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Reversible Chain Transfer Catalyzed Polymerizations (RTCPs) of Styrene and Methyl Methacrylate with Phosphorus Catalysts

Atsushi Goto, Norihiro Hirai, Yoshinobu Tsujii, Takeshi Fukuda**

Summary: Phosphorus compounds were employed as catalysts in Reversible Chain Transfer Catalyzed Polymerization (RTCP), a novel class of living radical polymerization (LRP) which we had recently developed. Low-polydispersity polystyrene and poly(methyl methacrylate) with predicted molecular weights were obtained with a fairly high conversion in a fairly short time. These catalysts are particularly featured by their *high reactivity* hence small amounts being required, *low toxicity*, and *low cost*. Some phosphorus catalysts used in this work are among the least expensive catalysts/mediators of LRP developed so far.

Keywords: iodide; living radical polymerisation; phosphorus; reversible chain transfer catalyzed polymerisation

Introduction

Living radical polymerization (LRP) has attracted much attention as a useful tool to synthesize well-defined 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 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 Polymer-X (X = I) is activated by Polymer$^\bullet$ (degenerative or exchange chain transfer: Scheme 1b).[4] However, due to a low exchange frequency of iodine, the controllability of polydispersity in this system is limited. The other is atom transfer radical polymerization (ATRP), in which Polymer-X (X = Cl, Br) is activated by the catalytic work of a transition metal complex (Scheme 1c, where A is an activator, and XA$^\bullet$ is a deactivator).[5] The addition of the catalyst allows a high frequency of activation-deactivation cycle, yielding low-polydispersity polymers.

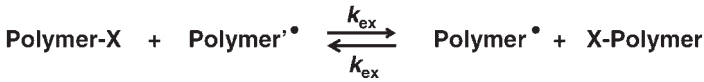
We recently developed a new and robust family of LRP. We added a germanium (Ge) or tin (Sn) compound, e.g., GeI_4, to the iodide-mediated polymerization.[6–8] GeI_4 works as a deactivator (XA) of Polymer$^\bullet$, in situ producing $GeI_3^\bullet$ (Scheme 1d). $GeI_3^\bullet$ works as an activator (A$^\bullet$) of a polymer-iodide (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) process in which GeI_4 works as a chain transfer agent. Polymer-X is catalytically activated via a RT process. This is a new reversible activation mechanism in LRP, and we have proposed to term the related polymerization the RT-catalyzed polymerization (RTCP).[8] In this paper, the chain transfer agents (the Ge, Sn, and phosphorus compounds (see below)) will be called RT catalysts or simply catalysts. The RTCP is also the first LRP using compounds of typical elements (non-transition metals) as effective catalysts.

Very recently, we extended the catalyst from Ge and Sn compounds to phosphorus

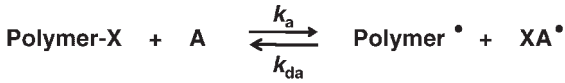
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
E-mail: fukuda@scl.kyoto-u.ac.jp

(a) Reversible activation (general scheme)

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

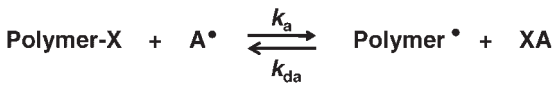


(c) Atom transfer (AT)



(A = transition metal complex)

(d) Reversible chain transfer (RT)



(A = typical element compound)

(X = I and XA = GeI_4, PI_3 etc.)

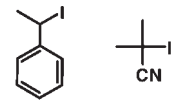
Scheme 1.
Reversible activation processes.

compounds.[8] In this proceeding, we will briefly summarize the studies on the phosphorus catalysts, demonstrating the controllability in molecular weight and molecular weight distribution for the polymerizations of styrene (St) and methyl methacrylate (MMA).

Styrene (St)

We examined the polymerization of St at 100 °C, using 1-phenylethyl iodide (PE-I: Figure 1) as a low-mass alkyl halide initiator, PI_3 (phosphorus triiodide) as a deactivator, and dicumyl peroxide (DCP) as a conventional radical initiator. In this polymerization, Polymer•, which is originally supplied by DCP, is supposed to react with PI_3, in situ producing the activator radical $PI_2^•$ (and Polymer-I). If $PI_2^•$ effectively abstracts I from PE-I (or Polymer-I) to produce PE• (or Polymer•), cycles of activation and deactivation (RT) will get started.

Table 1 (entries 1–5) and Figure 2 (filled circles) show the results. As shown in the figure, the number-average molecular weight M_n linearly increased with conversion and well agreed with the theoretical value $M_{n,theo}$. 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 (0.5-2 mM) of PI_3 required to control the polydispersity



(PE-I) (CP-I)

Figure 1.
Structures of PE-I and CP-I.

Table 1.
Polymerizations of St with PE-I in the Presence of Phosphorus Catalysts.

Entry	Catalyst	I	$[PE\text{-}I]_o/[I]_o/[catalyst]_o$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$)[a)]	PDI
1	PI_3	DCP	80/160/2	100	23	68	6200 (6800)	1.17
2	PI_3	DCP	80/80/2	100	23	46	4400 (4600)	1.18
3	PI_3	DCP	80/80/1	100	10	45	4000 (4500)	1.16
4	PI_3	DCP	80/80/0.5	100	23	52	5100 (5200)	1.25
5	PI_3	DCP	40/20/2	100	23	72	10000 (14000)	1.29
6	(EtO)PhPH(=O)	DCP	80/80/30	100	23	69	5200 (6900)	1.19
7	$(BuO)_2PH(=O)$	DCP	80/80/10	100	23	55	4200 (5500)	1.24
8	$(BuO)_2PH(=O)$	VR110	80/80/10	100	23	37	3200 (3700)	1.34

[a)] Theoretical M_n calculated with [St], [PE-I], and conversion.

(Table 1) suggests a high reactivity of PI_3. Notably, these concentrations are even lower than those (2–5 mM) needed for the previously studied highly effective Ge and Sn catalysts (GeI_4, GeI_2, SnI_4, and SnI_2), although the temperature in the PI_3 system (100 °C) is higher than those in the Ge (80 °C) and Sn (60 °C) systems.[6,7] For the PI_3 system (Table 1), we used relatively large amounts (80-160 mM) of DCP (conventional radical initiator) due to its slow decomposition (the half lifetime is ca. 80 h). The polymerization rate slightly decreased with an increase of the PI_3 concentration (entries 2 and 4). This is due to the cross-termination between Polymer$^\bullet$ and the activator radical $PI_2^\bullet$ (and the self-termination of $PI_2^\bullet$), as previously observed for the St/GeI_4 (catalyst) system.[6,8]

In RTCP, instead of adding a deactivator (such as PI_3), a precursor of a deactivator or an activator radical may be used as a starting compound. This concept is new and has not been attempted for the Ge and Sn compounds. For example, we used 5-valent phosphorus hydrides $R_2PH(=O)$ as starting compounds (precursors) to in situ produce an activator radical $R_2P^\bullet(=O)$ ($A^\bullet$ in Scheme 1d) and/or a deactivator $R_2PI(=O)$ (XA in Scheme 1d) in the presence of DCP and PE-I at 100 °C. DCP (peroxide) gives an oxygen-centered radical, which is known to abstract a hydrogen from $R_2PH(=O)$ to produce an

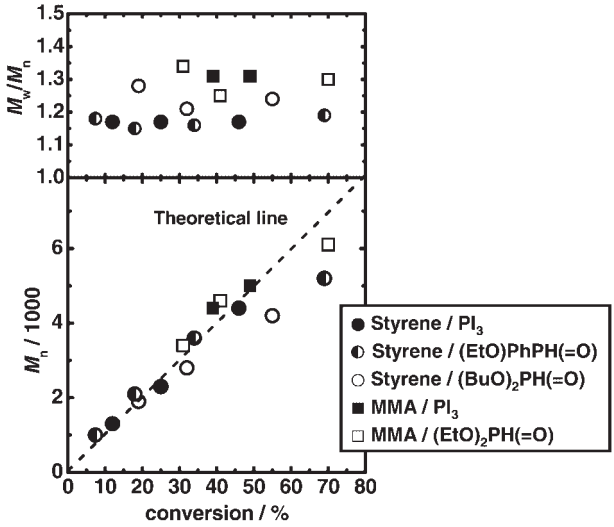


Figure 2.
Plot of M_n and PDI vs conversion for the polymerizations of St and MMA with the phosphorus catalysts for entries 2, 6, and 7 in Table 1 (St) and entries 2 and 4 in Table 2 (MMA).

Scheme 2.
Hydrogen abstraction from a phosphorus hydride by an oxygen-centered radical.

activator radical $R_2P^{\bullet}(=O)$ (Scheme 2).[9] PE-I (alkyl iodide) can be iodinating agents of $R_2PH(=O)$ to give a deactivator $R_2PI(=O)$ via a non-radical process.[10] In the polymerization, both processes (the productions of activator and deactivator) may be involved, and the relative contributions of the two processes would depend on the R group of the phosphorus hydride $R_2PH(=O)$.

We examined the St polymerizations with (EtO)PhPH(=O) (with a phenyl group) and $(BuO)_2PH(=O)$ (with no phenyl group) as precursors (Figure 2 (half-filled and open circles, respectively) and Table 1 (entries 6 and 7, respectively)). The two precursors gave similarly successful results. With 10–30 mM of the precursors, low polydispersity polymers (PDI $\leq$ 1.2) were obtained from an early stage of polymerization, and PDI was kept at a low level ($\sim$1.2) throughout the polymerization. Instead of DCP (peroxide), we also used an azo-initiator 2,2′-azobis(2,4,4-trimethylpentane) (VR110) as a conventional radical initiator for the $(BuO)_2PH(=O)$ system (entry 8). 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 7 and 8). This suggests that the production of the activator radical by DCP (peroxide) is important in this method. Thus, the proposed method was confirmed to work successfully with the two phosphorus hydrides, and the use of a peroxide significantly improved the polydispersity control.

Methyl Methacrylate (MMA)

We adopted the phosphorus catalysts to the MMA polymerization at 70 °C, in which we used a tertiary alkyl iodide 2-cyanopropyl iodide (CP-I: Figure 1) instead of the secondary one PE-I to achieve a sufficiently fast activation (initiation) from the alkyl iodide. With PI_3 as a deactivator and azobis(isobutyronitrile) (AIBN) as a conventional radical initiator (Figure 2 (filled squares) and Table 2 (entries 1–3)), low polydispersity ($\sim$1.2) was achieved with a small amount of the catalyst (2–5 mM). The results are as good as those with *p*-tolyl germanium triiodide (p-CH_3-C_6H_4-GeI_3) ($TGeI_3$) (at the same temperature (70 °C)),[7] which had been the only effective catalyst for MMA. The hydride precursor $(EtO)_2PH(=O)$ was also successfully adopted to the MMA polymerization, with benzoyl peroxide (BPO) as a peroxide (Figure 2 (open squares) and Table 2 (entries 4–6)). Notably, for all examined phosphorus catalysts, the temperature for the MMA system was 70 °C, which is lower than that (100 °C) for the St system.

Experimental Part

Materials

St (99%, Nacalai Tesque, Japan), MMA (99%, Nacalai), BPO (75% (25% water), Nacalai), DCP (98%, Nacalai), and AIBN (98%, Wako Pure Chemical, Japan) were purified by distillation or recrystallization

Table 2.
Polymerizations of MMA with CP-I in the Presence of Phosphorus Catalysts.

Entry	Catalyst	I	$[CP\text{-}I]_o/[I]_o/[catalyst]_o$ (mM)	T (°C)	t (h)	conv (%)	M_n ($M_{n,theo}$)[a)]	PDI
1	PI_3	AIBN	160/20/2.5	70	2.5	60	3800 (3000)	1.13
2	PI_3	AIBN	80/20/2	70	6	49	5000 (4900)	1.31
3	PI_3	AIBN	40/20/5	70	6	63	15000 (13000)	1.25
4	$(EtO)_2PH(=O)$	BPO	80/40/20	70	3	41	4600 (4100)	1.25
5	$(EtO)_2PH(=O)$	BPO	80/40/10	70	3	60	6900 (6000)	1.23
6	$(EtO)_2PH(=O)$	BPO	40/20/10	70	6	74	13000 (15000)	1.29

[a)] Theoretical M_n calculated with [MMA], [CP-I], and conversion.

from methanol. PE-I and CP-I were prepared according to Matyjaszewski[11] and Balczewski,[12] respectively. PI_3 (99%, Aldrich) was purified through an alumina column and stored under argon (PI_3 is (weakly) moisture-sensitive). VR-110 (99.9%, Wako), $(EtO)_2PH(=O)$ (98%, Aldrich), $(BuO)_2PH(=O)$ (95%, Tokyo Kasei, Japan), and (EtO)PhP(=O) (94%, Aldrich) were used as received.

Gel Permeation Chromatography (GPC)

The GPC analysis was made 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 μm; 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 made with a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in THF. The column system was calibrated with standard polystyrenes and poly(methyl methacrylate)s.

Polymerization

In a typical run, a mixture of St (3 mL), PE-I, BPO, and PI_3 in a Schlenk flask was heated at 100 °C under 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.

Conclusions

Phosphorus compounds were successfully used as catalysts for RTCP, well controlling the polymer molecular weight and its distribution for St and MMA. Attractive features of the phosphorus catalysts include their *high reactivity* hence small amounts being required, *high solubility* in organic media without ligands, *insensitivity to oxygen*, and *minor color and smell*, like the Ge and Sn catalysts. The phosphorus catalysts may also be attractive for their *low toxicity*, like the Ge catalysts, and their *low cost*, lower than those of the Ge and Sn catalysts. Perhaps, the phosphorus hydrides (precursor catalysts) are the least expensive LRP catalysts/mediators developed so far.

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