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Germanium- and Tin-Catalyzed Living Radical Polymerizations of Styrene and Methacrylates

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Summary: Ge and Sn (non-transition-metal) catalyzed living radical polymerizations were developed. Low-polydispersity ($M_w/M_n \sim 1.1$–1.3) polystyrenes, poly(methyl methacrylate)s, poly(glycidyl methacrylate)s, and poly(2-hydroxyethyl methacrylate) with predicted molecular weights were obtained with a 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, to explain 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 proved to be mainly due to the cross-termination between the propagating radical with $GeI_3^\bullet$. Attractive features of the Ge and Sn catalysts include their *high reactivity* hence small amounts (1–5 mM) being required under a mild condition (at 60–80 °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 Ge catalysts may also be attractive for their *low toxicity*.

Keywords: germanium; iodide; living radical polymerization; non-transition metal; tin

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 $P^\bullet$ (Scheme 1a). 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, in which P-X (X = I) is activated by $P^\bullet$ (degenerative or exchange chain transfer: Scheme 1b).[4] However, due to a low exchange frequency of iodine, the control in polydispersity is limited, in most cases. 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 is an activator, and XA is a deactivator).[5] The addition of the catalyst allows a high activation frequency, yielding low-polydispersity polymers.

We recently developed a new and robust LRP.[6] We added a germanium or tin compound such as GeI_4 to the iodide-mediated polymerization. GeI_4 works as a deactivator of $P^\bullet$, in situ producing $GeI_3^\bullet$ (Scheme 2). $GeI_3^\bullet$ radical works as an activator for polymer-iodide P-I, producing $P^\bullet$ and GeI_4. This cycle allows a frequent activation of P-I. This is the first living radical polymerization using a non-transition metal as a catalyst.

In this paper, we will briefly summarize our studies on this new LRP, demonstrating its controllability in molecular weight and molecular weight distribution for styrene (St) and methacrylates and kinetic features regarding the activation process and the polymerization rate for the St/GeI_4 system.

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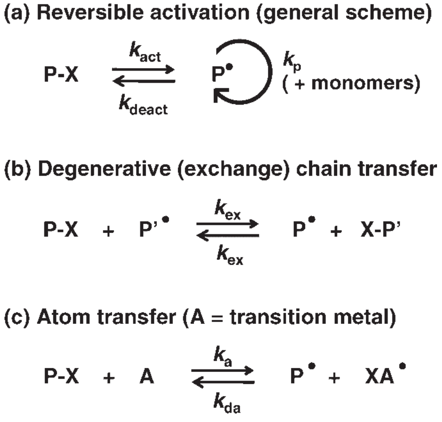


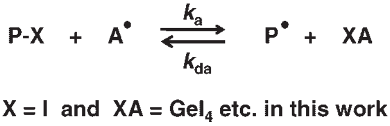
Scheme 1.
Reversible activation processes. (a) General Scheme, (b) degenerative (exchange) chain transfer, and (c) atom transfer.

Control in Molecular Weight and Its Distribution

Styrene

We 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 $GeI_3^\bullet$ (and P-I). If $GeI_3^\bullet$ effectively abstracts I from PE-I (or P-I) to produce $PE^\bullet$ (or $P^\bullet$), a useful sequence of activation and deactivation will be completed.

Table 1 (entries 1-4) and Figure 1 (filled squares) show the results. As shown in Figure 1, M_n linearly increased with conversion and agreed with the theoretical value $M_{n,theo}$. 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 (2–5 mM) of GeI_4 required to control the polydispersity suggests a high reactivity of this catalyst.



Scheme 2.
Catalytic Activation process with the Ge and Sn catalyst.

The activation of P-I occurs not only by the catalytic process (Scheme 2) 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 11: iodide-mediated polymerization) only gave a PDI as large as 1.55 for 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 the catalytic activation plays a main role in the GeI_4 system, with a small contribution of degenerative chain transfer.

Besides GeI_4, we also used GeI_2, SnI_4, and SnI_2 as deactivators (entries 5–10 in Table 1 and Figure 1). In all cases, low polydispersity was attained with a small amount (1–5 mM) of the catalyst. The Sn catalysts (entries 7–10) exhibited good polydispersity control at 60 °C, as the Ge catalysts (entries 1–6) did at 80 °C. This suggests that the Sn catalysts are even more active. Both GeI_2 and SnI_2 were effective catalysts, but the results with them (entries 5, 6, and 10 and Figure 1) were not as good as those with GeI_4 and SnI_4 (entries 1–4 and 7–9 and Figure 1).

Ge and Sn halides are Lewis acids. $SnCl_4$, which is a strong Lewis acid, can abstract a halogen anion from an alkyl halide to give the alkyl carbocation and is widely used for living cationic polymerizations.[7] On the other hand, Ge and Sn iodides (used in this work) are relatively weak Lewis acids. The tacticities of the produced polymers and the complete inhibition of the polymerization in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) confirmed that the polymerizations in this work proceeded in a radical mechanism.

Methacrylates

We examined the polymerization of methyl methacrylate (MMA) with the same low-mass alkyl iodide (PE-I) and catalysts

Table 1.
Polymerization of St with PE-I in the Presence of Ge and Sn Iodides.

entry	XA	$[PE\text{-}I]_0/[I^a]_0/[XA]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$)^b	PDI
1	GeI_4	80/20/5	80	4	26	2500 (2600)	1.19
				7	37	3500 (3700)	1.16
				21	47	4300 (4700)	1.16
2		80/20/2	80	7	47	4600 (4700)	1.16
3		80/40/2	80	7	85	8200 (8500)	1.24
4		25/10/5	80	21	40	11400 (13300)	1.29
5	GeI_2	80/20/5	80	21	59	5700 (5900)	1.15
6		80/40/5	80	25	85	6800 (8500)	1.16
7	SnI_4	80/20/5	60	21	36	3600 (3600)	1.13
8		80/40/5		27	72	6500 (7200)	1.21
9		8/4/1	60	21	24	22000 (24000)	1.18
10	SnI_2	80/20/5	60	21	50	4800 (5000)	1.23
11	none	80/20/0	80	4	41	4200 (4100)	1.55

[a] BPO for entries 1–6 and 11 and AIBN for entries 7–10.
[b] Theoretical M_n calculated with [St], [PE-I], and conversion.

(GeI_4, GeI_2, SnI_4, and SnI_2) as in the styrene 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) ($TGeI_3$)[8] as a catalyst. In this case (entries 1 and 2 in Table 2), low-polydispersity polymers were successfully obtained 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 the catalyst (entry 3 in Table 2), polydispersity was not controlled.

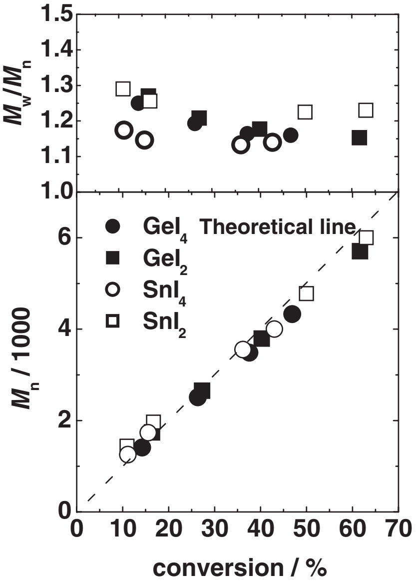


Figure 1.
Plot of M_n and PDI vs conversion for the Ge and Sn catalyzed polymerizations of St for entries1, 5, 7, and 10 in Table 1.

We also examined two functional methacrylates (Table 2), i.e., glycidyl methacrylate (GMA) with an epoxide and 2-hydroxyethyl methacrylate (HEMA) with a hydroxy group. For GMA (entry 4), we used GeI_4 as a catalyst and BPO as a conventional radical initiator, with other conditions set the same as those for MMA. 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 retained in GMA. For HEMA (entry 5), $TGeI_3$ and AIBN were used, as in the MMA system. Although a relatively large amount (20 mM) of the catalyst was required, a low-polydispersity polymer was successfully obtained.

Kinetic Studies for the St/GeI_4 System

We made kinetic studies on the activation process and polymerization rate R_p for the St polymerization with a polystyrene iodide (PSt-I) ($M_n = 2000$; PDI = 1.20), BPO, and

Table 2.
Polymerization of Methacrylates with CP-I in the Presence of Ge Iodides.

entry	monomer	XA	$[CP\text{-}I]_0/[I^a]_0/[XA]_0$ (mM)	T (°C)	t(h)	conv (%)	M_n ($M_{n,theo}$)[b]	PDI
1	MMA	$TGeI_3$	80/20/5	70	6	84	6900 (8400)	1.19
2			20/20/5	70	8	60	18400 (24000)	1.28
3			40/20/0	70	4	99	30300 (20000)	1.90
4	GMA	GeI_4	40/20/5	70	0.67	20	6600 (6300)	1.14
					1.67	64	21000 (18000)	1.27
5	HEMA[c]	$TGeI_3$	80/20/20	70	2.5	85	10000 (9700)	1.35

[a] AIBN for entries 1–3 and 5 and BPO for entry 4.
[b] Theoretical M_n calculated with [monomer], [PE-I], and conversion.
[c] In ethanol (50 vol%).

GeI_4 at 80 °C. We used the polymeric adduct PSt-I as a starting alkyl iodide to focus on the kinetics of polymer region.

Reversible Activation

As mentioned, in the presence of GeI_4 (deactivator XA), PSt-I can be activated by degenerative chain transfer (Scheme 1b: rate constant k_{ex}) and the catalytic process with $GeI_3^\bullet$ (activator $A^\bullet$) (Scheme 2: rate constant k_a.). Thus, the pseudo-first-order activation rate constant k_{act} is given by

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

In the quasi-equilibrium for the catalytic activation-deactivation process (Scheme 2), Eq. 1 takes the form

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

where k_{da} is the deactivation rate constant with XA (Scheme 2). The equation means that k_{act} increases with the ratio [XA]/[P-X].

By the gel permeation chromatography (GPC) method,[3,9] we determined k_{act} for the PSt-I/GeI_4 system with various $[GeI_4]_0/[PSt\text{-}I]_0$ ratios and a (nearly) fixed $[P^\bullet]$. As expected from Eq. 2, k_{act} linearly increased with this ratio in the examined range of 0–0.04 (data not shown), suggesting that for the typical case with $[GeI_4]/[PSt\text{-}I] = 5mM/80mM$, k_{act} would be about 12 times larger than in the absence of the catalyst GeI_4. This explains why low-polydispersity polymers were obtained from an early stage of polymerization for the GeI_4 system.

Polymerization Rate

In the presence of Ge and Sn iodides, R_p was somewhat smaller than in their absence (Tables 1 and 2). This is because Ge and Sn radicals ($A^\bullet$) undergo irreversible cross-termination with $P^\bullet$ (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 reversible addition-fragmentation chain transfer (RAFT) polymerization.[10,11]

In the quasi-equilibrium for the catalytic process (Scheme 2) and the stationary-state of radical concentrations ($d[P^\bullet]/dt = d[A^\bullet]/dt = 0$), R_p is theoretically given by[11]

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

where $R_{p,0}$ is the R_p without XA, K is the activation-deactivation equilibrium constant ($K = k_a/k_{da}$ (Scheme 2)), and k_t is the self-termination rate constant for $P^\bullet$. This means that R_p decreases with the ratio [XA]/[P-X]. At a small 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

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

The last term in Eq. 3 is also neglected, when the self-termination of $A^\bullet$ is reversible and is not a real termination.

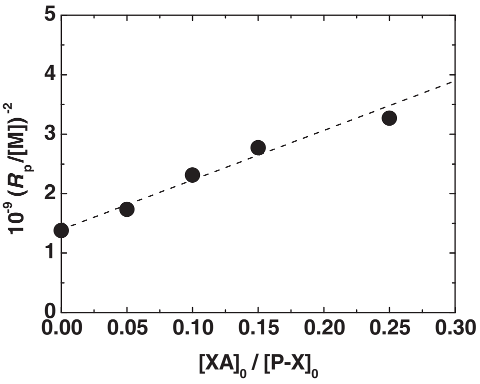


Figure 2.
Plot of $(R_p/[M])^{-2}$ vs $[XA]_0/[P\text{-}X]_0$ for the St/PSt-I/BPO/(GeI$_4$) system (80 °C): $[PSt\text{-}I]_0 = 20$ mM; $[BPO]_0 = 10$ mM; $[GeI_4]_0 = 0$–5 mM. [M] is the monomer concentration.

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. We studied an early stage of polymerization (for ≤35 min and at the conversion of ≤7%). 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. The R_p (hence $[P^\bullet]$) was stationary in the studied range of time in all cases, as the theory demands, and decreased with $[XA]_0/[P\text{-}X]_0$. Figure 2 shows the plot of R_p^{-2} vs $[XA]_0/[P\text{-}X]_0$. The plot was linear, confirming the validity of Eq. 4 in the studied range (0–0.25) of the ratio. Thus, for the GeI$_4$ system, at a relatively small ratio, as in entries 1–4 in Table 1 ($[XA]_0/[P\text{-}X]_0 \sim 0.1$), 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 2), we had $k_t'/(k_t K) = 3$.

Conclusions

The Ge and Sn (non-transition-metal) catalyzed LRPs were developed. The molecular weight and its distribution were well controlled for the St, MMA, GMA, and HEMA polymerizations. The k_{act} for the St/GeI$_4$ system was large enough, even with a small amount of GeI$_4$, which explained why low-polydispersity PSts are obtained 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 and Sn catalysts include their *high reactivity* hence small amounts being required under a mild temperature, *high solubility* in organic media without ligands, *insensitivity to air* hence sample preparation being allowed in the air, and *minor color and smell*. The Ge catalysts may also be attractive for their *low toxicity*.

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