# Macromolecules

# Systematic Study on Alkyl lodide Initiators in Living Radical Polymerization with Organic Catalysts

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**Supporting Information** 



**ABSTRACT:** Several low-molar-mass alkyl iodides were studied as initiating dormant species in living radical polymerization with organic catalysts. Primary, secondary, and tertiary alkyl iodides with different stabilizing groups (ester, phenyl, and cyano groups) were systematically studied for the rational design of initiating alkyl iodides. The activation rate constants of these alkyl iodides were experimentally determined for quantitative comparison. These alkyl iodides were used in the polymerizations of methyl methacrylate and butyl acrylate to examine their initiation ability in these polymerizations. A telechelic polymer was prepared using an alkyl iodide with a functional group. Alkyl iodides with multi-initiating sites were also studied.

# ■ INTRODUCTION

Living radical polymerization (LRP) has gained increased attention as a useful technique for preparing well-defined polymers with narrow molecular weight distributions.<sup>1-3</sup> LRP is based on the reversible activation of a dormant species (Polymer-X) to a propagating radical (Polymer<sup>•</sup>) (Scheme 1a). A sufficiently large number of activation—deactivation cycles are required for achieving low polydispersity.<sup>4</sup> We recently developed new LRP systems using iodine as a capping agent and organic molecules as catalysts. We developed two

Scheme 1. Reversible Activation: (a) General Scheme and (b) RCMP

(a) Reversible activation (general scheme)

Polymer-X 
$$\xrightarrow{k_{act}}_{k_{deact}}$$
 Polymer  $\xrightarrow{k_p}$  (+ monomers )  
(b) RCMP  
Polymer-I + catalyst  $\xrightarrow{k_a}_{k_{da}}$  Polymer  $\xrightarrow{\bullet}$  +  $\xrightarrow{\bullet}$ I···· catalyst  
( $\ominus$ I  $\circledast$ NR<sub>4</sub>) ( $\xrightarrow{\bullet}$ Olymer ( $\xrightarrow{\bullet}$ ) ( $\xrightarrow{\bullet}$ Olymer ( $\xrightarrow{\bullet}$ )

 $\left(\begin{array}{ccc} 2 & \bullet | \cdots & \text{catalyst} & \longrightarrow & I_2 \cdots & \text{catalyst} & + & \text{catalyst} \\ & (\bullet \ominus I_2 & \bullet NR_4 \ ) & (\ominus I_3 & \bullet NR_4 \ ) & (\ominus I & \bullet NR_4 \ ) \end{array}\right)$ 

mechanistically different systems referred to as reversible chain transfer catalyzed polymerization  $(RTCP)^{5,6}$  and reversible coordination mediated polymerization (RCMP).<sup>6–11</sup>

In this work, we focus on RCMP. The catalysts for RCMP include organic salts such as tetrabutylammonium iodide (BNI) and methyltributylphosphonium iodide (BMPI) (Figure 1). RCMP utilizes a reversible coordination of Polymer-I with a catalyst (activator) to generate Polymer\* and an \*I-catalyst complex (deactivator) (Scheme 1b). (The •I-catalyst complex is not a stable radical and reacts with another "I-catalyst complex to generate an I2-catalyst complex and a catalyst (Scheme 1b). Both of the <sup>•</sup>I-catalyst and I<sub>2</sub>-catalyst complexes work as deactivators of Polymer<sup>•,7,9</sup>) Attractive features of RCMP include no use of special capping agents or metals. The catalysts are inexpensive, relatively nontoxic, easy to handle, and amenable to a wide range of monomers including styrenes, methacrylates, acrylates, acrylonitrile, and those with various functional groups.<sup>7-9</sup> RCMP can serve as a facile methodology for various applications.

To achieve low polydispersity, a sufficiently fast initiation of initiating dormant species (low-molar-mass alkyl iodides) is required as well as a sufficiently high frequency of activation deactivation cycles in the polymer region (during the

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Figure 1. Structures and abbreviations of alkyl iodides and catalysts studied in this work. The  $k_a$  value with BMPI at 70 °C is given for several alkyl iodides. The arrows indicate the ranges of effective alkyl iodides in the polymerizations of MMA and BA.

polymerization). Thus, rational design of initiating alkyl iodides is of primary importance. If the carbon—iodine bond of the alkyl iodide is too strong, the radical is not effectively generated from the alkyl iodide, resulting in low initiation efficiency. Thus, the radical must be effectively generated. Another requisite is that the generated radical must undergo sufficiently fast addition to monomer to drive the initiation process.

In this work, we systematically studied several low-molarmass alkyl iodides shown in Figure 1. The abbreviations of the alkyl iodides are given in Figure 1. Primary, secondary, and tertiary alkyl iodides with different stabilizing groups (ester, phenyl, and cyano groups) were studied for the rational design of initiating alkyl iodides with high initiation efficiency. We experimentally determined the activation rate constant  $k_a$ (Scheme 1b) for several alkyl iodides for quantitative comparison. We then used these alkyl iodides in methyl methacrylate (MMA) and butyl acrylate (BA) polymerizations to probe their initiation ability, using BMPI and BNI as catalysts. We prepared a telechelic polymer (chain-endfunctionalized polymer) by employing an alkyl iodide with a functional group. Alkyl iodides with multi-initiating sites, i.e., alkyl di-iodides and alkyl tri-iodides, were also studied.

# RESULTS AND DISCUSSION

**Determination of**  $k_a$  **for Polymer–lodide.** Prior to lowmolar-mass alkyl iodides, we studied a polymer–iodide, i.e., poly(methyl methacrylate)–iodide (PMMA-I), which is the dormant species in the polymer region in the polymerization of MMA. We determined the  $k_a$  values of PMMA-I using BMPI and BNI as catalysts. The medium (solvent) is MMA monomer. We previously determined the  $k_a$  values at 90 °C.<sup>9</sup> In this work, we extended the study to other temperatures to establish the temperature dependence. The method for determining  $k_a$  was a previously reported gel permeation chromatography (GPC) peak resolution method<sup>12</sup> (Supporting Information). Figure 2 shows the Arrhenius plots, from which  $k_a$  is given as eqs 1 and 2.



Figure 2. Arrhenius plot for  $k_{\rm a}$  of PMMA-I with BMPI and BNI in bulk MMA.

$$k_{\rm a}/{\rm M}^{-1}\,{\rm s}^{-1} = 8.3 \times 10^{11}\,{\rm exp}(-86.8\,{\rm kJ\,mol}^{-1}/RT)$$
 for BNI (1)

$$k_{\rm a}/{\rm M}^{-1}\,{\rm s}^{-1} = 3.0 \times 10^{13}\,{\rm exp}(-97.6\,{\rm kJ\,mol}^{-1}/RT)$$
 for BMPI (2)

The  $k_a$  value extrapolated at 70 °C from the Arrhenius plot was 0.050 M<sup>-1</sup> s<sup>-1</sup> for BNI and 0.041 M<sup>-1</sup> s<sup>-1</sup> for BMPI in bulk MMA medium.

We also determined  $k_a$  for BMPI at 70 °C in a solution medium of MMA (90%) and acetonitrile (10%). Acetonitrile was used to ensure that BMPI (organic salt catalyst) was completely dissolved at the mild temperature of 70 °C. (BMPI was not completely dissolved in bulk MMA medium below 80 °C.) The  $k_a$  value in MMA/acetonitrile was 0.0070 M<sup>-1</sup> s<sup>-1</sup>, which is approximately 1/6 times smaller than that (0.041 M<sup>-1</sup> s<sup>-1</sup>) in bulk MMA (estimated by extrapolation). This result shows a solvent effect. The value for BMPI at 70 °C in MMA/ acetonitrile will be referred to in the subsequent section. **Determination of**  $k_a$  for Low-Molar-Mass Alkyl lodides. We determined the  $k_a$  values of several low-molarmass alkyl iodides by a radical trap experiment,<sup>7,13</sup> using BMPI as a catalyst at 70 °C. In each radical trap trial, we heated an alkyl iodide (5 mM), BMPI (20 mM), and the radical trap 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (20 mM) in a mixture of toluene- $d_8$  (90%) and acetonitrile- $d_3$  (10%). We assume that  $k_a$  would not significantly differ in toluene and MMA (used for the polymer iodide) used as a hydrophobic medium. If the alkyl iodide (R–I) reacts with BMPI, the generated radical R<sup>•</sup> is trapped by TEMPO, thereby yielding R-TEMPO. Figure 3 shows the <sup>1</sup>H NMR spectra at time zero and



**Figure 3.** <sup>1</sup>H NMR spectra (in the range of 0.75–2.25 ppm) of the solution of CP-I (5 mM), BMPI (20 mM), and TEMPO (20 mM) heated at 70 °C for 0 and 3 h. The solvent was a mixture of toluene- $d_8$  (90%) and acetonitrile- $d_3$  (10%).

at 3 h for CP-I. At 3 h, new signals appeared and matched the signals of independently prepared pure R-TEMPO. We obtained  $k_a$  by following the decay of the concentration of R-I with NMR. In some cases, NMR signals were difficult to distinguish, and HPLC (high performance liquid chromatography) was used to follow the decay of the R-I concentration.

Figure 1 summarizes the  $k_a$  values obtained at 70 °C. EMA-I is a unimer model of a polymeric PMMA-I. The different side chains, i.e., ethyl group for EMA-I and methyl group for

PMMA-I, would not significantly affect  $k_a$  because the side chain is far from the carbon–iodine bond. (In a coppercatalyzed ATRP, the  $k_a$  values for unimer model alkyl bromides with methyl and ethyl side chains (MMA-Br and EMA-Br) were very similar.<sup>14</sup>) The  $k_a$  value of EMA-I (0.0023 M<sup>-1</sup> s<sup>-1</sup>) is smaller than that of PMMA-I (0.0070 M<sup>-1</sup> s<sup>-1</sup>). This result clearly shows a polymer effect (chain length dependence (CLD)) in  $k_a$ . The CLD should be the strongest between the unimer and dimer and become less significant with increasing chain length.

For alkyl iodides possessing an ester stabilizing group,  $k_{a}$ increased in the order of a primary alkyl iodide E-I (<0.0001  $M^{-1} s^{-1}$  < a secondary one EA-I (0.0004  $M^{-1} s^{-1}$ ) < a tertiary one EMA-I (0.0023  $M^{-1}\ s^{-1}),$  as expected. For different stabilizing groups, a cyano group led to a larger  $k_a$  than an ester group, based on comparing CE-I (0.0040 M<sup>-1</sup> s<sup>-1</sup>) and EA-I  $(0.0004 \text{ M}^{-1} \text{ s}^{-1})$  for secondary alkyl iodides and CP-I  $(0.0058 \text{ s}^{-1})$  $M^{-1}$  s<sup>-1</sup>) and EMA-I (0.0023  $M^{-1}$  s<sup>-1</sup>) for tertiary ones. These results suggest that the cyano group is a more effective stabilizing group than the ester group for this radical reaction. Alkyl iodides with two stabilizing groups (ester, cyano, and phenyl groups) showed very large  $k_a$  values. In the case of PhCN-I, it was difficult to accurately determine  $k_{a}$  because the R-TEMPO species produced was not stable enough (easily dissociated) at 70 °C due to the weak carbon-TEMPO bond. This difficulty, in turn, indicates that PhCN-I has a very large  $k_a$ value, and the value for PhCN-I in Figure 1 is a rough estimation (0.25  $M^{-1} s^{-1}$ ).

The  $k_a$  value increased in the order of EA-I (1) < EMA-I (6) < CE-I (10) < PhE-I (33) in this RCMP. This order is the same as in an ATRP with the corresponding alkyl bromides, i.e., MA-Br (1) < MMA-Br (56) < CE-Br (340) < PhM-Br (2.8 × 10<sup>5</sup>), where the side chain is a methyl group for MA-Br, MMA-Br, and PhM-Br, and the catalyst was CuBr/(2-pyridylmethyl)-amine used in acetonitrile at 22 °C.<sup>15</sup> The numbers in the parentheses are the relative  $k_a$  values in each RCMP and ATRP system (compared with EA-I for RCMP and MA-Br for ATRP). Notably, whereas  $k_a$  is as much as 2.8 × 10<sup>5</sup> times different between PhM-Br and MA-Br in ATRP,  $k_a$  is only 33 times different between PhE-I and EA-I in RCMP. The weaker



**Figure 4.** Plots of (a)  $\ln([M]_0/[M])$  vs *t* and (b)  $M_n$  and  $M_w/M_n$  vs conversion for the MMA/R-I/BMPI systems (in 25% toluene):  $[MMA]_0 = 8 M_i$ ;  $[R-I]_0 = 80 \text{ mM}$ ;  $[BMPI]_0 = 80 \text{ mM}$ . The symbols, R-I, and temperatures are indicated in the figure. I<sub>2</sub> (2 mM) was added for EMA-I at 80 °C.



**Figure 5.** Plots of (a)  $\ln([M]_0/[M])$  vs t and (b)  $M_n$  and  $M_w/M_n$  vs conversion for the MMA/R-I/BMPI systems (in 25% toluene) (70 °C):  $[MMA]_0 = 8 M$ ;  $[R-I]_0 = 80 mM$ ;  $[BMPI]_0 = 80 mM$ . The symbols and R-I are indicated in the figure.



**Figure 6.** Plots of (a)  $\ln([M]_0/[M])$  vs *t* and (b)  $M_n$  and  $M_w/M_n$  vs conversion for the BA/R-I/BNI systems (in bulk) (110 °C): [BA]\_0 = 8 M; [R-I]\_0 = 80 mM; [BNI]\_0 = 320 mM. The symbols and R-I are indicated in the figure. I<sub>2</sub> (0.2 mM) was added for filled squares.

dependence of  $k_a$  on the alkyl groups in RCMP (alkyl iodides) would be an interesting feature.

**MMA Polymerizations.** We then examined the polymerization performance with these alkyl iodides in actual polymerizations. The studied system is a solution polymerization of MMA (8 M (100 equiv)) with an alkyl iodide (80 mM (1 equiv)) and BMPI (80 mM) in toluene (75% MMA and 25% toluene) at 70  $^{\circ}$ C.

Figure 4 shows the results for alkyl iodides possessing an ester group. PMMA-I (filled circles) showed well-controlled polymerization. The number-average molecular weight  $(M_n)$  agreed with the theoretical value  $(M_{n,theo})$ , and the polydispersity index (PDI =  $M_w/M_n$ ) was small, i.e., approximately 1.2, from an early stage of polymerization, where  $M_w$  is the weight-average molecular weight. In comparison with the polymeric PMMA-I, the unimer model EMA-I (open squares) showed a slightly lower polymerization rate. The  $M_n$  deviated from  $M_{n,theo}$ , and PDI was relatively large, i.e., approximately 1.5, throughout the polymerization. This result indicates that the

unimer model is not yet an efficient initiator in this particular condition (70  $^{\circ}$ C).

However, we would note that at a slightly higher temperature of 80 °C the unimer model EMA-I became an efficient initiator (filled squares). The  $k_a$  of EMA-I would be sufficiently large at 80 °C. In this case, we added a small amount (2 mM) of molecular iodine I<sub>2</sub> as a deactivator<sup>9</sup> to avoid too many monomers to add to the generated EMA• at an early stage of polymerization. The  $M_n$  agreed well with  $M_{n,theo}$  from a middle stage of polymerization (at a conversion >60%), and PDI was small, e.g., approximately 1.2. Thus, we may use the unimer model EMA-I for possible applications at slightly high temperatures.

We then studied 70 °C without I<sub>2</sub> again. The secondary alkyl iodide EA-I (open triangles) showed much slower polymerization and poorer control of  $M_n$  and PDI than the tertiary one EMA-I (open squares) because activation (initiation) is too slow for EA-I. No polymerization took place with the primary alkyl iodide E-I (open circle). All these observations (Figure 4) are consistent with the  $k_a$  values discussed above.



**Figure 7.** <sup>1</sup>H NMR spectrum (acetonitrile- $d_3$ ) of PMMA-I obtained from PhEOH-I: [MMA]<sub>0</sub> = 8 M; [PhEOH-I]<sub>0</sub> = 160 mM; [BMPI]<sub>0</sub> = 80 mM in 25% toluene for 4 h at 60% conversion (70 °C).

Figure 5 shows the results for alkyl iodides possessing a cyano group, i.e., CP-I (filled circles) and CE-I (filled squares). CP-I has a similar  $k_a$  value to that of PMMA-I (see above) and should work as an efficient initiator. In fact, the polymerization rate with CP-I was almost the same as that with the polymeric PMMA-I (Figure 4 (filled circles)). The  $M_n$  agreed well with  $M_{\rm n.theo}$ , and PDI was approximately 1.2 throughout the polymerization. While CP-I showed better polymerization performance than CE-I, CE-I also exhibited sufficiently good control in  $M_{\rm p}$  and PDI. These results clearly demonstrate the usefulness of both CE-I and CP-I as initiating alkyl iodides. Figure 5 also compares the results for alkyl iodides with two stabilizing groups, i.e., PhE-I (filled triangles), EEMA-I (filled pentagons), and PhCN-I (open circles). They have very large  $k_a$ values (see above). PhE-I (with a phenyl group and an ester group) and EEMA-I (with two ester groups and a methyl group) led to controlled polymerizations similarly to CP-I with a cyano group, as expected. However, PhCN-I (with a phenyl group and a cyano group) afforded a slower polymerization and a large deviation of  $M_{\rm n}$  from  $M_{\rm n,theo}$ . This result would be obtained because activation is very fast, but the released radical PhCN<sup>•</sup> is too stable to add to monomer. PhCN<sup>•</sup> would undergo radical-radical termination rather than addition to monomer, and the termination would significantly reduce the concentration of the dormant species and hence lead to the observed slow polymerization and large deviation of  $M_{\rm p}$ . Thus, efficient alkyl iodides should have sufficiently large  $k_a$  values, and at the same time, the released alkyl radicals should be reactive enough to add to monomer. The range of effective initiating alkyl iodides for this MMA system is depicted in Figure 1. Examples of the GPC chromatograms are given in the Supporting Information.

**BA** Polymerizations. We switched the monomer from MMA to BA, elevated the temperature from 70 to 110 °C, and changed the catalyst from BMPI to BNI. A higher temperature (110 °C) is required for the BA polymerization<sup>9</sup> because the carbon–iodine bond is stronger for poly(acrylate)–iodine than

poly(methacrylate)-iodine, as suggested in the above discussion. We studied the bulk polymerization of BA (8 M) with R-I (80 mM) and BNI (320 mM) at 110 °C. Figure 6 shows the results. In contrast to the MMA polymerization at 70 °C, this BA polymerization at the elevated temperature proceeded even with the primary alkyl iodide E-I (open circles), although its initiation efficiency was low. The secondary alkyl iodide EA-I (open squares) afforded relatively low PDI (= 1.4-1.5). EA-I (filled squares) afforded almost quantitative initiation and low PDI (= 1.3) with the addition of a small amount (0.2 mM) of  $I_2$ (deactivator). This result shows that EA-I can be used as a good initiator. Without the addition of I2, the tertiary alkyl iodide EMA-I (filled circles) exhibited quantitative initiation and yielded low-polydispersity polymers (PDI = 1.3). CP-I with a cyano group (filled triangles) also worked well and achieved even lower polydispersity (PDI = 1.2). PhE-I (open triangles) and EEMA-I (open pentagons) with two stabilizing groups, which were highly efficient in the MMA polymerization at 70 °C, led to slower polymerization. This would be because the addition of the released radicals (PhE<sup>•</sup> and EEMA<sup>•</sup>) to the less conjugated monomer BA is relatively slow and also because these labile alkyl iodides undergo decomposition (degradation) as a side reaction at the elevated temperature. (The generated byproducts may slow down the polymerization as retarders.) Thus, the range of effective initiating alkyl iodides depended on monomers and temperatures, as depicted in Figure 1.

**Telechelic Polymers.** Telechelic polymers have many useful applications. We prepared a telechelic polymer using a functional alkyl iodide, i.e., PhEOH-I with a hydroxyl group. Figure 7 shows the <sup>1</sup>H NMR spectrum of the polymer ( $M_n$  = 3100 and PDI = 1.14) synthesized in the polymerization of MMA (8 M) with PhEOH-I (160 mM) and BMPI (80 mM) at 70 °C for 4 h (conversion = 60%) and purified with a preparative GPC. The introduction of the hydroxyl group was clearly confirmed by the signals of  $CH_2CH_2OH$  (3.9–4.2 ppm). We estimated chain-end functionality from the relative peak areas of this moiety and the monomer units. The number



**Figure 8.** Plots of (a)  $\ln([M]_0/[M])$  vs *t* and (b)  $M_n$  and  $M_w/M_n$  vs conversion for the MMA/R-I/BMPI systems (in 25% toluene) (70 °C) and the BA/R-I/BNI system (in bulk) (110 °C): [monomer]\_0 = 8 M; [R-I]\_0 = 80 mM; [catalyst]\_0 = 80 mM for BMPI and 320 mM for BNI. The symbols, monomers, and R-I are indicated in the figure.

of monomer units (= 28) was calculated using the  $M_n$  determined by GPC. The estimated chain-end functionality was 105% (with  $\pm$ 5% experimental error). Thus, we successfully obtained a well-defined telechelic polymer with virtually quantitative chain-end functionality.

Multi-Initiating Alkyl lodides. We previously successfully prepared A-B-A triblock copolymers and 3-arm star polymers by employing alkyl di-iodide EMA-II and alkyl tri-iodide EMA-III, respectively.<sup>10</sup> EMA-II and EMA-III are methacrylate types (tertiary alkyl iodides with an ester group). Here, we compare EMA-I, EMA-II, and EMA-III in the MMA polymerization at 70 °C. As Figures 4 and 8 show, both EMA-II (Figure 8 (filled circles)) and EMA-III (Figure 8 (filled squares)) effectively initiated, whereas the corresponding monoiodide EMA-I (Figure 4 (open squares)) did not initiate very effectively, as mentioned. (The molecular weights of the star polymers from EMA-III were determined by GPC-MALLS (multiangle laser light scattering).) The effective initiation of EMA-II and EMA-III would be due to their larger steric hindrance compared with that of EMA-I. (The steric hindrance can weaken the carboniodine bond.) PhE-II with two stabilizing groups (phenyl and ester groups) (Figure 8 (filled triangles)) also achieved low polydispersity in the same polymerization condition.

In the BA polymerization at 110  $^{\circ}$ C, we studied an alkyl diiodide EA-II of the acrylate type (secondary alkyl iodide with an ester group). As Figures 6 and 8 show, EA-II (Figure 8 (open circles)) initiated effectively, whereas the monoiodide EA-I (Figure 6 (open squares)) did not initiated so effectively. This result again suggests the importance of the steric hindrance. These results for MMA and BA also demonstrate the effectiveness of the studied alkyl di-iodides and tri-iodide for the design of polymer architectures.

# CONCLUSIONS

The  $k_a$  value increased in the order of primary < secondary < tertiary alkyl iodides. The cyano group was a better stabilizing group than the ester group. Alkyl iodides with two stabilizing groups had very large  $k_a$  values. Figure 1 summarizes the  $k_a$  values with BMPI catalyst at 70 °C and also the ranges of effective alkyl iodides in the polymerizations of MMA (70 and 80 °C) and BA (110 °C). A telechelic polymer was prepared

using an alkyl iodide with a hydroxyl functional group. The studied alkyl di-iodides and alkyl tri-iodide were effective initiators and would be useful for the design of polymer architectures.

## EXPERIMENTAL SECTION

**Materials.** MMA (99%, Nacalai Tesque, Japan) and BA (99%, Nacalai) were purified through an alumina column. CP-I (99%, Tokyo Chemical Industry (TCI), Japan (contract service)), BNI (98%, TCI), BMPI (96%, Wako Pure Chemical, Japan), TEMPO (99%, Aldrich), acetonitrile (99.5%, Wako), and toluene (99.5%, Nacalai) were used as received.

**Ethyl 2-lodoisobutyrate (EMA-I).** The corresponding bromide, i.e., ethyl 2-bromoisobutyrate (EMA-Br) (39.0 g, 200 mmol), and NaI (149.9 g, 1000 mmol) were stirred in dry acetonitrile (300 mL) at 80 °C for 20 h. The reaction mixture was filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in dichloromethane, washed with saturated aqueous NaHSO<sub>3</sub> solution and water, and dried over MgSO<sub>4</sub>. After removal of solvent under reduced pressure, the purification by distillation afforded EMA-I (57% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): *δ* = 1.28 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.2 Hz), 2.06 (s, 6H, CI(CH<sub>3</sub>)<sub>2</sub>), 4.21 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): *δ* = 13.7 (OCH<sub>2</sub>CH<sub>3</sub>), 173.3 (OC(O)CI).

**Ethyl 2-lodopropionate (EA-I).** The corresponding bromide, i.e., ethyl 2-bromopropionate (EA-Br) (35.0 g, 193 mmol), and NaI (58.0 g, 387 mmol) were stirred in dry acetone (193 mL) at 25 °C for 2 h. The reaction mixture was filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in dichloromethane, washed with saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent under reduced pressure afforded EA-I (79% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.26 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.0 Hz), 1.93 (d, 3H, CHICH<sub>3</sub>, *J* = 7.0 Hz), 4.14–4.22 (m, 1H, CHICH<sub>3</sub>, *J* = 7.0 Hz), 4.45 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.2 (CHICH<sub>3</sub>), 13.7 (OCH<sub>2</sub>CH<sub>3</sub>), 23.3 (CHICH<sub>3</sub>), 61.8 (OCH<sub>2</sub>CH<sub>3</sub>), 171.9 (OC(O)CI).

**Ethyl 2-lodoacetate (E-l).** E-I was obtained from the same procedure as EA-I. Ethyl 2-bromoacetate (E-Br) was used instead of EA-Br to afford E-I (83% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.25 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.2 Hz), 3.65 (s, 2H, ICH<sub>2</sub>CO), 4.17 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = -5.3 (C(O)CH<sub>2</sub>I), 13.8 (OCH<sub>2</sub>CH<sub>3</sub>), 62.1 (OCH<sub>2</sub>CH<sub>3</sub>), 168.7 (C(O)CI).

**2-lodopropionitrile (CE-I).** CE-I was obtained from the same procedure as EA-I. 2-Bromopropionitrile (CE-Br) was used instead of EA-Br to afford CE-I (82% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.12 (d, 3H, CHICH<sub>3</sub>, J = 7.0 Hz) 4.26 (q, 1H, CNCHICH<sub>3</sub>, J = 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = -13.2 (CICH<sub>3</sub>), 25.5 (CICH<sub>4</sub>), 120.0 (CICN).

**Ethyl 2-lodo-2-phenylacetate (PhE-I).** PhE-I was obtained from the same procedure as EA-I. Ethyl 2-bromo-2-phenylacetate (PhE-Br) was used instead of EA-Br to afford PhE-I (82% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.27$  (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, J = 7.2 Hz), 4.15-4.27 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 5.51 (s, 1H, PhCHICO), 7.27-7.33 (m, 3H, PhH), 7.58-7.60 (m, 2H, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 13.8$  (OCH<sub>2</sub>CH<sub>3</sub>), 20.7 (PhCHI), 62.3 (OCH<sub>2</sub>CH<sub>3</sub>), 128.7 (Ph), 128.7 (Ph), 128.9 (Ph), 137.3 (Ph), 169.8 (OC(O)CI).

**Diethyl 2-lodo-2-methylmalonate (EEMA-I).** The corresponding bromide, i.e., diethyl 2-bromo-2-methylmalonate (EEMA-Br) (17.7 g, 70 mmol), and NaI (12.6 g, 84 mmol) were stirred in dry acetonitrile (44 mL) at 25 °C for 1 h. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in diethyl ether and filtered to remove insoluble salts. Removal of solvent under reduced pressure afforded EEMA-I (88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.21 (t, 6H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.2 Hz), 2.18 (s, 3H, CICH<sub>3</sub>), 4.18 (q, 4H, OCH<sub>2</sub>CH<sub>3</sub>, *J* = 7.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.6 (OCH<sub>2</sub>CH<sub>3</sub>), 29.4 (CH<sub>3</sub>CI), 35.1 (C(CH<sub>3</sub>)I), 62.9 (OCH<sub>2</sub>CH<sub>3</sub>), 168.7 (OC(O)CI).

α-lodobenzyl Cyanide (PhCN-I). Bromine (52.3 g, 308 mmol) was dropwisely added into benzyl cyanide (32.8 g, 280 mmol) over 1 h at 110 °C. After stirring for another 0.5 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane. The solution was washed with saturated aqueous NaHSO3 solution and water and dried over MgSO<sub>4</sub>. Removal of the solvent under reduced pressure afforded  $\alpha$ -bromobenzyl cyanide (PhCN-Br) (97% yield), which was used in the subsequent reaction without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 5.48 (s, 1H, PhCHICN), 7.40–7.44 (m, 3H, PhH), 7.53-7.56 (m, 2H, PhH). PhCN-Br (32.0 g, 160 mmol) and NaI (28.8 g, 192 mmol) were stirred in dry acetonitrile (100 mL) at 25 °C for 1 h. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in dichloromethane. After filtration to remove insoluble substances, the filtrate was washed with saturated aqueous Na2SO2 solution and water and dried over MgSO4. After removal of solvent under reduced pressure, the purification by recrystallization from acetonitrile afforded PhCN-I (57% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 5.60 (s, 1H, PhCHICN), 7.32–7.39 (m, 3H, PhH), 7.51-7.54 (m, 2H, PhH). <sup>13</sup>C NMR (CDCl<sub>2</sub>):  $\delta = -4.9$ (CHIPh), 118.2 (CHICN), 127.2 (Ph), 129.4 (Ph), 129.7 (Ph), 135.2 (Ph).

2-Hydroxyethyl 2-lodo-2-phenylacetate (PhEOH-I). 2-Bromo-2-phenylacetic acid (25.0 g, 115 mmol) and thionyl chloride (27.3 g, 229 mmol) were stirred at 80 °C for 1 h. After removal of thionyl chloride under reduced pressure, the residue was dropwisely added into the mixture of ethylene glycol (284.7 g, 4.6 mol) and pyridine (9.5 g, 120 mmol) over 0.5 h at 25 °C. The reaction mixture was stirred for another 1 h, diluted with dichloromethane, washed with saturated aqueous NaHSO3 solution and water, and dried over MgSO4. Removal of solvent under reduced pressure afforded 2-hydroxyethyl 2-bromo-2phenylacetate (PhEOH-Br) (80% yield), which was used in the subsequent reaction without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ = 1.73 (br s, 1H, OCH<sub>2</sub>CH<sub>2</sub>OH), 3.78-3.87 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>OH), 4.25-4.35 (m, 2H, OCH2CH2OH), 5.39 (s, 1H, PhCHBrCO), 7.31-7.38 (m, 3H, PhH), 7.52-7.56 (m, 2H, PhH). PhEOH-Br (5.0 g, 19.3 mmol) and NaI (5.8 g, 38.6 mmol) were stirred in dry acetone (20 mL) at 0 °C for 1 h. The reaction mixture was filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in dichloromethane, washed with saturated aqueous Na2SO3 solution and water, and dried over MgSO4. After removal of solvent under reduced pressure, the purification by flash chromatography (silica gel; ethyl acetate/hexane) afforded PhEOH-I (79% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 2.12$  (br s, 1H, OCH<sub>2</sub>CH<sub>2</sub>OH), 3.77-3.86 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>OH), 4.22-4.31 (m, 2H,  $OCH_2CH_2OH$ ), 5.58 (s, 1H, PhCHICO), 7.27–7.33 (m, 3H, PhH), 7.57–7.60 (m, 2H, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 20.1 (PhCHI), 60.5 (CH<sub>2</sub>OH), 67.5 (OCH<sub>2</sub>CH<sub>2</sub>), 128.7 (*Ph*), 128.8 (*Ph*), 128.9 (*Ph*), 136.8 (*Ph*), 170.0 (OC(O)CI).

Ethylene Glycol Bis(2-iodoisobutyrate) (EMA-II). The mixture of ethylene glycol (5.0 g, 80 mmol) and pyridine (13.9 g, 176 mmol) in dichloromethane (25 mL) was slowly added to the solution of 2bromoisobutyryl bromide (44.1 g, 192 mmol) in dichloromethane (15 mL) and stirred for 1 h. The reaction mixture was washed with aqueous HBr (5%), saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution, and water and dried over MgSO<sub>4</sub>. Removal of the solvent under reduced pressure afforded ethylene glycol bis(2-bromoisobutyrate) (EMA-BB), which was used in the subsequent reaction without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.92 (s, 12H, CCH<sub>3</sub>), 4.42 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O). EMA-BB (25.5 g, 71 mmol) and NaI (50.9 g, 340 mmol) were stirred in dry acetonitrile (110 mL) at 80 °C for 8 h. The reaction mixture was filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in dichloromethane, washed with saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution and water, and dried over MgSO4. After removal of solvent under reduced pressure, the purification by flash chromatography (silica gel; ethyl acetate/hexane) afforded EMA-II (35% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.08 (s, 12H, CCH<sub>3</sub>), 4.39 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (CDCl<sub>2</sub>):  $\delta = 32.8 (CI(CH_3)_2), 33.6 (CI(CH_3)_2), 63.1 (OCH_2CH_2O), 173.1$ (OC(O)CI).

**Glycerol Tris(2-lodoisobutyrate) (EMA-III).** EMA-III was obtained from the same process as EMA-II. Glycerol was used instead of ethylene glycol to afford pure EMA-III in a 35% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.08 (m, 18H, CCH<sub>3</sub>), 4.33 (dd, 2H, OCHHCHCH-HO), 4.48 (dd, 2H, OCHHCHCHHO), and 5.37 (m, 1H, OCHHCHCHHO). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 32.3 (CI(CH<sub>3</sub>)<sub>2</sub>), 32.5 (CI(CH<sub>3</sub>)<sub>2</sub>), 33.6 (CI(CH<sub>3</sub>)<sub>2</sub>), 33.6 (CI(CH<sub>3</sub>)<sub>2</sub>), 62.9 (OCH<sub>2</sub>CHCH<sub>2</sub>O), 70.3 (OCH<sub>2</sub>CHCH<sub>2</sub>O), 172.4 (OC(O)CI), 172.8 (OC(O)CI).

Ethylene Glycol Bis(2-iodo-2-phenylacetate) (PhE-II). 2-Bromo-2-phenylacetic acid (25.0 g, 115 mmol) and thionyl chloride (27.6 g, 232 mmol) were stirred at 80 °C for 1.5 h. After removal of thionyl chloride under reduced pressure, the residue was dissolved in dichloromethane and dropwisely added into the mixture of ethylene glycol (3.4 g, 55 mmol) and pyridine (8.7 g, 110 mmol) in dichloromethane at 0 °C. The reaction mixture was stirred at 0 °C for another 1 h, washed with aqueous HBr (5%), saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution, and water, and dried over MgSO<sub>4</sub>. Removal of solvent under reduced pressure afforded ethylene glycol bis(2-bromo-2-phenylacetate) (PhE-BB) (23.9 g, 95% yield), which was used in the subsequent reaction without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ = 4.31 - 4.38 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>O), 5.25 - 5.29 (m 2H, PhCH.), 7.24-7.36 (m, 6H, PhH), 7.42-7.50 (m, 4H, PhH). PhE-BB (15.1 g, 33 mmol) and NaI (14.8 g, 99 mmol) were stirred in dry acetone (33 mL) at 17 °C for 3.5 h. The reaction mixture was filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in dichloromethane, washed with saturated aqueous Na2SO3 solution and water, and dried over MgSO4. Removal of solvent under reduced pressure afforded EMA-II (88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.33 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O), 5.47 (s, 2H, PhCHICO), 7.22-7.26 (m, 6H, PhH), 7.51-7.53 (m, 4H, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 19.6 (PhCHI), 19.7 (PhCHI), 63.2 (OCH<sub>2</sub>CH<sub>2</sub>O), 128.8 (Ph), 128.9 (Ph), 129.0 (Ph), 136.8 (Ph), 169.6 (OC(O)CI).

**Diethyl 2,5-Diiodoadipate (EA-II).** EA-II was obtained from the same procedure as EA-I. Diethyl 2,5-dibromoadipate (EA-BB) was used instead of EA-Br to afford EA-II (73% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.27$  (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>, J = 7.2 Hz), 1.89–1.99 (m, 2H, CHICH<sub>2</sub>CH<sub>2</sub>CHI), 2.06–2.18 (m, 2H, CICH<sub>2</sub>CH<sub>2</sub>CI), 4.15–4.24 (m, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 4.25–4.30 (m, 2H, CHICH<sub>2</sub>CH<sub>2</sub>CHI). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 13.7$  (OCH<sub>2</sub>CH<sub>3</sub>), 18.6 (CH<sub>2</sub>CH<sub>2</sub>), 35.6 (OC(O)CHI), 62.0 (OCH<sub>2</sub>CH<sub>3</sub>), 170.8 (OC(O)CI).

**Analytical GPC.** The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7  $\mu$ m; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) with a flow rate of 0.8 mL/min (40 °C). Sample detection and

quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known polymer concentrations in solvent. The monomer conversion was determined from the GPC peak area. The column system was calibrated using standard PMMAs. For the polymerizations of BA and the polymerization of MMA from EMA-III, the samples were also detected using a Wyatt Technology DAWN EOS MALLS detector (Santa Barbara, CA) equipped with a Ga–As laser ( $\lambda = 690$  nm). The refractive index increment dn/dc was determined to be for 0.056 mL g<sup>-1</sup> for BA and 0.086 mL g<sup>-1</sup> for MMA with a Wyatt Technology OPTILAB DSP differential refractometer ( $\lambda$ = 690 nm).

**Preparative GPC.** The PMMA-I shown below was purified with a preparative GPC (LC-918, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns ( $600 \times 20$  mm; bead size =  $16 \mu$ m; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as eluent with a flow rate of 3.8 mL/min (room temperature).

**NMR.** The NMR spectra were recorded on a JEOL (Japan Electron Optics Laboratory, Tokyo) JNM-AL300 (300 MHz) at ambient temperature with flip angle  $45^{\circ}$  <sup>1</sup>H: spectral width 6006.01 Hz, acquisition time 2.7279 s, and pulse delay 4.272 s.

**HPLC.** The HPLC analysis was performed on an Agilent (Santa Clara, CA) 1120 compact liquid chromatograph equipped with an ODS-100S gel column. The eluent was a mixture of water (90%) and acetonitrile (10%) with a flow rate of 0.8 mL/min (40  $^{\circ}$ C).

**Determination of**  $k_a$  **for Low-Molar-Mass Alkyl lodides.** In a typical run, a mixture of toluene- $d_8$  (1.8 mL), acetonitrile-  $d_3$  (0.2 mL), CP-I (5 mM), a catalyst (20 mM), and TEMPO (20 mM) was heated in a Schlenk flask at 70 °C under an argon atmosphere with magnetic stirring and then quenched to room temperature at a prescribed time *t*. The mixtures before and after the heat treatment were analyzed by <sup>1</sup>H NMR or HPLC.

**Preparation of PMMA-I (for Figures 2 and 4).** A mixture of MMA (20 mL (8 M)), CP-I (80 mM), and BMPI (40 mM) in a 100 mL round-bottom flask was heated at 60 °C for 2.5 h under an argon atmosphere with magnetic stirring. After purification by reprecipitation from cold hexane and further purification with a preparative GPC to remove a trace of residual BMPI (catalyst), a PMMA-I with  $M_n$  = 4100 and PDI = 1.19 was isolated. The polymer was used as a probe adduct (P<sub>0</sub>-X) in the determination of  $k_{act}$  (Figure 2) and a macroinitiator (R-I) in the polymerization of MMA (Figure 4), as shown below. A chain extension test<sup>12</sup> showed that the polymer contained 9% of potentially inactive species (without the iodine moiety at the chain-end), for which the experimental data have been corrected.

**Determination of**  $k_a$  for PMMA-I. A mixture of MMA (3 mL (8 M)), P<sub>0</sub>-X (0.75 mM), and a catalyst (1–5 mM) in a Schlenk flask was heated under an argon atmosphere. After a prescribed time t, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF to a known concentration, and analyzed by GPC. The detailed procedure for determining  $k_a$  is given in the Supporting Information.

**Polymerization.** In a typical run, a Schlenk flask containing a mixture of MMA (2.5 mL), R-I, BMPI, and toluene was heated at 70  $^{\circ}$ C under an argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF to a known concentration, and analyzed by GPC.

**Preparation of PMMA-I from PhEOH-I (Figure 7).** A mixture of MMA (3 mL (8 M)), PhEOH-I (160 mM), BMPI (80 mM), and toluene (1 mL) in a Schlenk flask was heated at 70 °C for 4 h under an argon atmosphere with magnetic stirring. After purification with a preparative GPC, a PMMA-I with  $M_{\rm n}$  = 3100 and PDI = 1.14 was isolated.

# ASSOCIATED CONTENT

# **S** Supporting Information

Determination of  $k_a$  of PMMA-I and examples of GPC chromatograms in the MMA polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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