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Feature Article

Reversible chain transfer catalyzed polymerization (RTCP): A new class of living radical polymerization

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ABSTRACT

This article introduces the new family of living radical polymerizations with germanium (Ge), tin (Sn), phosphorus (P), and nitrogen (N) catalysts which we recently developed. The polymerizations are based on a new reversible activation mechanism, *Reversible chain Transfer* (RT) catalysis. Low-polydispersity polymers are obtained in the homopolymerizations and random and block copolymerizations of styrene, methyl methacrylate, and functional methacrylates. The background, performance, and kinetic features of the polymerizations are described. Attractive features of the catalysts include their high reactivity, low toxicity (Ge, P, and N), low cost (P and N), and ease of handling (robustness).

1. Introduction

Living radical polymerization (LRP) has received growing attention as a powerful synthetic tool for well-defined, low-polydispersity polymers [1]. The basic concept of LRP is the reversible activation of the dormant species (Polymer–X) to the propagating radical (Polymer$^\bullet$) (Scheme 1a). A sufficiently large number of activation–deactivation cycles is a requisite for good control of chain length distribution [2–4].

We recently developed a new class of LRP using a tin (Sn) [5,6], germanium (Ge) [5,6], phosphorus (P) [6,7], or nitrogen (N) [8] compound as a catalyst for the reversible activation and have proposed to term the polymerization reversible chain transfer catalyzed polymerization (RTCP) [6] for its new reversible activation mechanism. This is also the first LRP using compounds of typical elements (non-transition metals) as effective catalysts. In this article, we will describe the concept and mechanism (Section 3.1), background (Section 3.2), performance (Section 3.3), and kinetic features (Section 3.4) of RTCP, following a brief survey of currently known LRP systems (Section 2) in a mechanistic point of view.

2. Currently known LRP systems

2.1. Examples of capping agent X

Miscellaneous capping agents X are used for LRP. Examples are listed in Scheme 2. They include sulfur compounds (Scheme 2a [9] and g [10]), stable nitroxides (b) [11–13], stable nitrogen and carbon compounds (c) [14–17], transition metal complexes (d) [18,19], iodine (e) [20], halogens with transition metal catalysts (f) [21–23], and tellurium, stibine, and bismuth compounds (h) [24–26].

2.2. Mechanistic classification of reversible activation processes

The reversible activation reactions in the most successful LRPs currently known may mechanistically be classified into three types (Scheme 1b–d), which are the dissociation-combination (DC), degenerative chain transfer (DT), and atom transfer (AT) mechanisms.

2.2.1. Dissociation-combination (DC) mechanism

In this mechanism, Polymer–X is thermally or photochemically dissociated into Polymer$^\bullet$ and X$^\bullet$ (Scheme 1b), where a stable (persistent) radical X$^\bullet$ is supposed to be stable enough to undergo no reaction other than the combination with Polymer$^\bullet$. The best-known examples of the stable radical are nitroxides such as TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) [11] and DEPN (*N-tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide) [12] (Scheme 2b). Other examples include nitrogen compounds such as

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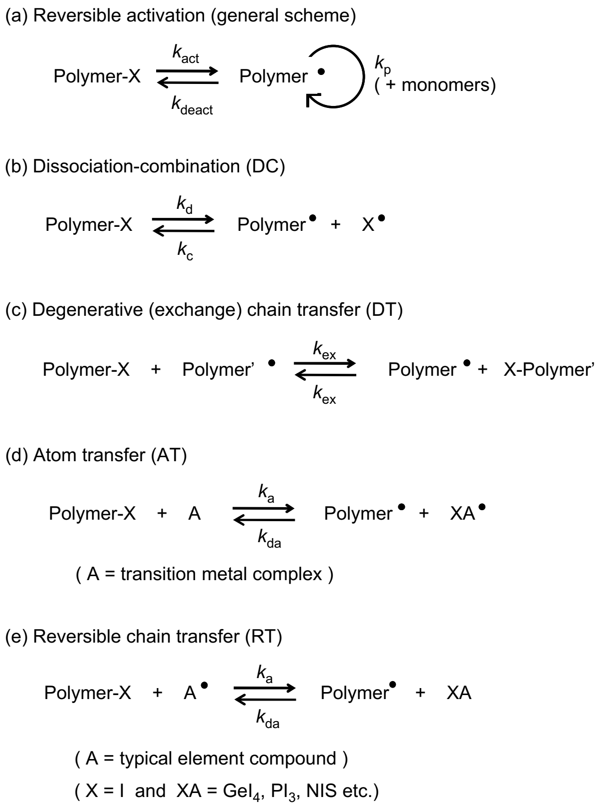


Scheme 1. (a) General scheme of reversible activation, (b, c, and d) three main mechanisms of reversible activation, and (e) new mechanism of reversible activation proposed for RTCP.

triazols [14] and verdazyls [15] (Scheme 2c), bulky carbon compounds such as triphenylmethyls [16] and vinyl compounds [17] (c), and transition metal complexes such as cobalt [18] and titanium [19] complexes (d).

2.2.2. Degenerative chain transfer (DT) mechanism

In this mechanism, Polymer–X is attacked by the propagating radical (Polymer$'^{\bullet}$) to form the active species (Polymer$^{\bullet}$) and the dormant species (Polymer′–X) (Scheme 1c). This is an exchange reaction of X. Two types of LRPs belong to this category. One is the case in which X is an atom or a simple group. In this case, X is simply transferred from radical to radical without forming any kinetically important intermediate. A typical example is the iodide-mediated polymerization (Scheme 2e), where X is iodine. Organotellurium-mediated living radical polymerization (TERP: X = MeR) (Scheme 2h) [24], organostibine one (SBRP: X = SbR$_2$) [25], and organobismuthine one (BIRP: X = BiR$_2$) [26] are also based on this mechanism, while interestingly the DC mechanism coexists in TERP and BIRP with the main mechanism being DT in both cases. The cobalt and titanium systems (X = Co and Ti complexes) (Scheme 2d) are also assumed to include the two mechanisms. The other is the case in which X is a group with a double bond that is accessible to the addition of Polymer$^{\bullet}$. The exchange reaction (Scheme 3) occurs via the addition of Polymer$'^{\bullet}$ to Polymer–X to form the intermediate radical Polymer–(X$^{\bullet}$)–Polymer′ followed by its fragmentation into Polymer$^{\bullet}$ and Polymer′–X. This process was named reversible addition–fragmentation chain transfer (RAFT) [10]. Dithioester compounds are representative RAFT agents (Scheme 2g).

2.2.3. Atom transfer (AT) mechanism

In this mechanism, Polymer–X is activated by the catalysis of activator A, and the capping agent is transferred to form a stable species XA$^{\bullet}$ (Scheme 1d). All currently known successful LRPs in this category use a halogen like Cl and Br as a capping agent X and a halide complex of transition metal like Cu [22] and Ru [21] as an activator A (Scheme 2f). These LRPs are often termed atom transfer radical polymerizations (ATRPs) [22].

2.2.4. Experimental establishment of activation mechanism for individual systems

The activation mechanism can experimentally and quantitatively be established by determining the activation rate constants for the three mechanisms k_d (Scheme 1b), k_{ex} (c), and k_a (d) for individual systems [3]. Such an experiment was carried out for the nitroxide (Scheme 2b) [27], iodide (e) [28], ATRP (f) [29], RAFT (g) [30], TERP (h) [31], SBRP (h) [25,32], and BIRP (h) [26] systems. The established mechanisms are summarized in Scheme 4, as the classification was mentioned in the above sections.

3. Reversible chain transfer catalyzed polymerization (RTCP)

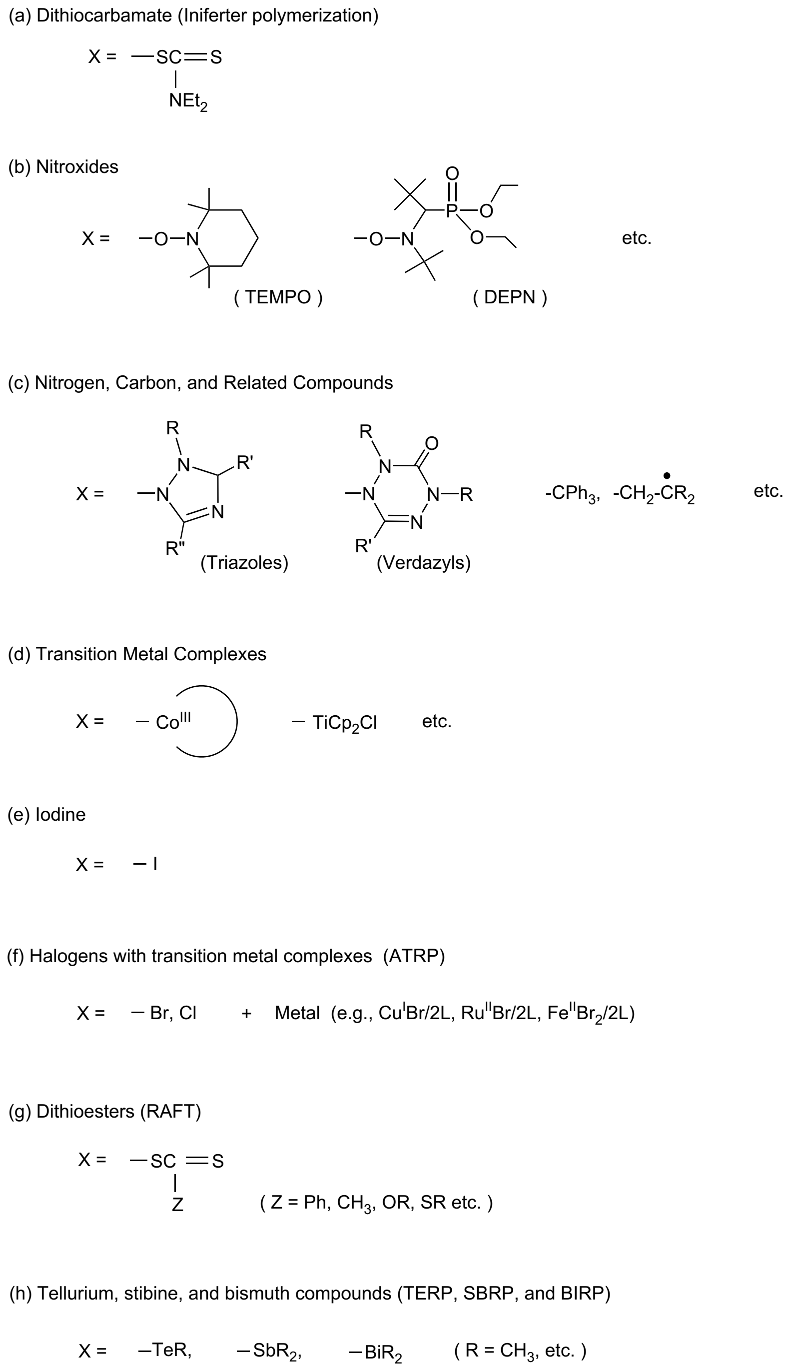
3.1. Concept and mechanism

The iodide-mediated polymerization (see above (Scheme 2e: X = I)) is a simple and robust LRP, as it contains only monomer, an alkyl iodide (initiating dormant species), and a conventional radical initiator (source of Polymer$^{\bullet}$). In this polymerization, as noted above, a polymer-iodide (Polymer–I) (dormant species) is activated by Polymer$^{\bullet}$ (DT: Scheme 1c). However, due to a low exchange frequency of iodine, the control of polydispersity is limited. To this polymerization, we added a Ge, Sn, P, or N compound such as GeI$_4$, developing a new family of LRP. The added GeI$_4$ works as a deactivator (I–A) of Polymer$^{\bullet}$, in situ producing GeI$_3^{\bullet}$ (Scheme 1e). GeI$_3^{\bullet}$ works as an activator (A$^{\bullet}$) of Polymer–I, producing Polymer$^{\bullet}$ and GeI$_4$. This cycle allows a frequent activation of Polymer–I. Mechanistically, this process is a *reversible chain transfer* (RT) with GeI$_4$ as a chain transfer agent, and Polymer–I is catalytically activated via an RT process. This is a new reversible activation mechanism, and we have proposed to term the related polymerization the RT-catalyzed polymerization (RTCP). In this article, the chain transfer agents (Sn, Ge, P, and N compounds) will be called RT catalysts or simply catalysts.

3.2. Background – radical reactions of Sn, Ge, P, and N compounds in organic chemistry

In organic chemistry, Sn and Ge radicals are known to abstract a halogen from an alkyl halide with a high reactivity to give the alkyl radical and their halides [33]. For best example, tributyltin radical (Bu$_3$Sn$^{\bullet}$) rapidly reacts with alkyl chlorides at a rate constant 10^2–10^4 M^{-1} s^{-1} [34,35], with alkyl bromides at 10^6–10^7 M^{-1} s^{-1} [34,36], and with alkyl iodides at 10^9 M^{-1} s^{-1} [34,36]. The last value is even close to those in the diffusion controlled limit (Table 1). Such high reactivity of Sn and Ge radicals urged us to use the reaction for the activation process of LRP. In organic chemistry, this reaction and the subsequent reduction of the alkyl radical with a hydride are widely utilized for the transformation of alkyl halide to alkyl hydride [33]. While Sn and Ge (group 14) are overwhelmingly frequently used, other group 14 elements and group 13, 15 (e.g., P and N), and 16 elements (Fig. 1) are also utilized for the transformation. This indicates that a wide variety of elements are possibly applicable to RTCP catalysts. In this article, we will focus on Sn, Ge, P, and N catalysts.

As well as a high reactivity of the activator radical, a high reactivity of the deactivator halide is also essential for RTCP. However, the reactions of a carbon-centered radical to Ge, Sn, and relevant halides are generally slow [33]. The counterparts of the mentioned Bu$_3$Sn$^{\bullet}$, i.e., the chloride Bu$_3$SnCl, the bromide Bu$_3$SnBr, and even the iodide Bu$_3$SnI, are also virtually unreactive (poor



Scheme 2. Examples of X.

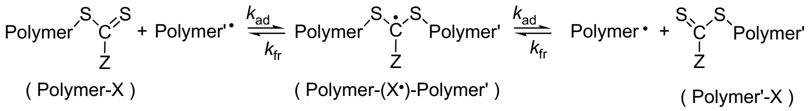
deactivators), and thus tributyltins are not useful for RTCP. Thus, we explored appropriate halides. We found that some Ge, Sn, P, and N iodides such as $\mathrm{GeI_4}$ work as very effective deactivators to be used in RTCP.

3.3. Performance

We examined the homopolymerizations and copolymerizations of styrene (St), methyl methacrylate (MMA), and functional methacrylates including benzyl (BzMA), glycidyl (GMA), 2-hydroxyethyl (HEMA), poly(ethylene glycol)methyl ether (PEGMA), and *N*,*N*-dimethylaminoethyl (DMAEMA) methacrylates as well as methacrylic acid (MAA) by using several catalysts (Fig. 1). The results will be summarized.

3.3.1. St with Ge, Sn, P, and N iodides as deactivators

The polymerization of St was carried out at 80 °C, using 1-phenylethyl iodide (PE–I: Fig. 1) as a low-mass alkyl iodide (dormant species), $\mathrm{GeI_4}$ as a catalyst (deactivator), and benzoyl peroxide (BPO) as a conventional radical initiator [5,6]. In this polymerization, Polymer$^{\bullet}$, which is originally supplied by BPO, is supposed to react with $\mathrm{GeI_4}$, in situ producing the activator radical $\mathrm{GeI_3^{\bullet}}$ (and Polymer–I). If $\mathrm{GeI_3^{\bullet}}$ effectively abstracts I from PE–I (or Polymer–I) to produce PE$^{\bullet}$ (or Polymer$^{\bullet}$), cycles of activation and deactivation (RT) will be started. Table 2 (entries 1 and 2) and Fig. 2 (filled circles) show the results. The M_{n} linearly increased with conversion and well agreed with the theoretical value $M_{\mathrm{n,theo}}$. The small deviations from $M_{\mathrm{n,theo}}$ at a later stage of polymerization are ascribed to the increase in the number of chains by the



Scheme 3. Reversible addition-fragmentation chain transfer (RAFT).

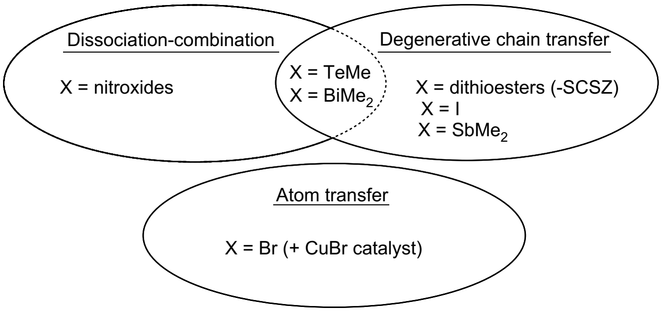
decomposition of BPO. The polydispersity index (PDI or M_w/M_n) reached a low value of about 1.2 from an early stage of polymerization, indicating a high frequency of the activation–deactivation cycle. The small amount of GeI_4 (2–5 mM (200–500 ppm)) required to control the polydispersity suggests a high reactivity of GeI_4. The activation of Polymer–I occurs not only by RT (Scheme 1e) but also by DT (c). However, the system without GeI_4 (iodide-mediated polymerization) (Fig. 2 (open circles)) gave much larger PDIs than that with GeI_4 (filled circles) (with other conditions set the same). This means that RT plays a main role in the GeI_4 system, with a small contribution of DT. Besides GeI_4, another Ge catalyst GeI_2 [5,6], Sn catalysts SnI_4 and SnI_2 [5,6], a P catalyst PI_3 [6,7], and a N catalyst *N*-iodosuccinimide (NIS: Fig. 1) [8] were also effective for St (entries 3–7 in Table 2 and Fig. 3a). Low polydispersity was achieved with a small amount (0.5–5 mM (50–500 ppm)) of the catalysts at 60–100 °C.

3.3.2. St with phosphorus hydrides as precursors

Instead of adding a deactivator, a precursor of a deactivator or an activator radical may be used as a starting compound to give a catalyst. For example, we used phosphorus hydrides $R_2PH(=O)$ as starting compounds (precursors) to in situ produce an activator radical $R_2P^{\bullet}(=O)$ ($A^{\bullet}$ in Scheme 1e) in the presence of a peroxide (radical initiator) [6,7]. The peroxide gives an oxygen-centered radical, which abstracts a hydrogen from $R_2PH(=O)$ to produce $R_2P^{\bullet}(=O)$ (Scheme 5). The abstraction by oxygen-centered radicals is known to be fast [37]. We carried out the polymerization of St with PE–I, dicumyl peroxide (DCP), and $(BuO)_2PH(=O)$ or $(EtO)PhPH(=O)$ as a precursor at 100 °C. With 10–30 mM of each precursor (entries 8 and 9 in Table 2 and Fig. 3a), small PDIs ($\leq$1.2) were achieved from an early stage of polymerization. Thus, with these two phosphorus hydrides, this alternative method was confirmed to be useful.

3.3.3. Methacrylates

The polymerization of MMA was carried out with Ge [6], P [6,7], and N [8] catalysts (entries 10–13 in Table 2 and Fig. 3b). To ensure a fast initiation from the alkyl iodide, we used a tertiary alkyl iodide, 2-cyanopropyl iodide (CP–I: Fig. 1), instead of the secondary one, PE–I. As a Ge catalyst, p-CH_3-C_6H_4-GeI_3 (tolyl-GeI_3) (entry 10) was used instead of GeI_4, which was effective for St but not active enough for MMA. With 5 mM of tolyl-GeI_3, low-polydispersity polymers were successfully obtained. As a P catalyst, PI_3 (entry 10) was effective for MMA as well as for St. A precursor catalyst, $(EtO)_2PH(=O)$, was also applicable to MMA with BPO as a peroxide (entry 13 in Table 2 and Fig. 3b). For the MMA polymerization, the N catalyst, NIS, exhibited particularly good performance (entry 12 in Table 2 and Fig. 3b). Even with 1 mM of NIS, which is among the lowest concentrations of the studied catalysts, PDI was small (1.15–1.4) from an early stage to a later stage of polymerization both in bulk and anisole solution. Notably, the temperature for MMA (70–80 °C) was even lower than that for St (80–100 °C) with the Ge, P, and N catalysts.



Scheme 4. Activation mechanisms experimentally established for several LRP systems.

Functional methacrylates, BzMA (with a benzyl group), GMA (with an epoxide), HEMA (with a hydroxy group), and PEGMA (with ethylene oxide units) were examined, using NIS, for example (entries 14–17 in Table 2 and Fig. 3b) [8]. NIS is attractive for its good tolerance to functional groups. In all cases, M_n well agreed with $M_{n,theo}$, and PDI was about 1.1–1.4 from low to high conversions. This suggests that the high reactivity of NIS retained in these monomers. BzMA and GMA are widely applied to photoresists (electronic materials), and HEMA and PEGMA, to biomaterials. No conductivity and low toxicity of NIS may be particularly attractive for these applications.

3.3.4. Random and block copolymerizations

With the NIS catalyst, the random copolymerizations of functional methacrylates, e.g., copolymerizations of BzMA with MAA (with a carboxylic acid), with DMAEMA (with a dimethylamino group), and with HEMA were also successful (entries 18–20 in Table 2) [8]. The compositions of MAA and DMAEMA were 15 mol% and that of HEMA was 22 mol%. With a small amount of NIS (1–2 mM), low-polydispersity polymers (PDI = 1.21–1.37) were obtained up to high conversions (60–90%). For methacrylates (both homopolymerizations (see above) and copolymerizations), the polymerization was fairly fast: the conversion reached 70–90% in 1–6 h, in the studied conditions (Table 2).

With the PI_3 [38] and NIS [8] catalysts, the block copolymerizations using a PMMA–I macroinitiator (first block) were attempted, where PMMA is poly(methyl methacrylate). Using St and BzMA for the second block monomers (entries 21 and 22 in Table 2), block copolymers with small PDIs (~1.2) were obtained. Instead of using an isolated macroinitiator (see above), successive addition of two monomers was also attempted. To a polymerization of MMA (100 equiv) (first monomer) with CP–I (1 equiv) (alkyl iodide) at a conversion of 54%, the addition of BzMA (100 equiv) (second monomer) yielded PMMA-*block*-(PMMA-*random*-PBzMA)s with reasonably small PDIs (~1.4) (entry 23 in Table 2), where PBzMA is poly(benzyl methacrylate).

3.3.5. Use of alkyl iodide in situ formed

Instead of using a preformed alkyl iodide, we may add molecular iodine I_2 and an azo compound to the system as starting compounds and use the alkyl iodide in situ formed in the polymerization. This method may be practically useful due to the general lack of the long-term stability of alkyl iodides upon storage. This method was invented by Lacroix-Desmazes et al. and adopted

Table 1
Rate constants for halogen abstraction of $Bu_3Sn^{\bullet}$ from alkyl halides ($R–X + Bu_3Sn^{\bullet} \rightarrow R^{\bullet} + Bu_3SnX$) (25 °C)

Alkyl halide (R–X)	Rate constant ($M^{-1}\,s^{-1}$)	Reference
n-$C_{10}H_{21}$–Cl	7×10^3	[35]
n-C_8H_{17}–Br	3×10^7	[36]
CH_3–I	4×10^9	[36]

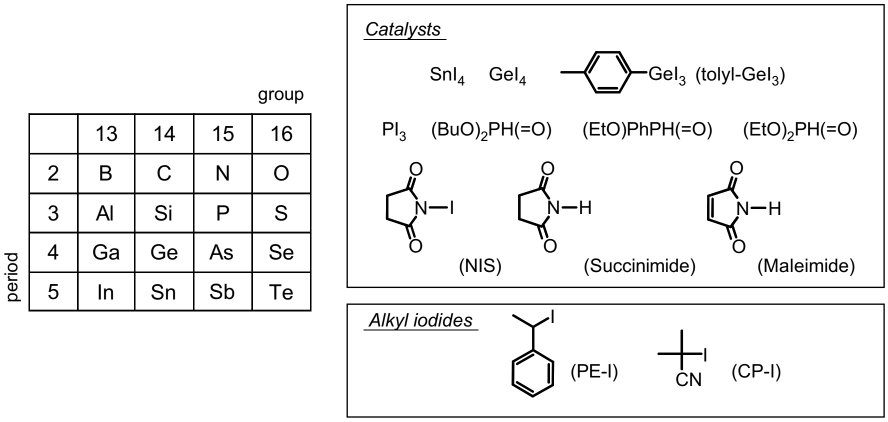


Fig. 1. Periodic table and structures of catalysts and alkyl iodides (low-mass dormant species).

to the iodide-mediated LRP [39]. The polymerization of MMA was examined with I_2 (40 mM), AIBN (80 mM), and NIS (5 mM) at 80 °C (entry 24 in Table 2 and Fig. 4) [8]. AIBN gives 2-cyanopropyl radical CP$^\bullet$, and CP$^\bullet$ reacts with I_2 to form CP–I [40]. It also works as a radical source to run the polymerization after the completion of CP–I formation. In view of the rather low efficiency ($f \sim 0.6$) of AIBN to produce free CP$^\bullet$, we used an excess of it (2 equiv to I_2). Virtually no polymerization occurred for 2.25 h, during which time CP$^\bullet$ predominantly reacted with I_2 (rather than monomer) and CP–I (theoretically 80 mM from 40 mM of I_2) accumulated. After this period, the polymerization smoothly proceeded. The M_n well agreed with $M_{n,theo}$, and PDI was 1.2–1.3 from a low conversion to a high conversion. A phosphorus hydride $(EtO)_2PH(=O)$ (precursor) and nitrogen hydrides succinimide (Fig. 1) and maleimide (Fig. 1) (precursors) were also successfully used in this method (entries 25–27 in Table 2) [38].

3.4. Kinetic features

Kinetic studies were carried out on the activation process and the polymerization rate R_p in the St polymerizations with a polystyrene iodide (PSt–I) ($M_n = 2000$; PDI = 1.20), BPO, and a catalyst (GeI_4, SnI_4, or NIS) at 80 °C [6,38]. (The systems correspond to those in Section 3.3.1 for St with Ge, Sn, and N iodides (catalysts).) The

Table 2
Polymerizations of St and methacrylates with Ge, Sn, P, and N catalysts

Entry	Monomer (equiv to [R–I])	Catalyst	R–I	In[a]	$[R–I]_0/[In]_0/[catalyst]_0$ (mM)	T (°C)	t (h)	Conv (%)	M_n[b] ($M_{n,theo}$)	PDI[b]
1	St (100 equiv)	GeI_4	PE–I	BPO	80/20/5	80	21	47	4300 (4700)	1.16
2	St (100 equiv)	GeI_4	PE–I	BPO	80/40/2	80	7	85	8200 (8500)	1.24
3	St (100 equiv)	GeI_2	PE–I	BPO	80/40/2	80	7	85	8200 (8500)	1.24
4	St (100 equiv)	SnI_4	PE–I	AIBN	80/40/5	60	27	72	6500 (7200)	1.21
5	St (100 equiv)	SnI_2	PE–I	AIBN	80/20/5	60	21	50	4800 (5000)	1.23
6	St (100 equiv)	PI_3	PE–I	DCP	80/80/0.5	100	23	52	5100 (5200)	1.25
7	St (100 equiv)	NIS	PE–I	DCP	80/80/5	100	10	56	5200 (5600)	1.16
8	St (100 equiv)	$(BuO)_2PH(=O)$	PE–I	DCP	80/80/10	100	23	55	4200 (5500)	1.24
9	St (100 equiv)	$(EtO)PhPH(=O)$	PE–I	DCP	80/80/30	100	23	69	5200 (6900)	1.19
10	MMA (100 equiv)	Tolyl-GeI_3	CP–I	AIBN	80/20/5	70	6	84	6900 (8400)	1.19
11	MMA (100 equiv)	PI_3	CP–I	AIBN	80/20/2	70	4	78	9600 (7800)	1.28
12	MMA (100 equiv)	NIS	CP–I	AIBN	60/10/1[c]	80	2	79	7000 (7900)	1.29
13	MMA (200 equiv)	$(EtO)_2PH(=O)$	CP–I	BPO	40/20/10	70	6	74	13 000 (15 000)	1.29
14	GMA (100 equiv)	NIS	CP–I	AIBN	60/10/1[c]	80	1	71	9700 (9100)	1.29
15	BzMA (100 equiv)	NIS	CP–I	AIBN	80/10/1	80	0.8	70	13 300 (13 000)	1.26
16	HEMA (100 equiv)	NIS	CP–I	AIBN	40/15/10[c]	80	1.5	57	7900 (7400)	1.36
17	PEGMA (100 equiv)[d]	NIS	CP–I	AIBN	80/10/2	80	1	39	8600 (9600)	1.33
18	MAA/BzMA (15/85 equiv)	NIS	CP–I	AIBN	80/40/1	80	1	60	6400 (9700)	1.21
19	DMAEMA/BzMA (15/85 equiv)	NIS	CP–I	AIBN	80/10/1	80	1.25	90	19 000 (15 600)	1.34
20	HEMA/BzMA (22/78 equiv)	NIS	CP–I	AIBN	80/20/2	80	1.25	90	18 500 (15 200)	1.37
21	St (200 equiv)	PI_3	PMMA–I[e]	DCP	40/40/1	100	24	90	27 000 (24 000)	1.25
22	BzMA (100 equiv)	NIS	PMMA–I[e]	AIBN	80/10/1	80	1	63	11 000 (15 000)	1.20
23	MMA (100 equiv)	NIS	CP–I	AIBN	40/10/1[c]	80	1.5	54	5400 (5400)	1.31
	+BzMA (100 equiv)						+0.5	108	9700 (13 600)	1.37
							+1.0	145	13 100 (19 300)	1.42
24	MMA (100 equiv)	NIS	I_2	AIBN	40/80/5	80	3	90	8200 (9000)	1.28
25	MMA (100 equiv)	$(EtO)_2PH(=O)$	I_2	AIBN	40/80/10	80	2.17	95	10 300 (9500)	1.22
26	MMA (100 equiv)	Succinimide	I_2	AIBN	40/80/30	80	3.08	90	7400 (9000)	1.38
27	MMA (100 equiv)	Maleimide	I_2	AIBN	40/80/30	80	3.16	62	6300 (6200)	1.29

[a] In = conventional radical initiator; BPO = benzoyl peroxide; AIBN = azobis(isobutyronitrile) and DCP = dicumyl peroxide.

[b] Determined by GPC with polystyrene-calibration for entries 1–9 and 21, poly(methyl methacrylate)-calibration for entries 10–13, 18–20, 22–27, and a multiangle laser light-scattering detector (MALLS) for entries 14–17.

[c] Solution polymerization with 25 vol% anisole for entries 12 and 14, 15 vol% 1-propanol and 35 vol% methyl ethyl ketone for entry 16, and 50 vol% anisole for entry 23.

[d] Molecular weight = 246.

[e] $M_n = 4100$ and PDI = 1.12 for entry 21, and $M_n = 3900$ and PDI = 1.14 for entry 22.

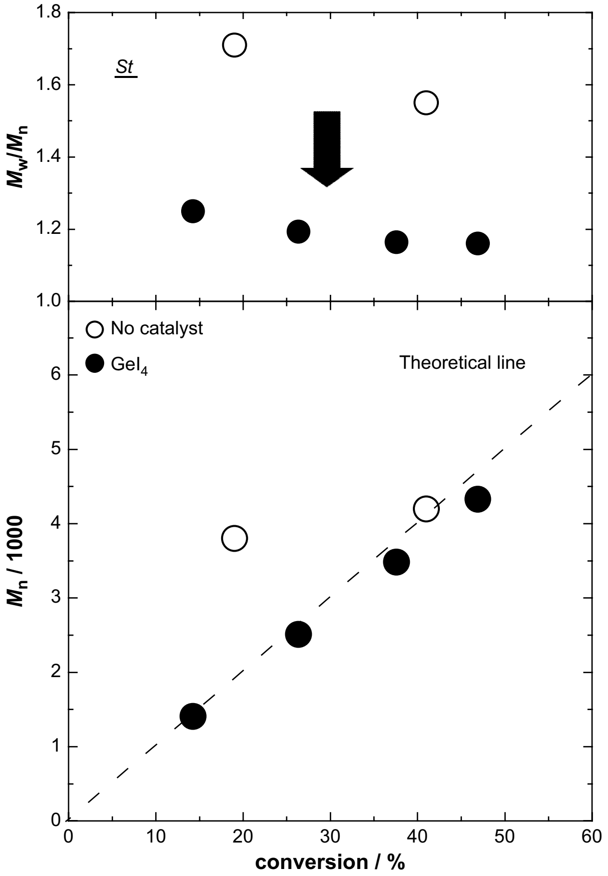


Fig. 2. Plots of M_n and M_w/M_n (PDI) vs conversion for the St/PE–I/BPO/(GeI_4) system (80 °C): $[PE–I]_0 = 80$ mM; $[BPO]_0 = 20$ mM; $[GeI_4]_0 = 0$ mM (open circles) and 5 mM (filled circles: for entry 1 in Table 2).

$$R_2PH(=O) + R\text{-}O^\bullet \longrightarrow R_2P^\bullet(=O) + R\text{-}OH$$

Scheme 5. Abstraction of a hydrogen from a phosphorus hydride with an alkoxy radical to form the phosphorus radical, which will work as an activator ($A^\bullet$ in Scheme 1e), and the alcohol.

polymeric adduct PSt–I was used as a starting alkyl iodide to focus on the kinetics of polymer region.

3.4.1. *Reversible activation*

In the presence of a deactivator XA (a catalyst), a Polymer-I can be activated via the RT process (Scheme 1e) with an activator radical $A^\bullet$ (rate constant k_a) and the DT process (Scheme 1c) (rate constant k_{ex}). Thus, k_{act} (Scheme 1a) is generally given by

$$k_{act} = k_{ex}[\text{Polymer}^\bullet] + k_a[\text{A}^\bullet] \tag{1}$$

In the quasi-equilibrium of the RT process (Scheme 1e), Eq. (1) takes the form

$$k_{act} = k_{ex}[\text{Polymer}^\bullet] + k_{da}[\text{Polymer}^\bullet]\left(\frac{[\text{XA}]}{[\text{Polymer–X}]}\right) \tag{2}$$

where k_{da} is the deactivation rate constant with XA (Scheme 1e). Thus, k_{act} increases with the ratio [XA]/[Polymer–X].

Fig. 5 shows the plots of k_{act} vs the ratio for the St/PSt–I/BPO systems (80 °C) with GeI_4 [6], SnI_4 [38], and NIS [38] as XA, where k_{act} was experimentally determined at a fixed value of [$\text{Polymer}^\bullet$]. In all cases, k_{act} linearly increased with the ratio, as expected from Eq. (2). The plot for GeI_4 suggests that in the typical case with $[GeI_4]/[PSt–I] = 5$ mM/80 mM = 0.0625 (entry 1 in Table 2), k_{act} is about 20 times larger than in the absence of GeI_4. This explains why low-polydispersity polymers were obtained from an early stage of polymerization for the GeI_4 system. SnI_4 and NIS also exhibited large k_{act} values at the same ratio, about 15 and 10 times larger than in their absence, respectively (Fig. 5). Of the three, GeI_4 was the

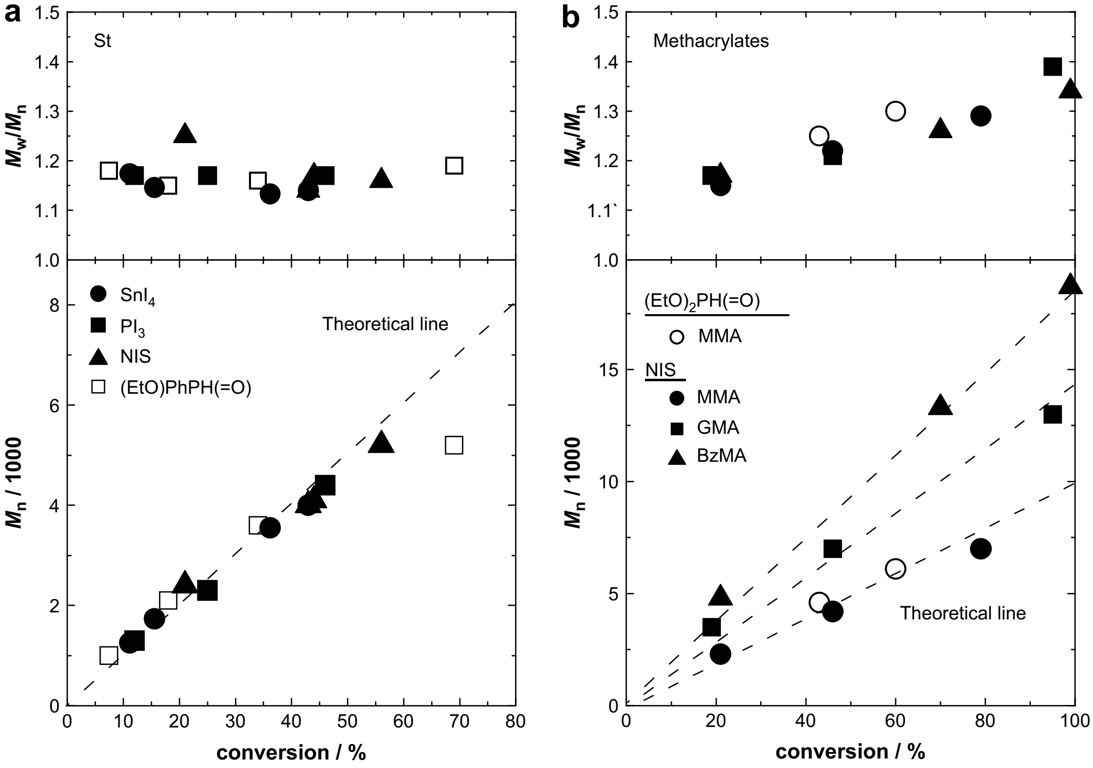


Fig. 3. Plots of M_n and M_w/M_n (PDI) vs conversion for the (a) St and (b) methacrylate systems for entries (a) 4, 6, 7, and 9, and (b) 12–15 in Table 2.

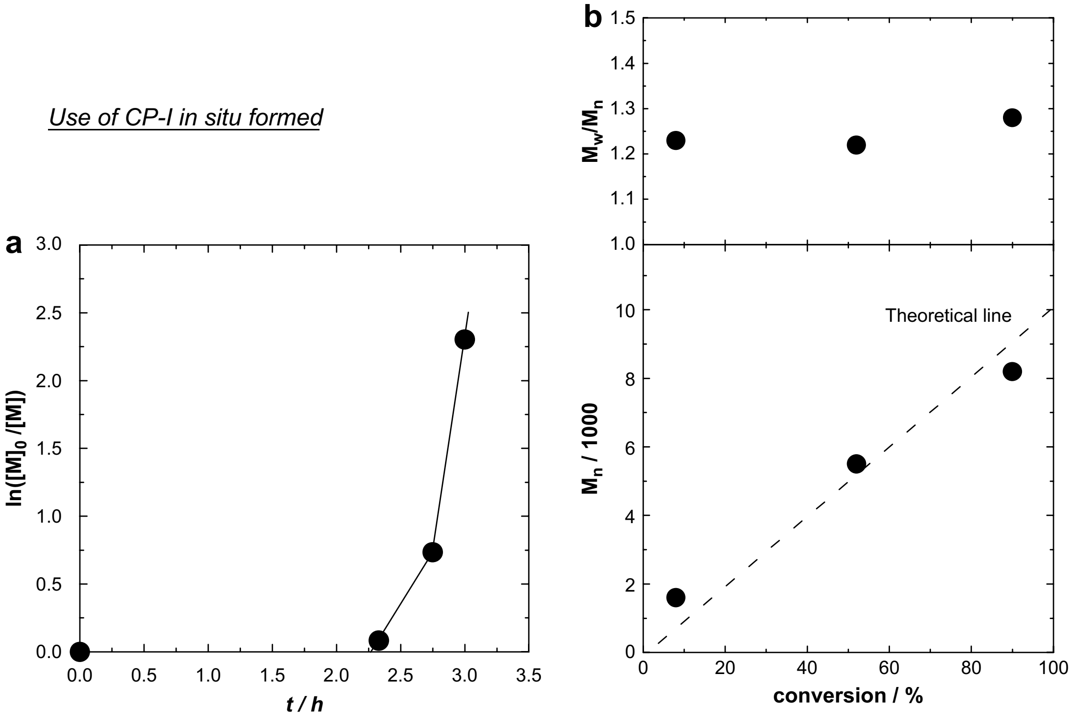


Fig. 4. Plots of M_n and M_w/M_n (PDI) vs conversion for the MMA/I$_2$/AIBN/NIS system (80 °C) for entry 24 in Table 2.

most active for St at 80 °C. It should be noted that the activity depends on temperature and monomer. For St at a lower temperature 60 °C, SnI$_4$ was the most active, and for MMA, NIS was the most active, for example (data not shown), as the details will be discussed in future publication.

For GeI$_4$, the slope of the line (Fig. 5) gives k_{da} of 6.0×10^5 M^{-1} s^{-1}. This is large, nearly as large as the deactivation rate constant (5.7×10^5 M^{-1} s^{-1} (120 °C)) [12] for a PSt radical with DEPN, an excellent deactivator for LRP. As shown below, the equilibrium constant K ($=k_a/k_{da}$) for the GeI$_4$ system was estimated to be about 10^0. It follows that, for a typical condition of [Polymer–I] = 10^{-2} M, [Polymer$^\bullet$] = 10^{-8} M, and [GeI$_4$] = 10^{-3} M, $[\mathrm{GeI}_3^{\bullet}]$ is 10^{-9} M (nano-molar). With these K and k_{da} values, k_a is estimated to be about 10^6 M^{-1} s^{-1}. This value is remarkably large, meaning that the observed large activation rate is achieved by a nano-molar level concentration of the activator. Such a large k_a is a unique kinetic feature of RTCP.

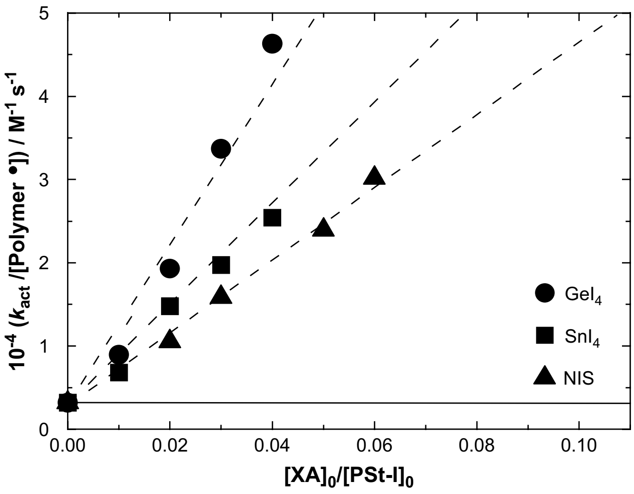


Fig. 5. Plots of k_{act} vs [XA]$_0$/[PSt–I]$_0$ for the St/PSt–I/BPO/XA systems (80 °C) with XA = GeI$_4$ (circles), SnI$_4$ (squares), and NIS (triangles): [PSt–I]$_0$ = 10 mM; [BPO]$_0$ = 1 mM; [XA]$_0$ = 0–0.6 mM.

3.4.2. Polymerization rate

In the presence of the RTCP catalysts, R_p is somewhat smaller than in their absence (iodide-mediated polymerization), as shown in Fig. 6a for the St/PSt–I/BPO systems with and without GeI$_4$ (80 °C) [6]. This is because the activator radicals (A$^\bullet$) undergo irreversible cross-termination with Polymer$^\bullet$ (rate constant k'_t) and irreversible self-termination between A$^\bullet$ (rate constant k''_t). This mechanism is analogous to the one for the rate retardation in the RAFT polymerization [41], where the intermediate radicals (Polymer–(X$^\bullet$)–Polymer) undergo the relevant terminations. In theory, when the quasi-equilibrium of RT holds and the radical concentrations [Polymer$^\bullet$] and [A$^\bullet$] are stationary, R_p is given by Eq. (3)

$$R_p = R_{p,0}\left(1+2\left(\frac{k'_t}{k_t K}\right)\frac{[\mathrm{XA}]}{[\mathrm{Polymer{-}X}]}+\left(\frac{k''_t}{k_t K^2}\right)\frac{[\mathrm{XA}]^2}{[\mathrm{Polymer{-}X}]^2}\right)^{-1/2} \tag{3}$$

where $R_{p,0}$ is the R_p without XA. Eq. (3) means that R_p decreases with increasing ratio [XA]/[Polymer–X]. At a small value of this ratio, the last term on the right-hand side for the self-termination of A$^\bullet$ may be neglected, and Eq. (3) takes the form

$$R_p = R_{p,0}\left(1+2\left(\frac{k'_t}{k_t K}\right)\frac{[\mathrm{XA}]}{[\mathrm{Polymer{-}X}]}\right)^{-1/2} \tag{4}$$

In the mentioned system (Fig. 6a), R_p (hence [Polymer$^\bullet$]) was stationary in the studied range of time in all cases and decreased with increasing ratio of [GeI$_4$]$_0$/[PSt–I]$_0$ as the theory demands. Fig. 6b shows the plot of R_p vs [GeI$_4$]$_0$/[PSt–I]$_0$. The plot was linear, confirming the validity of Eq. (4) for [GeI$_4$]$_0$/[PSt–I]$_0$ = 0–0.25. Thus, when this ratio is relatively small (~0.0625), as in entry 1 in Table 2, the cross-termination is the main cause for the retardation. The existence of the cross-termination brings about an increase of the termination rate hence the number of dead chain by, e.g., about 20%

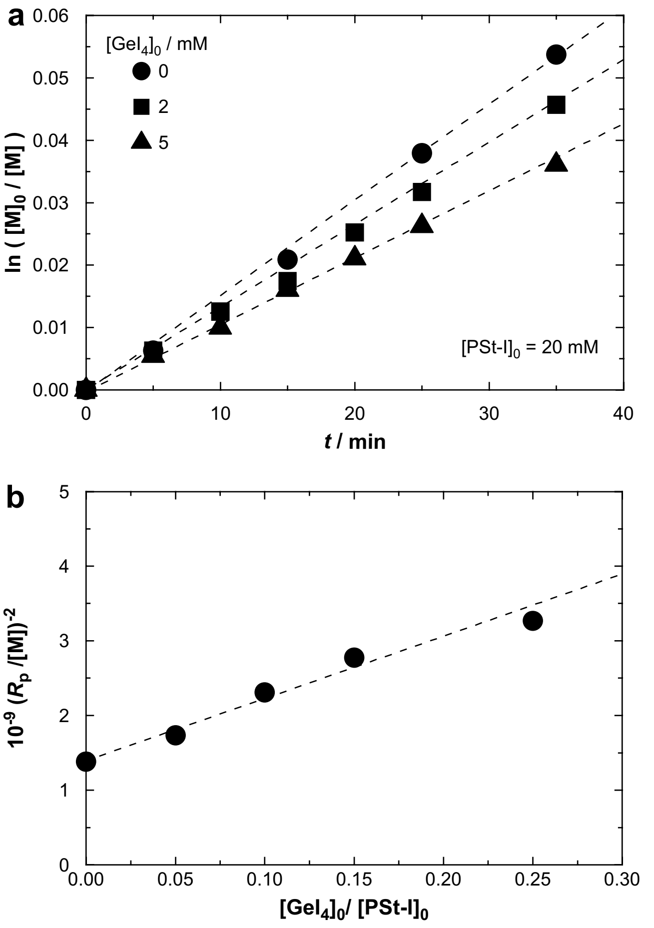


Fig. 6. Plots of (a) $\ln([M]_0/[M])$ vs time t and (b) $(R_p/[M])^{-2}$ vs $[GeI_4]_0/[PSt–I]_0$ for the St/PSt–I/BPO/GeI$_4$ system (80 °C): $[PSt–I]_0 = 20$ mM; $[BPO]_0 = 10$ mM; $[XA]_0 =$ 0–5 mM. The [M] denotes the concentration of monomer (St).

in a typical condition (entry 1 in Table 2). However, the effect of this much of dead chains on polydispersity is rather minor in this as well as other LRP systems. The cross-termination also results in a loss of GeI$_4$, but it is also minor, at least at an early stage of polymerization. In cases, the cross-termination products, such as PSt–GeI$_3$, may still work as XA, controlling the polydispersity. The slope of the line (Fig. 6b) gives $k'_t/(k_t K) = 3$. The k'_t between a polymer radical and a low-mass radical (A$^\bullet$) would be about 10^9 M^{-1} s^{-1}, and the k_t between polymer radicals would be about 10^8 M^{-1} s^{-1}, at the studied low conversions. Thus, K is estimated to be of the order of 10^0.

4. Conclusions

The addition of Ge, Sn, P, and N compounds to the iodide-mediated polymerization led to a new class of LRP called RTCP, which is based on a new reversible activation mechanism, reversible chain transfer (RT). Several Ge, Sn, P, and N compounds work as efficient catalysts, successfully controlling the homo- and co-polymerizations of St and (functional) methacrylates. Attractive features of the catalysts include their *high reactivity* (small amounts being required (e.g., ∼100 ppm)), *high solubility* in organic media without ligands, *insensitivity to air*, and *minor color and smell*. The Ge, P, and N catalysts may also be attractive for their *low toxicity*. The P catalysts, particularly the hydrides (precursors) may be attractive for their *low cost*. Perhaps, the hydrides are the least expensive LRP catalysts/mediators developed so far. Thus, while the addition of the catalyst to the iodide-mediated polymerization dramatically improves the polydispersity control, it causes little undesirable effects, retaining the robustness of the iodide-mediated polymerization. The good polydispersity controllability, the good tolerance to functional groups, and the prominent robustness may be great advantages for RTCP to serve as a useful synthetic tool for well-defined polymers.

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References

[1] (a) Matyjaszewski K, Davis TP, editors. Handbook of radical polymerization. New York: John Wiley & Sons; 2002;
(b) Matyjaszewski K, editor. ACS Symposium Ser 1998;685, 2000;768, 2003;854, 2006;944;
(c) Moad G, Solomon DH, editors. The chemistry of radical polymerization. Amsterdam: Elsevier; 2006;
(d) Braunecker WA, Matyjaszewski K. Prog Polym Sci 2007;32:93.
[2] Fukuda T. J Polym Sci Part A Polym Chem 2004;42:4743.
[3] Goto A, Fukuda T. Prog Polym Sci 2004;29:329.
[4] Fischer H. Chem Rev 2001;101:3581.
[5] (a) Goto A, Zushi H, Kwak Y, Fukuda T. ACS Symp Ser 2006;944:595;
(b) Goto A, Zushi H, Hirai N, Wakada T, Kwak Y, Fukuda T. Macromol Symp 2007;248:126.
[6] Goto A, Zushi H, Hirai N, Wakada T, Tsujii Y, Fukuda T. J Am Chem Soc 2007;29:13347.
[7] Goto A, Hirai N, Tsujii Y, Fukuda T. Macromol Symp 2008;261:18.
[8] Goto A, Hirai N, Wakada T, Nagasawa K, Tsujii Y, Fukuda T. Macromolecules 2008;41:6261.
[9] (a) Otsu T, Yoshida M. Makromol Chem Rapid Commun 1982;3:127;
(b) Otsu T. J Polym Sci Part A Polym Chem 2000;38:2121.
[10] (a) Le TPT, Moad G, Rizzardo E, Thang SH. International Pat. Appl. PCT/US97/12540 WO9801478; Chem Abstr 1998;128:115390;
(b) Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Macromolecules 1998;31:5559;
(c) Moad G, Rizzardo E, Thang SH. Aust J Chem 2005;58:379;
(d) Perrier S, Takolpuckedee P. J Polym Sci Part A Polym Chem 2005;43:5347;
(e) Moad G, Rizzardo E, Thang SH. Polymer 2008;49:1079.
[11] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Macromolecules 1993;26:2987.
[12] Benoit D, Grimaldi S, Robin S, Finet JP, Tordo P, Gnanou Y. J Am Chem Soc 2000;122:5929.
[13] (a) Solomon DH, Rizzardo E, Cacioli P. Eur Pat Appl EP135280; 1985.
(b) Benoit D, Chaplinski V, Braslau R, Hawker CJ. J Am Chem Soc 1999;121:3904;
(c) Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661;
(d) Sciannamea V, Jérôme R, Detrembleur C. Chem Rev 2008;108:1104.
[14] Colombani D, Steenbock M, Klapper M, Müllen K. Macromol Rapid Commun 1997;18:243.
[15] (a) Yamada B, Nobukane Y, Miura Y. Polym Bull 1998;41:539;
(b) Chen EKY, Teertstra SJ, Chan-Seng D, Otieno PO, Hicks RG, Georges MK. Macromolecules 2007;40:8609.
[16] (a) Bledzki A, Braun D. Polym Bull 1986;16:19;
(b) Chernikova EV, Pokataeva ZA, Garina ES, Lachinov MB, Golubev VB. Macromol Chem Phys 2001;202:188.
[17] Wieland PC, Raether B, Nuyken O. Macromol Rapid Commun 2001;22:700.
[18] (a) Wayland BB, Poszmik G, Mukerjee SL, Fryd M. J Am Chem Soc 1994;116:7943;
(b) Lu Z, Fryd M, Wayland BB. Macromolecules 2004;37:2686;
(c) Debuigne A, Caille JR, Jérôme R. Angew Chem Int Ed 2005;1101:44.
[19] Asandei AD, Moran IW. J Am Chem Soc 2004;126:15932.
[20] (a) Yutani Y, Tatemoto M. Preparing polymers with iodine compounds. Eur. Pat. Appl. 1992;EP489370 A1.
(b) Kato M, Kamigaito M, Sawamoto M, Higashimura T. Polym Prepr Jpn 1994;43:225;
(c) Matyjaszewski K, Gaynor S, Wang JS. Macromolecules 1995;28:2093;
(d) David G, Boyer C, Tonnar J, Ameduri B, Lacroix-Desmazes P, Boutevin B. Chem Rev 2006;106:3936.
[21] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721.
[22] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[23] (a) Matyjaszewski K, Xia J. Chem Rev 2001;101:2921;
(b) Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689;
(c) Kamigaito M, Ando T, Sawamoto M. Chem Record 2004;4:159;
(d) Tsarevsky NV, Matyjaszewski K. Chem Rev 2007;107:2270;
(e) Pintauer T, Matyjaszewski K. Chem Soc Rev 2008;37:1087.

[24] (a) Takagi K, Soyano A, Kwon TS, Kunisada H, Yuki Y. Polym Bull 1999;43:143;
(b) Yamago S, Iida K, Yoshida J. J Am Chem Soc 2002;124:2874;
(c) Yamago S. J Polym Sci Part A Polym Chem 2006;44:1.

[25] Yamago S, Ray B, Yoshida J, Tada T, Yoshizawa K, Kwak Y, et al. J Am Chem Soc 2004;126:13908.

[26] Yamago S, Kayahara E, Kotani M, Ray B, Kwak Y, Goto A, et al. Angew Chem Int Ed 2007;46:1304.

[27] Goto A, Fukuda T. Macromolecules 1997;30:5183.

[28] Goto A, Ohno K, Fukuda T. Macromolecules 1998;31:2809.

[29] Ohno K, Goto A, Fukuda T, Xia J, Matyjaszewski K. Macromolecules 1998;31:2699.

[30] Goto A, Sato K, Tsujii Y, Fukuda T, Moad G, Rizzardo E, et al. Macromolecules 2001;34:402.

[31] (a) Goto A, Kwak Y, Fukuda T, Yamago S, Iida K, Nakajima M, et al. J Am Chem Soc 2003;125:8720;
(b) Kwak Y, Goto A, Fukuda T, Kobayashi Y, Yamago S. Macromolecules 2006;39:4671.

[32] Kwak Y, Goto A, Fukuda T, Yamago S. Z Chem Phys 2005;219:283.

[33] (a) Neumann WP. Synthesis 1987:665;
(b) Chatgilialoglu C, Newcomb M. Adv Organomet Chem 1999;44:67;
(c) Studer A, Amrein S. Synthesis 2002:835.

[34] Curran DP, Jasperse CP, Totleben MJ. J Org Chem 1991;56:7169.

[35] Beckwith ALJ, Pigou PE. Aust J Chem 1986;39:77.

[36] Ingold KU, Lusztyk J, Scaiano JC. J Am Chem Soc 1984;106:343.

[37] (a) Brunton G, Ingold KU. Org Magn Reson 1975;7:527;
(b) Anpo M, Suteliffe R, Ingold KU. J Am Chem Soc 1983;105:3580.

[38] Goto A, Tsujii Y, Fukuda T. et al., in press.

[39] Lacroix-Desmazes P, Severac R, Boutevin B. Macromolecules 2005;38:6299.

[40] Balczewski P, Mikolajczyk M. New J Chem 2001;35:659.

[41] (a) de Brouwer H, Schellekens MAJ, Klumperman B, Monteiro MJ, German AL. J Polym Sci Part A Polym Chem 2000;38:3596;
(b) Barner-Kowollik C, Buback M, Charleux B, Coote ML, Drache M, Fukuda T, et al. J Polym Sci Part A Polym Chem 2006;44:5809.

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