). The  $M_n$  value was also comparable to that of the polymer obtained before irradiation, indicating that side reactions, such as chain transfer reactions, occurred at 0 °C. In contrast, a polymer with a high MW was obtained at –78 °C (entry 8; see Figure S1 for the <sup>1</sup>H NMR spectrum), but the MWD was broader than that of the product obtained at –40 °C (entry 1).

The effects of the time before UV irradiation were also examined. Even when UV light was irradiated after 5 min or 10 s (entries 9 and 10 in Table 1; Figure S6), the polymerizations were accelerated and resulted in the generation of polymers with controlled  $M_n$ , similar to the case of UV

irradiation after 30 min (entry 1).

### Experiments in the Absence of DAI Salts or with a Triarylsulfonium Salt

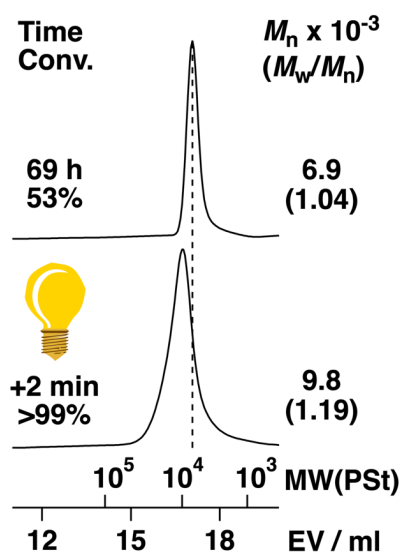
As demonstrated above, the polymerization acceleration associated with livingness via UV irradiation was different from our initial expectation [i.e., the decomposition of the DAI salts via UV irradiation would result in stop of the polymerization or loss of polymerization control (Scheme 2)]. To reveal the role of DAI salts, we then examined polymerizations in the absence of DAI salts.

Thus, UV light was irradiated during cationic polymerization in the absence of DAI salts. Isopropyl VE (IPVE), which is a more reactive VE than IBVE, was used because living polymerization of IPVE proceeded at a moderate rate even in the absence of Lewis acid catalysts with a TfOH/*n*Bu<sub>4</sub>NI system via spontaneous cleavage of the carbon–iodine bonds at the propagating ends.<sup>30</sup> UV light was irradiated when the IPVE conversion reached approximately 50% in 2 h. However, polymerization was not accelerated at all [Figure S7; cf. In the presence of DAI 1, the polymerization of IPVE was accelerated associated with livingness (Figure S8)]. These results implied that DAI salts were needed for acceleration. In addition, UV light was irradiated for 7 h during the IPVE polymerization in the absence of DAI salts (Figure S9). The result was similar to that obtained without UV irradiation in terms of monomer conversion and MW, which suggests that special effects of UV irradiation on propagating species or other components, such as the cleavage of the carbon–iodine bonds and the photodegradation of *n*Bu<sub>4</sub>NI by UV irradiation, were not exerted.

DAI salts are often used as photoinitiators in cationic polymerization because cationic species, such as protonic acids, are generated via the decomposition of DAI salts by using UV irradiation. To examine the effects of protonic acids, TfOH was added during the catalyst-free cationic polymerization of IPVE with TfOH/*n*Bu<sub>4</sub>NI. As a result, polymerization was accelerated after 2.0 mM TfOH was added at 34% conversion (Figure S10). However, the polymerization was

uncontrolled, resulting in a polymer with a broad MWD. The result indicated that very fast and uncontrolled polymerization likely proceeded due to the added acid. Therefore, acceleration associated with livingness via UV irradiation was not related to acid generation from the DAI salts. Acceleration could potentially occur before the acids were generated by the decomposition of the DAI salts.

Interestingly, polymerization acceleration associated with livingness was observed when (4-phenylthiophenyl)diphenylsulfonium triflate (PSDPS) was used instead of DAI salts. PSDPS is used as a photoinitiator in cationic polymerization.<sup>8</sup> However, PSDPS does not function as a Lewis acid catalyst, different from DAI salts, because halogen bonding is not formed at the sulfur atom. Cationic polymerization of IBVE was conducted with the TfOH/*n*Bu<sub>4</sub>NI system in the presence of PSDPS. The polymerization was very slow compared to the reaction using **1**, which was consistent with the absence of the Lewis acidity of PSDPS. The polymerization occurred via the spontaneous cleavage of the carbon–iodine bonds. When UV was irradiated at 55% conversion that needed 69 h, the polymerization was accelerated and resulted in >99% conversion in 2 min (entry 11 in Table 1; Figure 4). Moreover, the unimodal MWD of the product shifted to the higher-MW region, suggesting that the polymerization proceeded in a living manner even after UV irradiation. The results indicate that the Lewis acidity of DAI salts was not important and that decomposition of the photoinitiators likely contributed to acceleration by UV irradiation.



**Figure 4.** MWD curves of poly(IBVE)s:  $[\text{IBVE}]_0 = 0.46 \text{ M}$ ,  $[\text{TfOH}]_0 = 4.0 \text{ mM}$ ,  $[\text{nBu}_4\text{NI}]_0 = 4.2 \text{ mM}$ ,  $[\text{PSDPS}]_0 = 2.0 \text{ mM}$ , in dichloromethane at  $-40 \text{ }^\circ\text{C}$ . Entry 11 in Table 1.

### Experiments Based on the Hypothesis that the Consumption of $\text{I}^-$ Triggers Acceleration

From the results obtained above, we hypothesized that polymerization acceleration occurred from the consumption of some species triggered by the decomposition of DAI salts via UV irradiation. A candidate species consumed was an iodide anion because decomposition of DAI salts generated radical and cationic species in past studies.<sup>6,8,9</sup> If sufficient amounts of iodide anions were consumed by the reactions with radical and cationic species, a part of the carbon–iodine bonds at the propagating ends was broken to generate propagating carbocations that did not contain iodide anions but contained triflate anions, which did not form dormant covalent bonds with the VE-derived carbocations.

To examine the effects of the amount of iodide anions, polymerizations were conducted at different  $\text{nBu}_4\text{NI}$  concentrations.<sup>31</sup> When the  $\text{nBu}_4\text{NI}$  concentration was increased from 4.2 mM to 5.0 or 5.4 mM, the polymerizations were still accelerated while maintaining livingness (entries 2 and 3 in Table 2; Figure S11B and S11C). In contrast, acceleration did not occur at 5.8 mM  $\text{nBu}_4\text{NI}$  even when UV irradiation was applied for 60 min (entry 4; Figure S11D). Similar inert behavior was also observed in the polymerization of IPVE at 6.2 mM  $\text{nBu}_4\text{NI}$  (entry 5; Figure S11E). The results

indicated that acceleration via UV irradiation was suppressed when adequate amounts of iodide anions were present during polymerization.

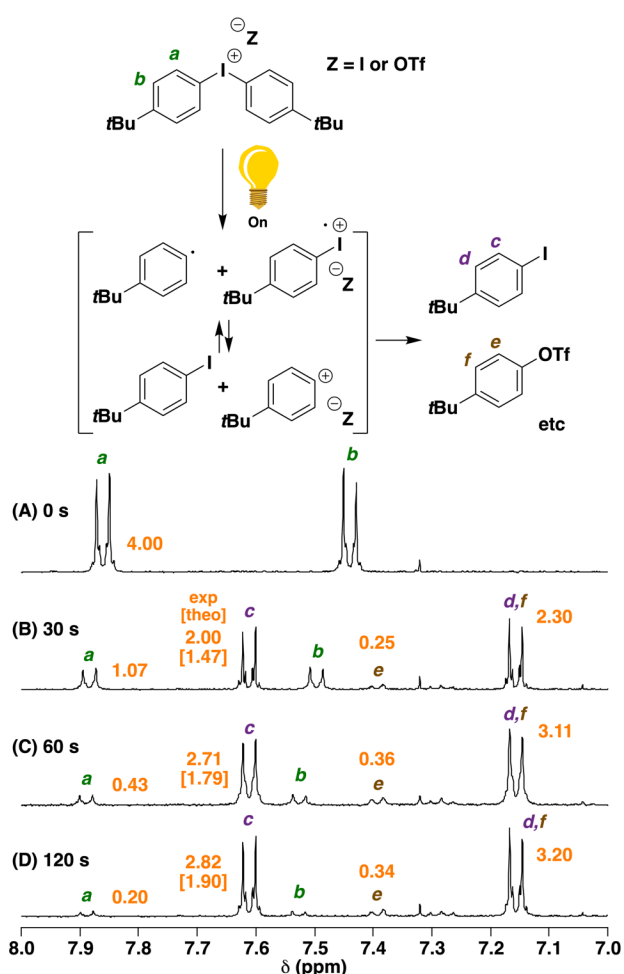
**Table 2. Cationic Polymerization of IBVE or IPVE at Various Concentrations of  $n\text{Bu}_4\text{NI}$ <sup>a</sup>**

entry	$[\text{nBu}_4\text{NI}]_0$ (mM)	time before irradiation	irradiation time	conv. (%)	$M_n \times 10^{-3}$ (GPC) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Polymerization behavior
1	4.2	30 min	–	55	6.8	1.05	
		30 min	50 s	99	12.4	1.09	Accelerated
2	5.0	60 min	–	32	3.9	1.07	
		60 min	90 s	98	13.2	1.11	Accelerated
3	5.4	60 min	–	20	1.5	1.11	
		60 min	90 s	98	12.1	1.19	Accelerated
4	5.8	60 min	–	12	0.9	1.09	
		60 min	2 min	11	0.9	1.08	
		60 min	60 min	14	1.3	1.13	Not accelerated
5 (IPVE)	6.2	75 min	–	45	6.5	1.07	
		75 min	40 min	64	7.9	1.08	Not accelerated

<sup>a</sup>  $[\text{IBVE}]_0 = 0.46$  M (entry 1–4) or  $[\text{IPVE}]_0 = 0.52$  M (entry 5),  $[\text{TfOH}]_0 = 4.0$  mM,  $[\text{nBu}_4\text{NI}]_0 = 4.2$ – $6.2$  mM,  $[\mathbf{1}]_0 = 2.0$  mM, in dichloromethane at  $-40$  °C. Entry 1 corresponds to entry 1 in Table 1 and Figure 1. See Figure S11 for the time–conversion curves. <sup>b</sup> By GPC (polystyrene calibration).

The consumption of iodide anions was confirmed in the experiment that monitored the UV-induced decomposition of a DAI salt by <sup>1</sup>H NMR spectroscopy. When a solution containing TfOH,  $n\text{Bu}_4\text{NI}$ , and **1** in  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$  was irradiated with UV light for 30 s, peaks assigned to *p*-*tert*-butyliodobenzene (peaks *c* and *d*) and *p*-*tert*-butyl(trifluoromethanesulfonyl)benzene (peaks *e* and *f*) were observed (Figure 5B).<sup>32,33</sup> These species were generated via the decomposition of **1**. After UV irradiation for 120 s, the peaks assigned to **1** (peaks *a* and *b*) became very small (Figure 5D). If *p*-*tert*-butyliodobenzene was derived from only the positively charged iodine atom of **1**, the amount of *p*-*tert*-butyliodobenzene would have corresponded to the consumed amount of **1**. The orange numbers in the parentheses in Figure 5 were the theoretical integral ratios calculated from the consumed amounts of **1**. However, the experimental integral ratios were clearly larger than the theoretical ratios. This result suggested that *p*-*tert*-butyliodobenzene was generated both from the positively charged iodine atom of **1** and the iodide anion derived from  $n\text{Bu}_4\text{NI}$ . In other words, iodide anions derived

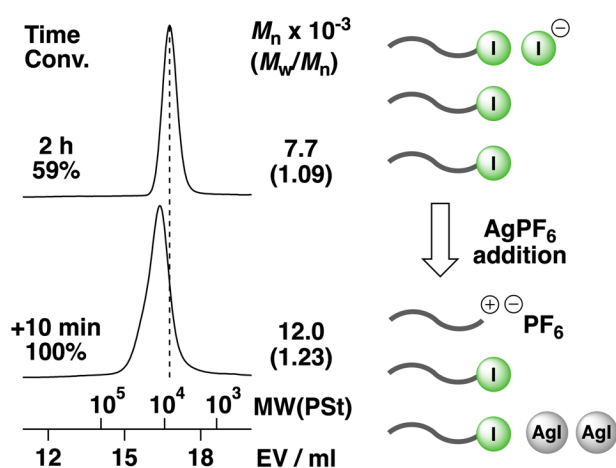
from  $n\text{Bu}_4\text{NI}$  were possibly consumed by the decomposition of the DAI salts in the polymerizations. For example, in Figure 5D, the remaining **1** was 0.10 mM, which theoretically corresponds to the generation of 1.90 mM *p-tert*-butyliodobenzene, whereas the actual amount of *p-tert*-butyliodobenzene was 2.82 mM, indicating that 0.92 mM (= 2.82 mM – 1.90 mM)  $n\text{Bu}_4\text{NI}$  was consumed for *p-tert*-butyliodobenzene generation.



**Figure 5.**  $^1\text{H}$  NMR spectra (recorded at 30 °C) of **1** (A) before and after UV irradiation for (B) 30, (C) 60, or (D) 120 s in the presence of  $n\text{Bu}_4\text{NI}$  at  $-40$  °C. ( $[\text{TfOH}]_0 = 4.0$  mM,  $[n\text{Bu}_4\text{NI}]_0 = 4.2$  mM,  $[\mathbf{1}]_0 = 2.0$  mM, in  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$  (4/1 v/v)). A solution was sealed in an NMR sample tube and UV light was irradiated to the tube. Orange numbers are integral ratios. (Numbers in parentheses are theoretical values based on that *p-tert*-butyliodobenzene was derived from only the positively charged iodine atom of **1**. The experimental values were larger than the theoretical values, which means that *p-tert*-butyliodobenzene was also derived from the iodine anions of  $n\text{Bu}_4\text{NI}$ .)

To reproduce the acceleration via the consumption of iodide anions without using DAI salts,

AgPF<sub>6</sub> was gradually added during the catalyst-free polymerization of IPVE with the TfOH/*n*Bu<sub>4</sub>NI system. AgPF<sub>6</sub> would react with an iodide anion to generate AgI precipitates. When the monomer conversion reached 59% in 2 h, a solution of AgPF<sub>6</sub> was gradually added for approximately 5 min with a syringe. Interestingly, the monomer conversion reached >99% in 10 min, and a polymer with a controlled MW and narrow MWD was obtained (Figure 6); this result indicated that the acceleration associated with livingness was reproduced without using DAI salts based on the hypothesis of iodide consumption.



**Figure 6.** MWD curves of poly(IPVE)s: [IPVE]<sub>0</sub> = 0.52 M, [TfOH]<sub>0</sub> = 4.0 mM, [*n*Bu<sub>4</sub>NI]<sub>0</sub> = 4.2 mM, [AgPF<sub>6</sub>]<sub>added</sub> = 0.60 mM, in dichloromethane at -40 °C. AgPF<sub>6</sub> was gradually added.

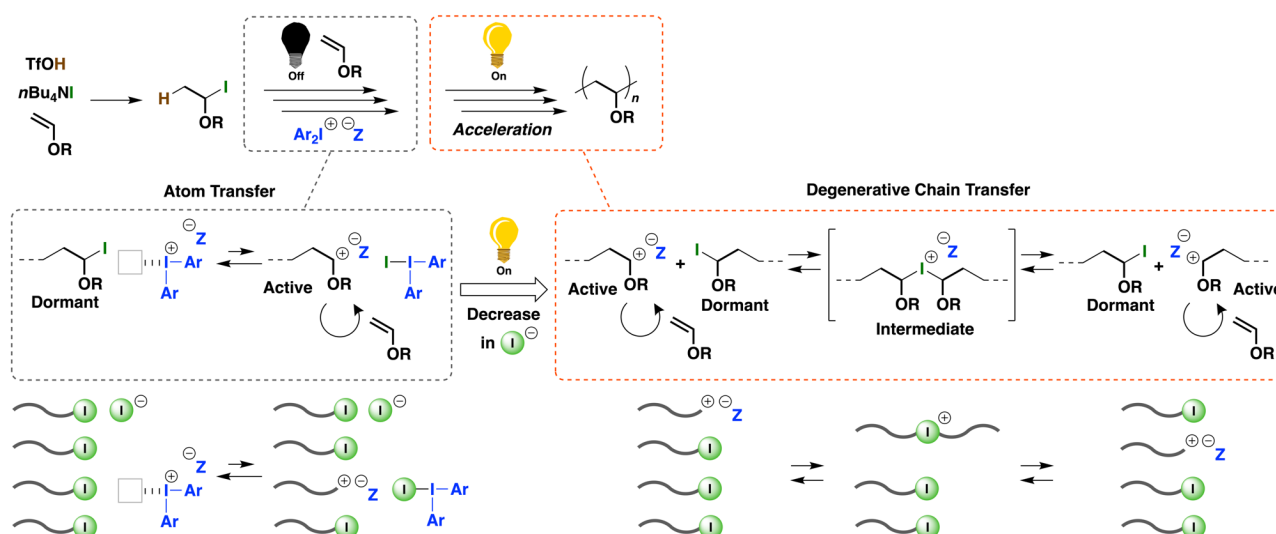
### Possible Mechanisms of Acceleration via UV Irradiation

Based on the experimental results obtained (Chart 1), we propose that the change in the polymerization mechanisms from the atom transfer type to degenerative chain transfer type, which is represented by the cationic RAFT polymerization,<sup>13,14</sup> is responsible for the acceleration of living polymerization using DAI salts by UV irradiation (Scheme 3). Before UV irradiation, the polymerization proceeded via the dormant–active equilibrium consisting of carbocation generation through iodide anion abstraction from the carbon–iodide bond at the propagating end caused by a DAI salt and reversible deactivation to regenerate the carbon–iodide bond (Scheme 3, left).<sup>27</sup> In this

state, 4.0 mM propagating chains and 0.2 mM iodide anions were present in the polymerization of  $[\text{TfOH}]_0/[\text{nBu}_4\text{NI}]_0$  with 4.0 mM/4.2 mM. After UV irradiation, decomposition of DAI salts smoothly occurred to consume iodide anions (see Scheme 4 for possible consumption mechanisms<sup>6,7,9</sup>). When excess iodide anions (0.2 mM in the above example) were completely consumed, iodine anions were removed from part of the carbon–iodine bonds at the propagating ends, which most likely triggered polymerization via the degenerative chain transfer mechanism (Scheme 3, right).<sup>34</sup>

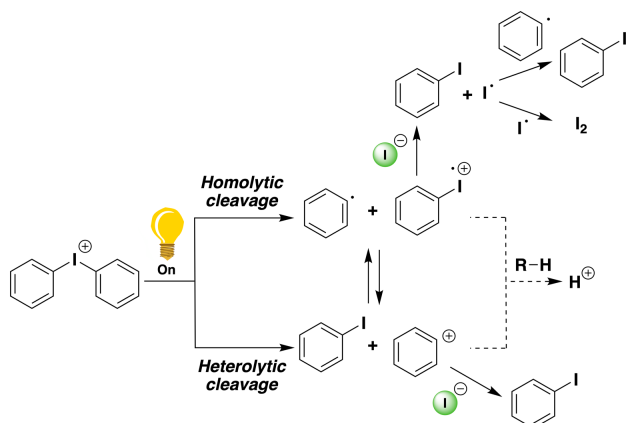
**Chart 1.** Experimental Results and Obtained Information

Experiment	Polymerization behavior	Obtained information concerning acceleration
UV irradiation without DAI salts (Figures S7 and S9)	Not accelerated; A similar result to that obtained without UV irradiation	DAI salts are necessary; UV irradiation does not trigger some reactions such as C–I bond cleavage
TfOH addition instead of UV irradiation (Figure S10)	Accelerated but uncontrolled	$\text{H}^+$ generation may not occur and/or may not be related to living polymerization
Use of PSDPS instead of DAI salts (Figure 4)	Accelerated and long-lived species were generated	Lewis acidity of DAI salts is not important
Use of suitable amounts of $\text{nBu}_4\text{NI}$ (Table 2 and Figure S11)	Accelerated and long-lived species were generated	Decrease in the amount of $\text{I}^-$ triggers acceleration
Use of extra amounts of $\text{nBu}_4\text{NI}$ (Table 2 and Figure S11)	Not accelerated	
$\text{AgPF}_6$ addition without DAI salts (Figure 6)	Accelerated and long-lived species were generated	Decrease in the amount of $\text{I}^-$ triggers acceleration



**Scheme 3.** Postulated Mechanism of Acceleration Associated with Livingness by Photoirradiation of Metal-Free Living Cationic Polymerization Using a Diaryliodonium Salt.<sup>a</sup>

<sup>a</sup> Z is a non- or weakly-coordinating anions such as TfO<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, derived from DAI salts and TfOH.



**Scheme 4.** Examples of I<sup>-</sup> Consumption Pathways by Decomposition of DAI Salts.

Gradual consumption of the iodide anions and a gradual increase in the amount of propagating cations that do not have an iodide anion but contain non- or weakly coordinating anions, such as TfO<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>, derived from DAI salts and TfOH are highly important for both acceleration and living polymerization. If propagating cations bearing non- or weakly coordinating anions as a counteranion are rapidly generated, uncontrolled propagation reactions probably occur because dormant species with covalent bonds are not formed between the carbocations and these non- or weakly coordinating anions. Indeed, rapid addition of TfOH, not gradual addition, resulted in uncontrolled polymerization (Figure S10). Gradual generation of these "active" propagating chains with the gradual decomposition of DAI salts via UV irradiation triggers the smooth shift to the iodine transfer-type degenerative chain transfer mechanism without losing polymerization control (Scheme 3).

The acceleration mechanism proposed above is supported by the experimental results. Polymerization was not accelerated at high concentrations of *n*Bu<sub>4</sub>NI (Table 2, Figure S11), which indicated that only excess iodide anions were consumed in the decomposition of DAI salts and that the carbon–iodine bonds at the propagating ends remained intact. The results listed in Table 2 likely

mean that approximately 1.4 to 1.8 mM iodide anions derived from  $n\text{Bu}_4\text{NI}$  were consumed under the examined conditions with 2.0 mM DAI salt **1**. The use of  $n\text{Bu}_4\text{NCl}$  resulted in a polymer with a bimodal MWD (entry 6 in Table 1; Figure S4) because the degenerative chain transfer mechanism was ineffective at the carbon–chlorine bonds. Specifically, the inertness of the carbon–chlorine bonds was suggested by the result that the lower-MW peak of the bimodal MWD curve after UV irradiation remained at the same position as that before UV irradiation (Figure S4). The higher-MW peak of the bimodal MWD curve was generated from cationic species derived from DAI decomposition, whereas the propagating chains with carbon–chlorine bonds remained intact even in the presence of the cationic species. Accelerations associated with livingness in the absence of DAI salts, which were achieved via PSDPS (Figure 4) or  $\text{AgPF}_6$  (Figure 6), were also consistent with our proposed mechanism. The broader MWD of the polymer obtained at  $-78\text{ }^\circ\text{C}$  (entry 8 in Table 1) than that at  $-40\text{ }^\circ\text{C}$  likely resulted from relatively slow degenerative chain transfer reactions compared to propagation reactions at the low temperature.

### **UV-Irradiation-Triggered Acceleration of the Polymerizations of Functional Group-Containing VEs and Styrene Derivatives**

The acceleration by UV irradiation was applied to cationic polymerizations of other monomers. 2-Methoxyethyl VE (MOVE), 2-chloroethyl VE (CEVE), and 2-acetoxyethyl VE (AcOVE) were used as functional group-containing VEs. MOVE exhibited slightly higher reactivity, and CEVE and AcOVE exhibited lower reactivity than IBVE. As a result, cationic polymerizations of the three VEs using **2** were accelerated via UV irradiation, resulting in polymers with unimodal MWDs (entries 1–3 in Table 3; Figure 7A, 7B, and 7C). However, the  $M_n$  values of the polymers were lower than the theoretical values in the cases of MOVE and AcOVE, which suggests the occurrence of side reactions. In addition, CEVE and AcOVE polymers had very broad MWDs, likely

indicating uneven propagation reactions of polymer chains due to the small rates of the iodine-transfer reactions (Scheme 3, right).

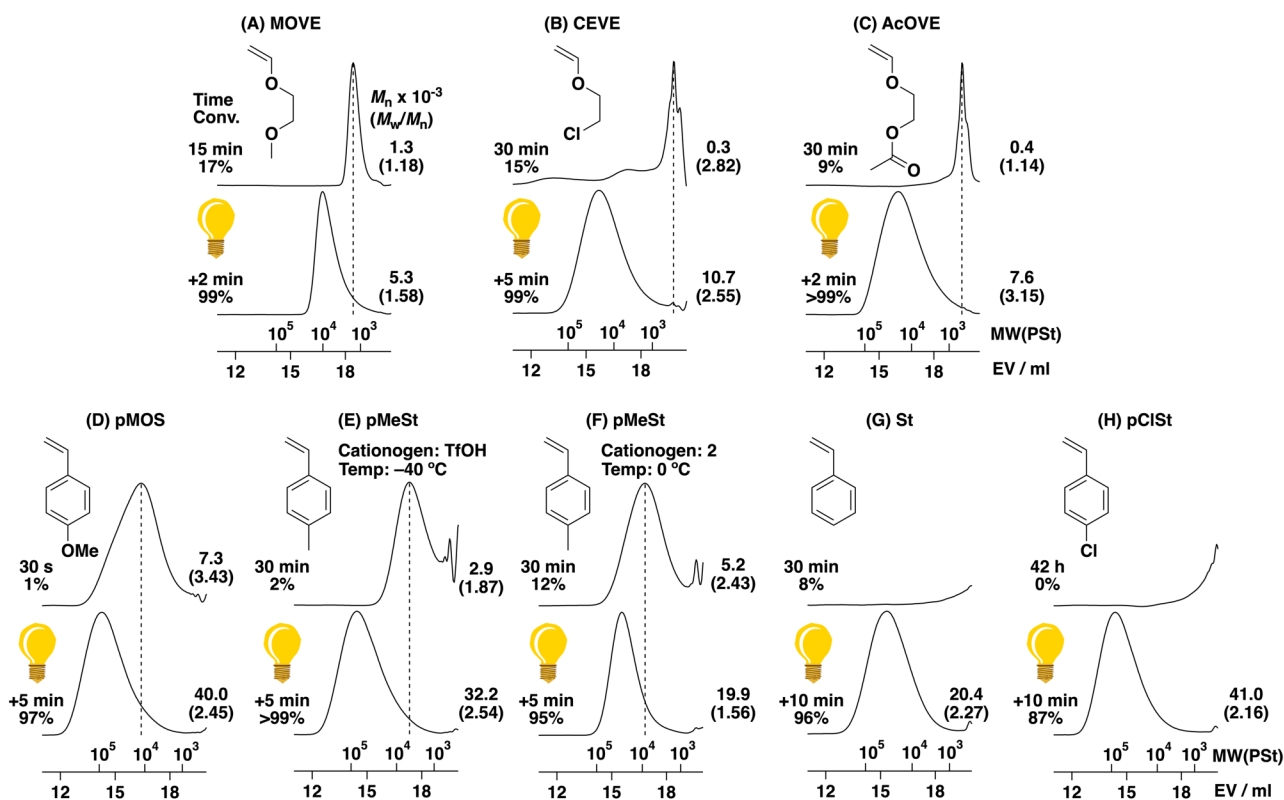
Cationic polymerization of styrenes using DAI salts was also accelerated by UV irradiation. *p*-Methoxystyrene (pMOS), *p*-methylstyrene (pMeSt), styrene (St), and *p*-chlorostyrene (pClSt), whose reactivities decrease in this order, were polymerized with **2**. All polymerization reactions were accelerated to attain more than approximately 90% monomer conversion in 5 or 10 min after UV irradiation (entries 4, 5, 7, and 8 in Table 3). In particular, the monomer conversion was almost 0% in 42 h in the polymerization of pClSt before UV irradiation, while 87% conversion was achieved in 10 min after irradiation. The  $M_n$  values were larger than the theoretical values in all cases, indicating low initiation efficiency. In addition, MWDs were broad, probably due to small rates of the iodine-transfer reactions; however, it was not clear whether cationic polymerizations of styrenes proceeded via the degenerative chain transfer mechanism involving the iodine-transfer reactions. Alkoxy groups were reported to function as reversible chain transfer agents in the cationic polymerization of pMOS.<sup>16,35</sup> Further investigation is needed to elucidate the polymerization mechanisms.

The possibility of improving controllability was demonstrated by the design of suitable reaction conditions. Instead of using TfOH, **2** with a PF<sub>6</sub><sup>-</sup> counteranion was used as both photoinitiator and Lewis acid catalyst because TfO<sup>-</sup> anions most likely induced β-proton elimination reactions in the polymerization of styrenes.<sup>27,36,37</sup> A solution containing pMeSt, **2**, and *n*Bu<sub>4</sub>NI was irradiated with UV light, which resulted in the generation of initiating species. After UV irradiation was stopped, **2** was newly added to the solution as a Lewis acid catalyst. When the monomer conversion reached 12% in 30 min at 0 °C, UV light was used, triggering acceleration of the polymerization and resulting in 95% conversion in 5 min. The obtained polymer had a narrower MWD than that obtained with TfOH at -40 °C. We are further investigating suitable conditions for the UV-accelerated cationic polymerization of styrenes.

**Table 3. Cationic Polymerization of Vinyl Monomers Using Diaryliodonium Salt 2<sup>a</sup>**

entry	monomer	cationogen	Lewis acid	temp. (°C)	time before irradiation	irradiation time	conv. (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ (GPC) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
1	MOVE	TfOH	2	-40 °C	15 min	–	17	2.3	1.3	1.18
					15 min	2 min	99	13.3	5.3	1.58
2	CEVE	TfOH	2	-40 °C	30 min	–	15	1.5	0.3	2.82
					30 min	5 min	99	10.4	10.7	2.55
3	AcOVE	TfOH	2	-40 °C	30 min	–	9	1.4	0.4	1.14
					30 min	2 min	>99	15.1	7.6	3.15
4	pMOS	TfOH	2	-40 °C	30 s	–	1	0.2	7.3	3.43
					30 s	5 min	97	14.6	40.0	2.45
5	pMeSt	TfOH	2	-40 °C	30 min	–	2	0.3	2.9	1.87
					30 min	5 min	>99	13.5	32.2	2.54
6	pMeSt	2 <sup>c</sup>	2	0 °C	30 min	–	12	1.6	5.2	2.43
					30 min	5 min	95	12.8	19.9	1.56
7	St	TfOH	2	-40 °C	30 min	–	8	–	–	–
					30 min	10 min	96	13.2	20.4	2.27
8	pClSt	TfOH	2	-40 °C	42 h	–	0	–	–	–
					42 h	10 min	87	14.3	41.0	2.16

<sup>a</sup> [Monomer]<sub>0</sub> = 4 vol % (entry 2, [CEVE]<sub>0</sub> = 0.39 M) or 6 vol % (entry 1 and 3–8, [MOVE]<sub>0</sub> = 0.53 M, [AcOVE]<sub>0</sub> = 0.46 M, [pMOS]<sub>0</sub> = 0.45 M, [pMeSt]<sub>0</sub> = 0.46 M, [St]<sub>0</sub> = 0.52 M, or [pClSt]<sub>0</sub> = 0.47 M), [cationogen]<sub>0</sub> = 4.0 mM, [*n*Bu<sub>4</sub>NI]<sub>0</sub> = 4.2 mM, [2]<sub>0</sub> = 8.0 mM, in dichloromethane. <sup>b</sup> By GPC (polystyrene calibration). <sup>c</sup> Photoinitiation by UV irradiation for 20 min at 0 °C.



**Figure 7.** MWD curves of the products obtained by the polymerizations of (A) MOVE (entry 1 in Table 3), (B) CEVE (entry 2), (C) AcOVE (entry 3), (D) pMOS (entry 4), (E), (F) pMeSt (entries 5 and 6), (G) St (entry 7), and (H) pClSt (entry 8) using DAI salt 2. See Table 3 for the polymerization

conditions.

## Conclusion

In conclusion, living cationic polymerization using DAI salts was accelerated after UV irradiation, while polymerization controllability was maintained, resulting in polymers with predictable MWs and narrow MWDs. As a result of our investigation that focused on various factors, such as photodegradability, Lewis acidity, types of carbon–halogen bonds, and *n*Bu<sub>4</sub>NI amounts, the acceleration associated with livingness likely occurred by the change in the polymerization mechanism from the atom transfer mechanism to the degenerative chain transfer mechanism. The decomposition of the DAI salts involved the consumption of iodide anions, inducing the gradual generation of carbocations that did not contain iodide but contained non- or weakly coordinating counteranions derived from DAI salts and TfOH. In the gradual generation of these "active" propagating chains, the iodine transfer-type degenerative chain transfer mechanism resulted in acceleration while maintaining livingness. The photoinduced acceleration system was also applied to the cationic polymerizations of functional group-containing VEs and styrenes. We are currently investigating the photoinduced acceleration system in more detail to confirm the polymerization mechanism and improve the controllability of polymerizations of various monomers.

## Associated Content

### *Supporting Information*

Experimental section, polymerization data, and NMR spectra of polymerization products.

### *Corresponding Author*

E-mail: aoshima@chem.sci.osaka-u.ac.jp (S.A.)

### *Notes*

The authors declare no competing financial interest.

## Acknowledgments

We thank Ms. Rui Haraguchi (Osaka University) for helpful discussion. This work was partially supported by JSPS KAKENHI Grant 21K05168.

## References and Notes

1. Dadashi-Silab, S.; Doran, S.; Yagci, Y. Photoinduced Electron Transfer Reactions for Macromolecular Syntheses. *Chem. Rev.* **2016**, *116*, 10212–10275.
2. Yagci, Y.; Jockusch, S.; Turro, N. J. Photoinitiated Polymerization: Advances, Challenges, and Opportunities. *Macromolecules* **2010**, *43*, 6245–6260.
3. Shanmugam, S.; Xu, J.; Boyer, C. Photocontrolled Living Polymerization Systems with Reversible Deactivations through Electron and Energy Transfer. *Macromol. Rapid Commun.* **2017**, *38*, 1700143.
4. Aydogan, A.; Yilmaz, G.; Shegiwal, A.; Haddleton, D. M.; Yagci, Y. Photoinduced Controlled/Living Polymerizations. *Angew. Chem. Int. Ed.* **2022**, *61*, e202117377.
5. Chen, M.; Zhong, M.; Johnson, J. A. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. *Chem. Rev.* **2016**, *116*, 10167–10211.
6. Crivello, J. V.; Lam J. H. W. Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization. *Macromolecules* **1977**, *10*, 1307–1315.
7. Crivello, J. V.; Lam J. H. W. Complex Triarylsulfonium Salt Photoinitiators. I. The Identification, Characterization, and Syntheses of a New Class of Triarylsulfonium Salt Photoinitiators. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2677–2695.
8. Crivello, J. V. The Discovery and Development of Onium Salt Cationic Photoinitiators *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241–4254.
9. Dektar, J. L.; Hacker, N. P. Photochemistry of Diaryliodonium Salts. *J. Org. Chem.* **1990**, *55*, 639–647.
10. Knapczyk, J. W.; McEwen, W. E. Photolysis of Triarylsulfonium Salts in Alcohol. *J. Org. Chem.* **1970**, *35*, 2539–2543.
11. Dektar, J. L.; Hacker, N. P. Photochemistry of Triarylsulfonium Salts *J. Am. Chem. Soc.* **1990**, *112*, 6004–6015.
12. Nishikawa, T.; Kanazawa, A.; Aoshima, S. Metal-Free Photoinitiated Controlled Cationic Polymerization of Isopropyl Vinyl Ether Using Diaryliodonium Salts. *Polym. Chem.* **2019**, *10*, 1056–1061.
13. Uchiyama, M.; Satoh, K.; Kamigaito, M. Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid. *Angew. Chem., Int. Ed.* **2015**, *54*, 1924–1928.
14. Uchiyama, S.; Satoh, K.; Kamigaito, M. Cationic RAFT and DT polymerization. *Prog. Polym. Sci.* **2022**, *124*, 101485.
15. Kottisch, V.; Michaudel, Q.; Fors, B. P. Cationic Polymerization of Vinyl Ethers Controlled by Visible Light. *J. Am. Chem. Soc.* **2016**, *138*, 15535–15538.
16. Perkowski, A. J.; You, W.; Nicewicz D. A. Visible Light Photoinitiated Metal-Free Living Cationic Polymerization of 4-Methoxystyrene. *J. Am. Chem. Soc.* **2015**, *137*, 7580–7583.
17. Michaudel, Q.; Kottisch, V.; Fors, B. P. Cationic Polymerization: From Photoinitiation to Photocontrol. *Angew. Chem. Int. Ed.* **2017**, *56*, 9670–9679.
18. Zhang, X.; Jiang, Y.; Ma, Q.; Hu, S.; Liao, S. Metal-Free Cationic Polymerization of Vinyl Ethers with Strict Temporal Control by Employing an Organophotocatalyst. *J. Am. Chem. Soc.* **2021**, *143*, 6357–6362.
19. Matsuda, M.; Uchiyama, M.; Yuki Itabashi, Y.; Ohkubo, K.; Kamigaito, M. Acridinium Salts as Photoredox Organocatalysts for Photomediated Cationic RAFT and DT Polymerizations of Vinyl Ethers. *Polym. Chem.* **2022**, *13*, 1031–1039.
20. Wang, L.; Xu, Y.; Zuo, Q.; Dai, H.; Huang, L.; Zhang, M.; Zheng, Y.; Yu, C.; Zhang, S.; Zhou,

- Y. Visible Light-Controlled Living Cationic Polymerization of Methoxystyrene. *Nat. Commun.* **2022**, *13*, 3621.
21. Zhang, Y.; Han, J.; Liu, Z.-J. Diaryliodonium Salts as Efficient Lewis Acid Catalysts for Direct Three Component Mannich Reactions. *RSC Adv.* **2015**, *5*, 25485–25488.
  22. Zeng, Y.; Li, G.; Hu, J. Diphenyliodonium-Catalyzed Fluorination of Arynes: Synthesis of *ortho*-Fluoroiodoarenes. *Angew. Chem. Int. Ed.* **2015**, *54*, 10773–10777.
  23. Heinen, F.; Engelage, E.; Dreger, A.; Weiss, R.; Huber, S. M. Iodine(III) Derivatives as Halogen Bonding Organocatalysts. *Angew. Chem. Int. Ed.* **2018**, *57*, 3830–3833.
  24. Cavallo, G.; Mentrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* **2016**, *116*, 2478–2601.
  25. Sutar, L. R.; Huber, M. S. Catalysis of Organic Reactions through Halogen Bonding. *ACS Catal.* **2019**, *9*, 9622–9639.
  26. Cavallo, G.; Murray, S. J.; Politzer, P.; Pilati, T.; Ursini, M.; Resnati, G. Halogen Bonding in Hypervalent Iodine and Bromine Derivatives: Halonium Salts. *IUCrJ* **2017**, *4*, 411–419.
  27. Haraguchi, R.; Nishikawa, T.; Kanazawa, A.; Aoshima, S. Metal-Free Living Cationic Polymerization Using Diaryliodonium Salts as Organic Lewis Acid Catalysts. *Macromolecules* **2020**, *53*, 4185–4192.
  28. Takagi, K.; Yamauchi, K.; Murakata, H. Halogen-Bonding-Mediated and Controlled Cationic Polymerization of Isobutyl Vinyl Ether: Expanding the Catalytic Scope of 2-Iodoimidazolium Salts. *Chem. Eur. J.* **2017**, *23*, 9495–9500.
  29. Takagi, K.; Murakata, H.; Yamauchi, K.; Hashimoto, K. Cationic Polymerization of Vinyl Monomers Using Halogen Bonding Organocatalysts with Varied Activity. *Polym. Chem.* **2020**, *11*, 6739.
  30. Hashizume, R.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. Design of Benign Initiator for Living Cationic Polymerization of Vinyl Ethers: Facile in Situ Generation of Vinyl Ether–Hydrogen Halide Adducts and Subsequent Controlled Polymerization without a Lewis Acid Catalyst. *Macromolecules* **2014**, *47*, 1578–1585.
  31. Smaller amounts of *n*Bu<sub>4</sub>NI than that of TfOH are not effective for living polymerization as reported in our previous study (reference 30).
  32. Hubbard, A.; Okazaki, T.; Laali, K. K. Halo- and Azidodediazoniating of Arenediazonium Tetrafluoroborates with Trimethylsilyl Halides and Trimethylsilyl Azide and Sandmeyer-Type Bromodediazoniating with Cu(I)Br in [BMIM][PF<sub>6</sub>] Ionic Liquid. *J. Org. Chem.* **2008**, *73*, 316–319.
  33. Hartman, R. L.; Naber, J. R.; Buchwald, S. L.; Jensen, K. F. Multistep Microchemical Synthesis Enabled by Microfluidic Distillation. *Angew. Chem. Int. Ed.* **2010**, *49*, 899–903.
  34. The atom transfer mechanism probably also operates even after the acceleration. However, the polymerization via the degenerative transfer mechanism occurs at a very large rate, which results in much smaller contribution of the atom transfer mechanism than the degenerative chain transfer mechanism.
  35. Boeck, P. T.; Tanaka, J.; Liu, S.; You, W. Importance of Nucleophilicity of Chain-Transfer Agents for Controlled Cationic Degenerative Chain-Transfer Polymerization. *Macromolecules* **2020**, *53*, 4303–4311.
  36. Higashimura, T.; Hiza, M.; Hasegawa, H. Catalytic Difference between Oxo Acids and Metal Halides in the Cationic Oligomerization of Styrene. *Macromolecules* **1979**, *12*, 217–222.
  37. Hiza, M.; Hasegawa, H.; Higashimura, T. Cationic Oligomerization of Chlorostyrene and *p*-Methoxystyrene: Selective Dimerization of Styrene Derivatives by Oxo Acids. *Polym. J.* **1980**, *12*, 379–385.