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Reversible chain Transfer Catalyzed Polymerization (RTCP)

Polymer-X + A• ⇌ Polymer• + XA

(A = Ge, Sn, or P compound and X = I in this work)

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Living Radical Polymerizations with Germanium, Tin, and Phosphorus Catalysts − Reversible Chain Transfer Catalyzed Polymerizations (RTCPs)

Atsushi Goto, Hirokazu Zushi, Norihiro Hirai, Tsutomu Wakada, Yoshinobu Tsujii,* and Takeshi Fukuda*

Contribution from Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received July 26, 2007; E-mail: tsujii@scl.kyoto-u.ac.jp; fukuda@scl.kyoto-u.ac.jp

Abstract: A novel class of living radical polymerizations with germanium, tin, and phosphorus catalysts were developed. The polymerizations are based on a new reversible activation mechanism, *Reversible chain Transfer (RT)* catalysis. Low-polydispersity ($M_w/M_n \approx 1.1-1.3$) polystyrene, poly(methyl methacrylate), poly(glycidyl methacrylate), and poly(2-hydroxyethyl methacrylate) with predicted molecular weight were obtained with fairly high conversion in a fairly short time. The pseudo-first-order activation rate constant k_{act} for the styrene/GeI$_4$ (catalyst) system was large enough, even with a small amount of GeI$_4$, explaining why the system provides low-polydispersity polymers from an early stage of polymerization. The retardation in the polymerization rate observed for the styrene/GeI$_4$ system was kinetically proven to be mainly due to the cross-termination between the propagating radical with GeI$_3$•. Attractive features of the germanium, tin, and phosphorus catalysts include their *high reactivity* hence small amounts (1−10 mM) being required under relatively mild conditions (at 60−100 °C), *high solubility* in organic media without ligands, *insensitivity to air* hence sample preparation being allowed in the air, and *minor color and smell*. The germanium and phosphorus catalysts may also be attractive for their *low toxicity*. The phosphorus catalysts may also be attractive for their *low cost*.
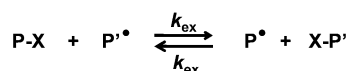
1. Introduction

Living radical polymerization (LRP) has attracted much attention as a robust and versatile synthetic route for well-defined polymers.[1] LRP is based on the reversible activation of the dormant species P−X to the propagating radical P• (Scheme 1a). In this article, P denotes a polymer, and phosphorus will explicitly be expressed. A number of activation−deactivation cycles are requisite for good control of chain length distribution.[2,3] As the capping agent X, halogens have been used mainly in two systems. One is iodide-mediated polymerization,[4] in which P−X (X = I) is activated by P• (degenerative or exchange chain transfer:[4,5] Scheme 1b). However, due to a low exchange frequency of iodine, the controllability of polydis-
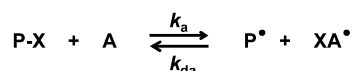
Scheme 1. Reversible Activation Processes[a]

(a) Reversible activation (general scheme)

$$P\text{-}X \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} P^\bullet \quad \overset{k_p}{\curvearrowright} (\text{+ monomers})$$

(b) Degenerative (exchange) chain transfer (DT)

$$P\text{-}X + P'^\bullet \underset{k_{ex}}{\overset{k_{ex}}{\rightleftarrows}} P^\bullet + X\text{-}P'$$

(c) Atom transfer (AT)

$$P\text{-}X + A \underset{k_{da}}{\overset{k_a}{\rightleftarrows}} P^\bullet + XA^\bullet$$

(A = transition metal complex)

(d) Reversible chain transfer (RT)

$$P\text{-}X + A^\bullet \underset{k_{da}}{\overset{k_a}{\rightleftarrows}} P^\bullet + XA$$

(A = typical element compound)
(X = I and XA = GeI$_4$ etc. in this work)

[a] (a) General scheme, (b) degenerative (exchange) chain transfer (DT), (c) atom transfer (AT), and (d) reversible chain transfer (RT).

persity in this system is limited. The other is atom transfer radical polymerization (ATRP), in which P−X (X = Cl, Br) is activated by a transition metal complex (Scheme 1c, where A

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is an activator and XA is a deactivator).[6] The addition of the catalyst[6,7] allows a high activation frequency, yielding low-polydispersity polymers.

In this work, we propose a new and robust LRP. We add a Ge, Sn, or phosphorus compound, e.g., GeI_4, to the iodide-mediated polymerization. GeI_4 works as a deactivator of $P^\bullet$, in situ producing $GeI_3^\bullet$ (Scheme 1d). $GeI_3^\bullet$ works as an activator of a polymer–iodide P–I, producing $P^\bullet$ and GeI_4. This cycle allows the frequent activation of P–I.

Mechanistically, this process is a reversible chain transfer (RT) process in which GeI_4 works as a chain transfer agent. P–X is catalytically activated via an RT process. This is a new reversible activation mechanism in LRP. The polymerization may be termed RT-catalyzed polymerization (RTCP) as a new class of LRP. In this paper, Ge, Sn, and phosphorus compounds will be called RT catalysts or simply catalysts. By a kinetic study,[8] we and Yamago recently uncovered that organotellurium-mediated LRP (TERP: $X = TeCH_3$) includes an RT process when ditelluride (($TeCH_3)_2$) is added ($X = A = TeCH_3$ in Scheme 1d), which gave a mechanistic reason for the previous finding[9] of Yamago et al. that the polydispersity control in TERP is improved by the addition of ditelluride.

In RTCP, instead of adding a deactivator, a precursor of a deactivator or an activator radical may be used as a starting compound. We examined such an alternative polymerization method too.

A key factor for RTCP is a high reactivity of the activator radical. In organic chemistry, Ge, Sn, and phosphorus radicals are known to abstract a halogen from an alkyl halide with high reactivity to give the alkyl radical and their halides.[10] This reaction and the subsequent reduction of the alkyl radical with a hydride are widely utilized for the transformation of an alkyl halide to an alkyl hydride. Another key factor is a high reactivity of the deactivator halide. However, the reactions of a carbon-centered radical to Ge, Sn, and phosphorus halides are generally slow[10] (particularly slow to the bromides and chlorides) and have not attracted much attention for synthetic purposes. In this work, we found that some Ge, Sn, and phosphorus iodides such as GeI_4 are highly reactive to carbon-centered radicals working as an effective deactivator for LRP. In this work, we determined the deactivation rate constant for GeI_4, which is the first quantitative study on this kind of reaction in organic chemistry.

The RTCP is the first LRP using compounds of typical elements (non-transition metals) as effective catalysts. In an ATRP manner, Percec et al.[11] used non-transition metals, $Na_2S_2O_4$, and its analogues as *irreversible* activators, which only once activated alkyl halides forming no effective deactivator. The Ge, Sn, and phosphorus compounds used in this study work as *reversible* activators and deactivators.

In this article, we will demonstrate the results of the RTCP of styrene (St), methyl methacrylate (MMA), glycidyl methacrylate (GMA), and 2-hydroxyethyl methacrylate (HEMA) with several Ge, Sn, and phosphorus catalysts. We will also examine the kinetic features of the St/GeI_4 system. This work was partly and briefly introduced in conference proceedings.[12]

2. Results and Discussion

2.1. Control in Molecular Weight and Its Distribution. 2.1.1. St with Ge, Sn, and Phosphorus Iodides as Deactivators. We first examined the polymerization of St at 80 °C, using 1-phenylethyl iodide (PE–I) as a low-mass alkyl halide initiator, GeI_4 as a deactivator, and benzoyl peroxide (BPO) as a conventional radical initiator. In this polymerization, $P^\bullet$, which is originally supplied by BPO, is supposed to react with GeI_4, in situ producing the activator radical $GeI_3^\bullet$ (and P–I). If $GeI_3^\bullet$ effectively abstracts I from PE–I (or P–I) to produce $PE^\bullet$ (or $P^\bullet$), cycles of activation and deactivation (RT) will be started.

Table 1 (entries 1–4) and Figures 1 and 2 (filled circles) show the results. The first-order plot of the monomer concentration [M] (Figure 1) showed a curvature in a long time range (for 21 h) due to a decrease of [BPO] with time t. In a relatively short time range (for ∼1 h), the polymerization rate was approximately constant, as will be discussed below. The number-average molecular weight M_n linearly increased with conversion and agreed with the theoretical value $M_{n,theo}$ (Figure 2). The small deviations from $M_{n,theo}$ at a later stage of polymerization are ascribed to the increase in the number of chains by the decomposition of BPO. The polydispersity index (PDI or M_w/M_n, where M_w is the weight-average molecular weight) reached a low value of about 1.2 from an early stage of polymerization (Figure 2), indicating a high frequency of the activation–deactivation cycle. The small amount (2–5 mM) of GeI_4 required to control the polydispersity (Table 1) suggests a high reactivity of GeI_4.

The activation of P–I occurs not only by RT (Scheme 1d) but also by degenerative chain transfer (Scheme 1b). However, for example, the system with PE–I (80 mM) and BPO (20 mM) but without GeI_4 (entry 16: iodide-mediated polymerization) gave a PDI as large as 1.55 (4 h at 80 °C), while that with GeI_4 (5 mM) (entry 1) achieved a fairly small PDI of 1.17 (with other conditions set the same). This means that RT plays a main role in the GeI_4 system, with a small contribution of degenerative chain transfer.

Besides PE–I, we also used a common alkyl iodide CHI_3 (entry 5 in Table 1). A small PDI (∼1.2) and a good agreement of M_n with $M_{n,theo}$ were achieved at an early stage of polymerization, meaning a sufficiently fast initiation (activation) from CHI_3. At a later stage of polymerization, a small shoulder appeared on the higher-molecular-weight side in the GPC chromatogram due to the slow initiation from the second iodine of CHI_3. However, this initiation was practically negligible and little affected PDI (∼1.25). The use of CH_2I_2 (data not shown) gave only high polydispersity polymers (PDI ∼2.0) throughout the polymerization (up to 80% conversion), meaning the lack of, or very poor, initiation ability of CH_2I_2.
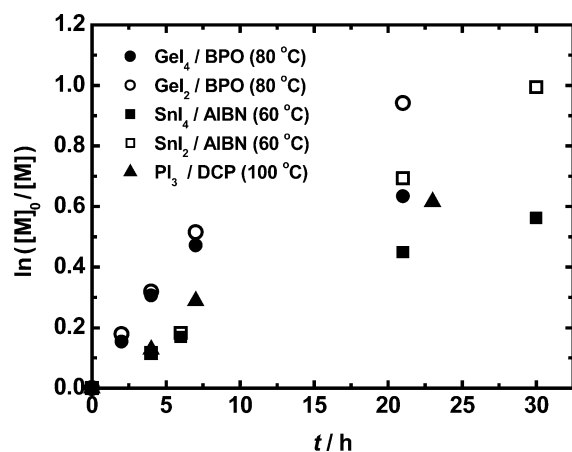
We then used GeI_2, SnI_4, SnI_2, and PI_3 (phosphorus triiodide) as deactivators with PE–I (entries 6–15 in Table 1 and Figures

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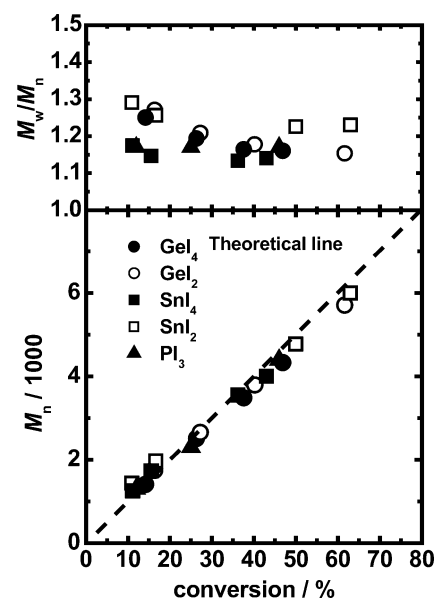
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Table 1. Polymerizations of St with Ge, Sn, and Phosphorus Iodides ($[M]_0 = 8$ M (8000 mM))

entry	XA	R–I	I	$[R–I]_0/[I]_0/[XA]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$)	PDI
1	GeI_4	PE–I	BPO	80/20/5	80	4	26	2500 (2600)	1.19
						7	37	3500 (3700)	1.16
						21	47	4300 (4700)	1.16
2		PE–I	BPO	80/20/2	80	7	47	4600 (4700)	1.16
3		PE–I	BPO	80/40/2	80	7	85	8200 (8500)	1.24
4		PE–I	BPO	25/10/5	80	21	40	11 400 (13 300)	1.29
5		CHI_3	BPO	80/20/2	80	4	29	2400 (2900)	1.21
						7	42	3900 (4200)	1.25
						21	69	5600 (6900)	1.25
6	GeI_2	PE–I	BPO	80/20/5	80	21	61	5700 (6100)	1.15
7		PE–I	BPO	80/40/5	80	25	85	6800 (8500)	1.16
8	SnI_4	PE–I	AIBN	80/20/5	60	21	36	3600 (3600)	1.13
9		PE–I	AIBN	80/40/5	60	27	72	6500 (7200)	1.21
10		PE–I	AIBN	8/4/1	60	21	24	22 000 (24 000)	1.18
11	SnI_2	PE–I	AIBN	80/20/5	60	21	50	4800 (5000)	1.23
12	PI_3	PE–I	DCP	80/80/2	100	23	46	4400 (4600)	1.17
13		PE–I	DCP	80/160/2	100	23	68	6200 (6800)	1.17
14		PE–I	DCP	80/80/1	100	10	45	4000 (4500)	1.16
15		PE–I	DCP	40/80/2	100	23	72	10 000 (14 000)	1.29
16	none	PE–I	BPO	80/20/0	80	4	41	4200 (4100)	1.55

Figure 1. Plot of $\ln([M]_0/[M])$ vs t for the St polymerizations with Ge, Sn, and phosphorus iodides for entries 1, 6, 8, 11, and 12 in Table 1.


Figure 2. Plots of M_n and PDI vs conversion for the St polymerizations with Ge, Sn, and phosphorus iodides for entries 1, 6, 8, 11, and 12 in Table 1.

1 and 2). In all cases, low polydispersity was achieved with a small amount (1−5 mM) of the catalyst. The Sn catalysts (entries 8−11) exhibited good polydispersity control at 60 °C, as the Ge catalysts (entries 1−4, 6, and 7) did at 80 °C. This suggests that the Sn catalysts are even more active than the Ge ones. Both GeI_2 and SnI_2 were effective catalysts, but the polydispersity control with them (entries 6, 7, and 11 and Figure 2) was not as good as that with GeI_4 and SnI_4 (entries 1−4 and 8−10 and Figure 2). PI_3 exhibited good control with very low concentrations (1−2 mM) (entries 12−15). These concentrations are among the lowest of the five examined catalysts, although the temperature was the highest for PI_3 (100 °C). The exact differences in the catalyst activity among the five catalysts are not clear at the moment and can be clarified by a systematic kinetic study. We carried out a kinetic study for GeI_4, as will be shown below, and are currently extending it to the other catalysts, which will be reported in a future publication. (The PI_3 systems included relatively large amounts (80−160 mM) of a conventional radical initiator, dicumyl peroxide (DCP), due

to its slow decomposition (the half-lifetime is ca. 80 h).[13]) The polymerization rates with the catalysts (entries 1−15) were somewhat smaller than those without them (e.g., entry 16), as will be discussed below.

Mechanistically, GeI_2 and SnI_2 may work as deactivators by themselves, or they may react with alkyl iodide (R−I), in situ producing the four-valent compounds,[14] $RGeI_3$ and $RSnI_3$, respectively, which may then work as deactivators. To examine the latter possibility, we heated a toluene-d_8 solution of GeI_2 (5 mM) and PE−I (5 mM) (1:1 equiv) at 80 °C for 10 h. Proton nuclear magnetic resonance (¹H NMR) measurements showed the formation of PE−GeI_3 in >95% yield (Supporting Informa-

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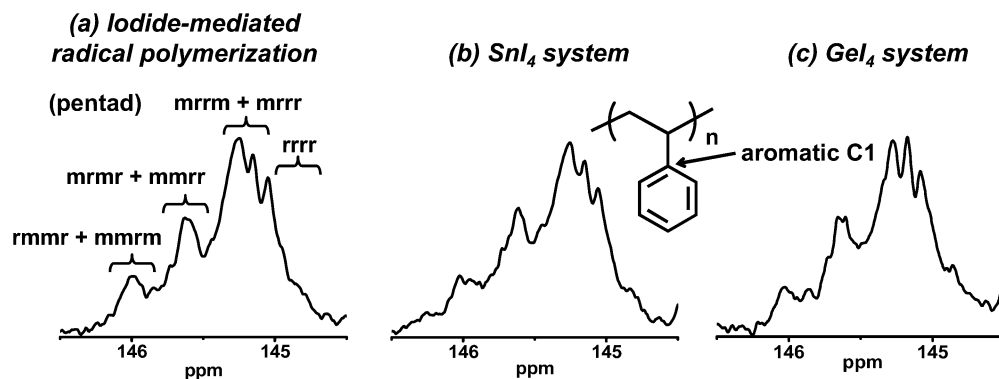
Figure 3. ^{13}C NMR spectra (in the range of 144.5−146.5 ppm) of PSts produced in (a) iodide-mediated radical polymerization (without catalyst) (60 °C), (b) SnI$_4$ system (60 °C), and (c) GeI$_4$ system (80 °C).
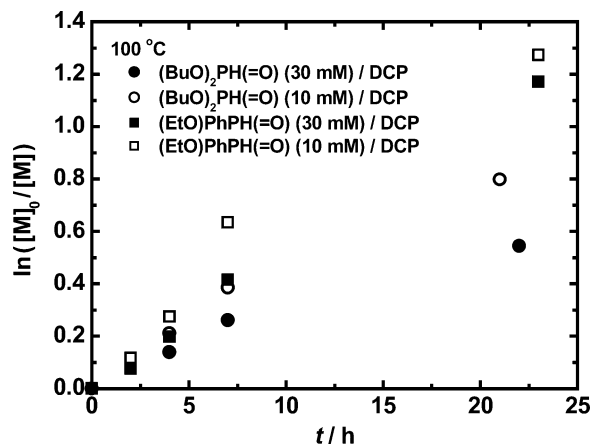
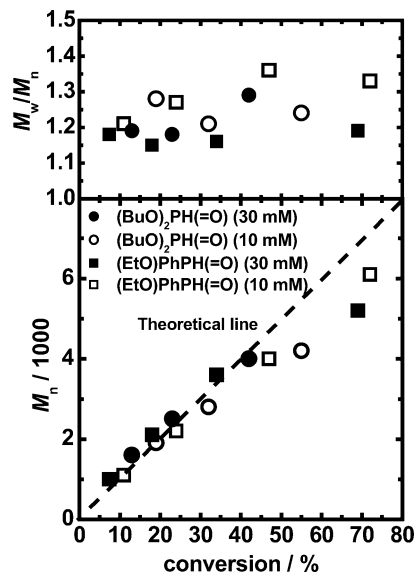**Scheme 2.** Hydrogen Abstraction from a Phosphorus Hydride by an Oxygen-Centered Radical

$$R_2PH(=O) \ + \ R\text{-}O^{\bullet} \longrightarrow R_2P^{\bullet}(=O) \ + \ R\text{-}OH$$
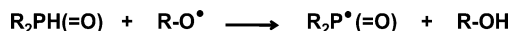
tion). This suggests involvement of the latter mechanism in the polymerization.

Ge and Sn halides are Lewis acids. SnCl$_4$ is a strong Lewis acid and is widely used as a catalyst for living cationic polymerizations.[15] On the other hand, Ge and Sn iodides (used in this work) are relatively weak Lewis acids. To confirm that the present systems are radical polymerizations, we examined the tacticities of the polystyrenes produced in the GeI$_4$ system (80 °C), the SnI$_4$ system (60 °C), and the iodide-mediated system without the catalyst (60 °C). The ^{13}C NMR signal pattern for the aromatic C1 carbon (Figure 3), which reflects the pentad distribution,[16] was almost the same in the three systems. (The tacticity was very similar in the iodide-mediated systems at 80 °C (data not shown) and 60 °C (Figure 3a). It is known that there is little temperature dependence of tacticity in conventional radical polymerization at 0−80 °C.[17]) By a cationic polymerization mechanism, a more isotactic-rich polymer should be formed. Moreover, the present polymerizations were completely inhibited in the presence of TEMPO. These support the radical mechanism.

2.1.2. St with Phosphorus Hydrides as Precursors. As another polymerization method, we used five-valent phosphorus hydrides R$_2$PH(=O) as starting compounds (precursors) to in situ produce an activator radical R$_2$P$^{\bullet}$(=O) (A$^{\bullet}$ in Scheme 1d) and/or a deactivator R$_2$PI(=O) (XA in Scheme 1d) in the presence of DCP and PE−I at 100 °C. DCP (peroxide) gives an oxygen-centered radical. Oxygen-centered radicals are known to abstract a hydrogen from R$_2$PH(=O) to produce an activator radical R$_2$P$^{\bullet}$ (=O) (Scheme 2).[18] Alkyl iodides can be iodinating agents of R$_2$PH(=O) to give a deactivator R$_2$PI(=O) via a non-radical process.[19] PE−I (used in this work) in fact works as a moderate iodinating agent of (BuO)$_2$PH(=O) (used in this work), for example. This was demonstrated by a model experiment: a heat treatment of a toluene-d_8 solution of PE−I

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(19) Mielniczak, G.; Lopusinski, A. *Synth. Commun.* **2003**, *33*, 3851−3859.

Figure 4. Plot of ln([M]$_0$/[M]) vs t for the St polymerizations with phosphorus hydrides for entries 1, 3, 5, and 6 in Table 2.

Figure 5. Plots of M_n and PDI vs conversion for the St polymerizations with phosphorus hydrides for entries 1, 3, 5, and 6 in Table 2.

(80 mM) and (BuO)$_2$PH(=O) (10 mM) at 100 °C yielded a deactivator in 12% yield for 1 h (Supporting Information). In the polymerization, both processes (the productions of activator and deactivator) can be involved, and the relative contributions of the two processes would depend on the R group of the phosphorus hydride R$_2$PH(=O).

We examined the St polymerizations with (BuO)$_2$PH(=O) and (EtO)PhPH(=O) (with a Ph group) as precursors (Figures

Table 2. Polymerizations of St with Phosphorus Hydrides ($[M]_0 = 8$ M (8000 mM))

entry	hydride	I	$[PE–I]_0/[I]_0/[hydride]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$)	PDI
1	$(BuO)_2PH(=O)$	DCP	80/80/30	100	7	23	2500 (2300)	1.18
2		DCP	80/160/30	100	7	51	5900 (5100)	1.24
3		DCP	80/80/10	100	7	32	2800 (3200)	1.21
					23	55	4200 (5500)	1.24
4		VR110	80/80/10	100	7	25	2400 (2500)	1.33
					23	37	3200 (3700)	1.34
5	$(EtO)PhPH(=O)$	DCP	80/80/30	100	7	34	3600 (3400)	1.16
					23	69	5200 (6900)	1.19
6		DCP	80/80/10	100	23	72	6100 (7200)	1.33
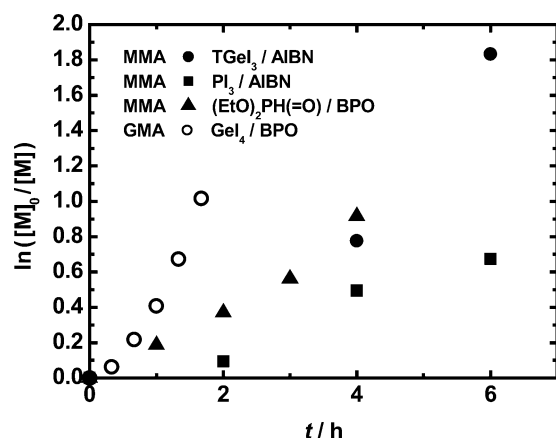
Figure 6. Plot of $\ln([M]_0/[M])$ vs t for the MMA and GMA polymerizations with Ge and phosphorus compounds for entries 1, 3, 5, and 9 in Table 3.

Figure 7. Plots of M_n and PDI vs conversion for the MMA and GMA polymerizations with Ge and phosphorus compounds for entries 1, 3, 5, and 9 in Table 3.

4 and 5 and Table 2). With 30 mM of the precursors (filled symbols in Figures 4 and 5 and entries 1, 2, and 5 in Table 2), low polydispersity polymers (PDI ≤ 1.2) were successfully obtained from an early stage of polymerization, and the PDI was kept at a low level (∼1.2) throughout the polymerization. Even with a lower concentration (10 mM) of the precursors (open symbols and entries 3 and 6), fairly low polydispersity (PDI ∼1.2−1.3) was achieved. Instead of DCP (peroxide), an azo-initiator 2,2′-azobis(2,4,4-trimethylpentane) (VR110) was used as a conventional radical initiator for the $(BuO)_2PH(=O)$ system (entry 4). The PDI was larger with VR110 than with DCP (1.33 vs 1.21 for 7 h, for example) at the same precursor concentration (10 mM) (entries 3 and 4). This suggests that the production of the activator radical by DCP (peroxide) is important in this method. Thus, with the two phosphorus hydrides, this method was successful, and the use of a peroxide significantly improved the polydispersity control.

2.1.3. Methacrylates. We adopted RTCP to methacrylates (Figures 6 and 7 and Table 3). We first examined the polymerization of MMA with the same low-mass alkyl iodide (PE–I) and Ge and Sn deactivators (GeI_4, GeI_2, SnI_4, and SnI_2) as in the St system. However, the initiation of PE–I was slow, and the polydispersity was not controlled. To increase the initiation rate, we used a tertiary alkyl iodide 2-cyanopropyl iodide (CP–I) instead of the secondary one PE–I, and to increase the activation rate, we used *p*-tolyl germanium triiodide (p-CH_3–C_6H_4–GeI_3) ($TGeI_3$) as a deactivator (filled circles in Figures 6 and 7 and entries 1 and 2 in Table 3). In this case, low polydispersity (∼1.2) was achieved with a small amount of the catalyst (5 mM) at 70 °C, in which azobis(isobutyronitrile) (AIBN) was used as a conventional radical initiator. Without
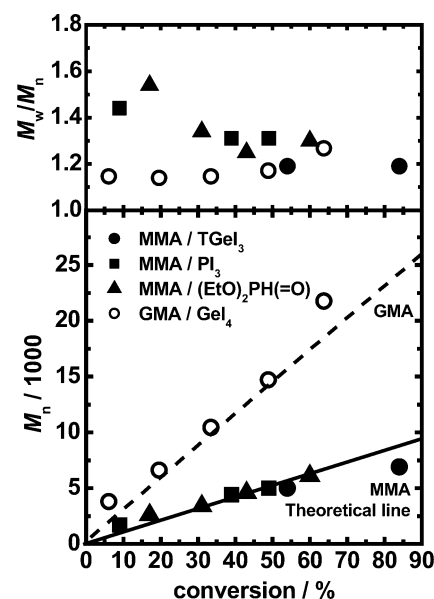
$TGeI_3$ (entry 8), polydispersity was not controlled. On the other hand, PI_3 was applicable to MMA as well as to St, but CP–I was used, instead of PE–I, as an alkyl iodide (squares and entries 3 and 4). PI_3 gave results as good as those for $TGeI_3$ with respect to the polydispersity control (e.g., PDI = 1.25 (PI_3) and 1.28 ($TGeI_3$) for M_n ∼15 000−18 000). The hydride precursor $(EtO)_2PH(=O)$ was also successfully adopted to the MMA polymerization, with BPO as a peroxide at 70 °C (triangles and entries 5−7). Notably, the temperature for the MMA polymerization was 70 °C for all examined catalysts, which is lower than those for St polymerization with the Ge (80 °C) and phosphorus (100 °C) catalysts (Tables 1 and 2).

We then examined two functional methacrylates, i.e., GMA (with an epoxide) and HEMA (with a hydroxy group) with Ge deactivators (with CP–I at 70 °C, as in the MMA system). For GMA (open circles and entry 9), we used GeI_4 as a deactivator. The M_n well agreed with $M_{n,theo}$, and PDI was about 1.2 from an early stage to a later stage of polymerization, suggesting that the high reactivity of the catalyst was retained. For HEMA (entry 10), $TGeI_3$ was used. Although a relatively large amount (20 mM) of $TGeI_3$ was required, a low-polydispersity polymer was successfully obtained. (The M_n and M_w for GMA and HEMA were determined by gel permeation chromatography equipped with a multiangle laser light-scattering detector (GPC-MALLS).)

Thus, with Ge, Sn, and phosphorus catalysts (deactivators

Table 3. Polymerizations of Methacrylates with Ge and Phosphorus Iodides and Hydride ($[M]_0 = 8$ M (8000 mM))

entry	monomer	XA	I	$[CP-I]_0/[I]_0/[XA]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n^a ($M_{n,theo}$)	PDI^a
1	MMA	TGeI$_3$	AIBN	80/20/5	70	6	84	6900 (8400)	1.19
2		TGeI$_3$	AIBN	20/20/5	70	8	60	18 000 (24 000)	1.28
3		PI$_3$	AIBN	80/20/2	70	6	49	5000 (4900)	1.31
4		PI$_3$	AIBN	40/20/5	70	6	63	15 000 (13 000)	1.25
5		(EtO)$_2$PH(=O)^b	BPO	80/40/20	70	3	43	4600 (4300)	1.25
6		(EtO)$_2$PH(=O)^b	BPO	80/40/10	70	3	60	6900 (6000)	1.23
7		(EtO)$_2$PH(=O)^b	BPO	40/20/10	70	6	74	13 000 (15 000)	1.29
8		none	AIBN	40/20/0	70	4	99	30 300 (20 000)	1.90
9	GMA	GeI$_4$	BPO	40/20/5	70	0.67	20	6600 (6300)	1.14
						1.67	64	21 000 (18 000)	1.27
10	HEMA^c	TGeI$_3$	AIBN	40/20/20	70	2.5	85	10 000 (9700)	1.35

^{a} M_n and M_w were determined by GPC-MALLS (multiangle laser light-scattering) for GMA and HEMA. ^{b}Hydride (precursor). ^{c}In ethanol (50 vol %), hence $[HEMA]_0 = 4$ M (4000 mM).

and precursors), molecular weight and its distribution were well controlled for St, MMA, GMA, and HEMA.

2.2. Kinetic Studies for the St/GeI$_4$ System. We made kinetic studies on the activation process and polymerization rate R_p for St polymerization with a polystyrene iodide (PSt−I) (M_n = 2000; PDI = 1.20), BPO, and GeI$_4$ at 80 °C. We used the polymeric adduct PSt−I as a starting alkyl iodide to focus on the kinetics of the polymer region.

2.2.1. Reversible Activation. As mentioned, in the presence of GeI$_4$ (deactivator XA in Scheme 1d), PSt−I can be activated via the RT process with GeI$_3{}^{\bullet}$ (activator radical A$^{\bullet}$: rate constant k_a) and the degenerative chain transfer process (DT, Scheme 1b: rate constant k_{ex}). Thus, the pseudo-first-order activation rate constant k_{act} (Scheme 1a) is generally given by

$$k_{act} = k_{ex}[P^{\bullet}] + k_a[A^{\bullet}] \qquad (1)$$

In the quasi-equilibrium of the RT process (Scheme 1d), eq 1 takes the form

$$k_{act} = k_{ex}[P^{\bullet}] + k_{da}[P^{\bullet}]\left(\frac{[XA]}{[P-X]}\right) \qquad (2)$$

where k_{da} is the deactivation rate constant with XA (Scheme 1d). Hence, k_{act} increases with the ratio $[XA]/[P-X]$.

We determined k_{act} in the polymerizations of St with various concentrations of GeI$_4$ (0−0.4 mM) and fixed concentrations of PSt−I (10 mM) and BPO (1 mM) by the polydispersity analysis method[3,20] (Supporting Information). In these polymerizations, due to the fixed value of $[BPO]_0$, $[P^{\bullet}]$ was nearly the same for all cases (the retardation in R_p with GeI$_4$ was insignificant for the examined low values of $[GeI_4]_0$ (see below)). As expected from eq 2, k_{act} linearly increased with the $[GeI_4]_0/[PSt-I]_0$ ratio in the examined range (0−0.04) of the ratio (Figure 8), suggesting that for a typical case with $[GeI_4]/[PSt-I] = 5$ mM/80 mM = 0.0625 (entry 1 in Table 1), k_{act} would be about 12 times larger than that 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.

From the slope of the straight line in the plot (Figure 8), k_{da} was determined to be 6.0×10^5 M^{-1} s^{-1}. This is large, nearly
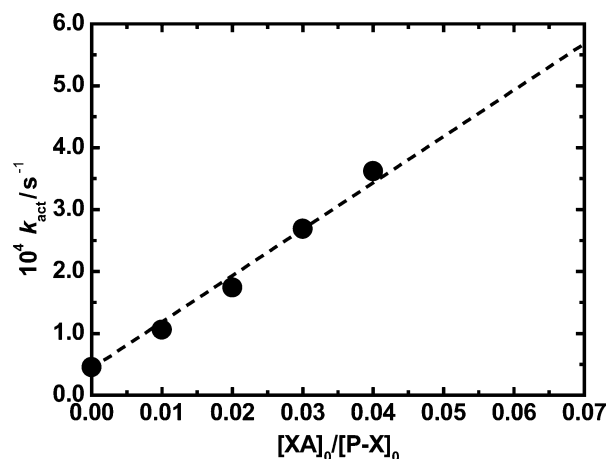
Figure 8. Plot of k_{act} vs $[XA]_0/[P-X]_0$ for the St/PSt−I/BPO/(GeI$_4$) system (80 °C): $[PSt-I]_0 = 10$ mM; $[BPO]_0 = 1$ mM; $[GeI_4]_0 = 0-0.4$ mM.

as large as the deactivation rate constant (5.7×10^5 M^{-1} s^{-1} (120 °C))[21] for a PSt radical with *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN), which is known to be an excellent deactivator for LRP. As shown below, the equilibrium constant K ($=k_a/k_{da}$) for this system was estimated to be about 10^0. It follows that, for a typical condition of conventional polymerization of $[P-I] = 10^{-2}$ M, $[P^{\bullet}] = 10^{-8}$ M, and $[GeI_4] = 10^{-3}$ M, $[GeI_3{}^{\bullet}]$ is 10^{-9} M (nanomolar). With the K and k_{da}, 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 nanomolar level concentration of the activator. Thus, these k_{da} and k_a values confirm a high deactivating ability of GeI$_4$ and a high activation ability of the in situ formed radical GeI$_3{}^{\bullet}$.

2.2.2. Polymerization Rate. As mentioned above, in the presence of the catalysts, R_p was somewhat smaller than that in their absence. This is because the Ge, Sn, and phosphorus radicals (A$^{\bullet}$) undergo irreversible cross-termination with P$^{\bullet}$ and irreversible self-termination between A$^{\bullet}$. This mechanism is analogous to the one for the rate retardation in reversible addition−fragmentation chain transfer (RAFT) polymerization.[22,23]

In theory,[23] when a system includes conventional initiation (rate R_i), propagation (rate constant k_p), self-termination of P$^{\bullet}$ (rate constant k_t), cross-termination between P$^{\bullet}$ and A$^{\bullet}$ (rate

(20) Fukuda, T.; Goto, A. *Macromol. Rapid Commun.* **1997**, *18*, 683−688: the factor −2 appearing in eq 4 is a misprint for *C*−2.

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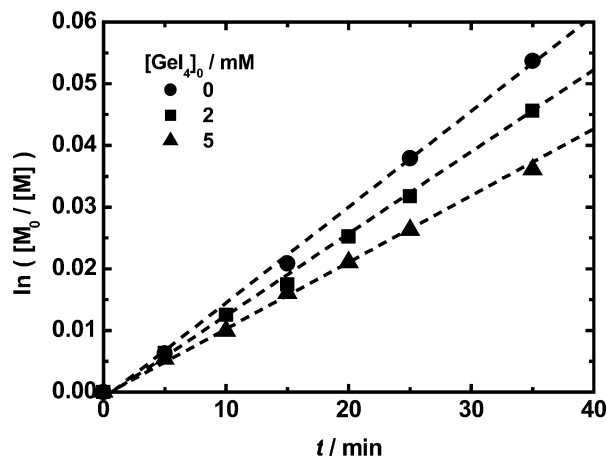
Figure 9. Plot of $\ln([M]_0/[M])$ vs t for the St/PSt−I/BPO/(GeI$_4$) system (80 °C): $[PSt−I]_0 = 20$ mM; $[BPO]_0 = 10$ mM; $[GeI_4]_0$ as indicated in the figure.

Figure 10. Plot of $(R_p/[M])^{-2}$ vs $[XA]_0/[P−X]_0$ for the St/PSt−I/BPO/(GeI$_4$) system (80 °C): $[PSt−I]_0 = 20$ mM; $[BPO]_0 = 10$ mM; $[GeI_4]_0 = 0−5$ mM.

constant k_t'), self-termination of A$^\bullet$ (rate constant k_t''), RT (Scheme 1d), and DT (Scheme 1b) as elementary reactions, the following equations should hold in the stationary state of the radical concentrations $[P^\bullet]$ and $[A^\bullet]$:

$$0 = d[P^\bullet]/dt =$$
$$R_i - k_t[P^\bullet]^2 - k_t'[P^\bullet][A^\bullet] + k_a[P−X][A^\bullet] - k_{da}[P^\bullet][XA] \quad (3)$$

$$0 = d[A^\bullet]/dt =$$
$$- k_t'[P^\bullet][A^\bullet] - k_t''[A^\bullet]^2 - k_a[P−X][A^\bullet] + k_{da}[P^\bullet][XA] \quad (4)$$

The sum of eqs 3 and 4 reads

$$R_i - k_t[P^\bullet]^2 - 2k_t'[P^\bullet][A^\bullet] - k_t''[A^\bullet]^2 = 0 \quad (5)$$

In the quasi-equilibrium of RT ($k_a[P−X][A^\bullet] = k_{da}[P^\bullet][XA]$), R_p ($=k_p[P^\bullet][M]$) is given by

$$R_p = R_{p,0}\left(1 + 2\left(\frac{k_t'}{k_tK}\right)\frac{[XA]}{[P−X]} + \left(\frac{k_t''}{k_tK^2}\right)\frac{[XA]^2}{[P−X]^2}\right)^{-1/2} \quad (6)$$

where $R_{p,0}$ is the R_p without XA ($R_{p,0} = k_p(R_i/k_t)^{1/2}[M]$), and K is the equilibrium constant ($K = k_a/k_{da}$). Equation 6 means that R_p decreases with the ratio $[XA]/[P−X]$. 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 6 takes the form

$$R_p = R_{p,0}\left(1 + 2\left(\frac{k_t'}{k_tK}\right)\frac{[XA]}{[P−X]}\right)^{-1/2} \quad (7)$$

This last term in eq 6 may also be neglected, when the self-termination of A$^\bullet$ is reversible and is not a real termination.

We examined the R_p for the St/GeI$_4$ system with various amounts of GeI$_4$ (0−5 mM) and fixed amounts of PSt−I (20 mM) and BPO (10 mM) at 80 °C at an early stage of polymerization. The use of the polymer adduct PSt−I instead of the low-mass adduct PE−I minimizes the possible effect of chain length dependence of k_t on R_p. As shown in Figure 9, R_p (hence $[P^\bullet]$) was stationary in the studied range of time in all cases and decreased with $[XA]_0/[P−X]_0$, as the theory demands. Figure 10 shows the plot of R_p^{-2} vs $[XA]_0/[P−X]_0$. The plot was linear, confirming the validity of eq 7 in the studied range of the ratio (0−0.25). Thus, when $[XA]_0/[P−X]_0$ is relatively small (∼0.1), as in entries 1−3 in Table 1, the cross-termination is the main cause for the retardation. The cross-termination results in a loss of GeI$_4$, but it is a minor one at an early stage of polymerization. Moreover, the cross-termination products such as PSt−GeI$_3$ (by recombination) are Ge(IV) iodides and would still work as XA, contributing to polydispersity control. From the slope of the line (Figure 10), we had $k_t'/(k_tK) = 3$. 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},[24] at the studied low conversions. Thus, K is estimated to be on the order of 10^0.

3. Conclusions

RTCP was developed as a novel class of LRPs. With Ge, Sn, and phosphorus catalysts, the polymer molecular weights and its distribution were well controlled in the polymerizations of St, MMA, GMA, and HEMA. The k_{act} for the St/GeI$_4$ system was large enough, even with a small amount of GeI$_4$, explaining why the system provides low-polydispersity polymers from an early stage of polymerization. The rate retardation observed for the St/GeI$_4$ system was due to the cross-termination between P$^\bullet$ with GeI$_3$$^\bullet$. Attractive features of the Ge, Sn, and phosphorus catalysts include their *high reactivity* hence small amounts being required under a mild temperature,[25] *high solubility* in organic media without ligands, *insensitivity to air* hence sample preparation being allowed in the air, and *minor color and smell*. The

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Ge and phosphorus catalysts may also be attractive for their *low toxicity*. The phosphorus catalysts, particularly the hydrides, may also be attractive for their *low cost*. Perhaps, the hydrides are the least expensive LRP catalysts/mediators developed so far. RTCP would be applicable to a wider variety of monomers, and a wider variety of compounds with various central elements would be used as catalysts. These are currently examined in our laboratory.

(25) The catalysts can be removed from polymer by regular procedures (reprecipitation, etc.), although the catalyst covalently attached to polymer via cross-termination is difficult to remove. In any case, the amount of the catalyst used in the polymerization is so low that the residual catalyst may not be a large problem in most practical usage.

Supporting Information Available: Experimental section, ^{1}H NMR spectra for the reaction of GeI_2 and PE$-$I, ^{31}P NMR spectra for the reaction of $(BuO)_2PH(=O)$ and PE$-$I, and the procedure of the determination of k_{act}. The material is available free of charge via the Internet at http://pubs.acs.org.

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