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Living Radical Polymerization with Nitrogen Catalyst: Reversible Chain Transfer Catalyzed Polymerization with *N*-Iodosuccinimide

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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$^\bullet$):

$$\text{Polymer}-\text{X} \rightleftarrows \text{Polymer}^\bullet \quad \text{(general scheme)} \qquad (1a)$$

A sufficiently large number of activation−deactivation cycles is a requisite for good control of chain length distribution.[2] Iodide-mediated polymerization using iodine as a capping agent X 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$^\bullet$).[3] In this polymerization, a polymer−iodide (Polymer−I) (dormant species) is activated by Polymer$^\bullet$ (degenerative or exchange chain transfer (DT)):[3,4]

$$\text{Polymer}-\text{I} + \text{Polymer}'^\bullet \rightleftarrows \text{Polymer}^\bullet + \text{I}-\text{Polymer} \quad \text{(DT)} \qquad (1b)$$

However, due to a low exchange frequency of iodine, the control of polydispersity is limited.

We recently developed a new family of LRP,[5−7] in which we added a Ge (germanium),[5,6] Sn (tin),[5,6] or P (phosphorus)[6,7] compound to the iodide-mediated polymerization:

$$\text{Polymer}-\text{I} + \text{A}^\bullet \rightleftarrows \text{Polymer}^\bullet + \text{I}-\text{A} \quad (\text{I}-\text{A} = \text{GeI}_4, \text{NIS, etc.}) \quad \text{(RT)} \qquad (1c)$$

For example, the added GeI_4 works as a deactivator (I−A) of Polymer$^\bullet$, in situ producing $GeI_3^\bullet$. $GeI_3^\bullet$ 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).[6] In this paper, the chain transfer agents (Sn, Ge, P, and N (nitrogen) compounds (see below)) will be called RT catalysts or simply catalysts. Attractive features of the Sn, Ge, and P catalysts include their (1) high reactivity (a small amount being required), (2) high solubility in organic media without ligands, (3) insensitivity to air, and (4) minor color and smell. The Ge and P catalysts may also be attractive for their (5) low toxicity. Thus, while the addition of the catalyst dramatically improves the polydispersity control, it causes little practical problems, retaining the robustness of the iodide-mediated polymerization.

To explore a wider variety of catalysts, we have attempted the elemental extension from Sn, Ge, P to N and found that the common compound *N*-iodosuccinimide (NIS: Table 1) works as a highly efficient catalyst for RTCP. While NIS also retains the mentioned robustness, it exhibits even better polydispersity controllability for methacrylates than the previous catalysts and is tolerant to functional groups, allowing the application to a variety of functional monomers. Thus, NIS can make significant advances in RTCP. Herein, we will report the homopolymerizations and the random and block copolymerizations of styrene (St) and (functional) methacrylates with NIS. Copolymerizations will be reported for the first time for RTCP. The studied monomers include methyl (MMA), 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) and St. In RTCP, instead of adding an isolated low-mass alkyl iodide initiator, the one formed in situ in the polymerization system may also be used. This alternative polymerization method will also be demonstrated.

We examined the polymerization of St at 100 °C, using 1-phenylethyl iodide (PE-I: Table 1) as a low-mass alkyl iodide (initiating dormant species), NIS as a catalyst (deactivator I−A), and dicumyl peroxide (DCP) as a conventional radical initiator. In this polymerization, Polymer$^\bullet$, which is originally supplied

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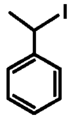
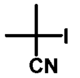
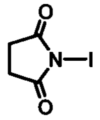
Table 1. Polymerizations of Styrene and Methacrylates with *N*-Iodosuccinimide (NIS)


(PE-I)


(CP-I)


(NIS)

entry	monomer[a] (equiv to [R−I])	R-I[b]	In[c]	$[\text{R-I}]_0/[\text{In}]_0/[\text{NIS}]_0$	T (°C)	t (h)	conv (%)	M_n[d,g] ($M_{n,theo}$[e])	PDI[f,g]
1	St (100)	PE-I	DCP	80/80/5	100	10	56	5200 (5600)	1.16
2	MMA (100)	CP-I	AIBN	80/10/1	80	2	90	7900 (9000)	1.38
3	MMA (100)	CP-I	AIBN	60/10/1[h]	80	2	79	7000 (7900)	1.29
4	GMA (100)	CP-I	AIBN	80/10/1	80	0.75	95	13000 (12200)	1.39
5	GMA (100)	CP-I	AIBN	60/10/1[h]	80	1	71	9700 (9100)	1.29
6	BzMA (100)	CP-I	AIBN	80/10/1	80	0.8	70	13300 (13000)	1.26
7	HEMA (100)	CP-I	AIBN	40/15/10[h]	80	1.5	57	7900 (7400)	1.36
8	PEGMA (100)[i]	CP-I	AIBN	80/10/2	80	1	39	8600 (9600)	1.33
9	MAA/BzMA (15/85)	CP-I	AIBN	80/40/1	80	1	60	6400 (9700)	1.21
10	DMAEMA/BzMA (15/85)	CP-I	AIBN	80/10/1	80	1.25	90	19000 (15600)	1.34
11	HEMA/BzMA (22/78)	CP-I	AIBN	80/20/2	80	1.25	90	18500 (15200)	1.37
12	BzMA (100)	PMMA-I[j]	AIBN	80/10/1	80	1	63	11000 (15000)	1.20
13	MMA (100)	CP-I	AIBN	40/10/1[h]	80	1.5	54	5400 (5400)	1.31
	+ BzMA (100)					+0.5	108	9700 (13600)	1.37
						+1.0	145	13100 (19300)	1.42
14	MMA (100)	I_2	AIBN	40/80/5	80	3	90	8200 (9000)	1.28

[a] St = styrene. MMA = methyl methacrylate. GMA = glycidyl methacrylate. BzMA = benzyl methacrylate. HEMA = 2-hydroxyethyl methacrylate. PEGMA = poly(ethylene glycol) methyl ether methacrylate. MAA = methacrylic acid. DMAEMA = *N*,*N*-dimethylaminoethyl methacrylate. [b] R-I = alkyl iodide. PE-I = 1-phenylethyl iodide (structure shown under the title of this table). CP-I = 2-cyanopropyl iodide (structure shown under the title of this table). PMMA-I = poly(methyl methacrylate) iodide. [c] In conventional radical initiator. DCP = dicumyl peroxide. AIBN = azobis(isobutyronitrile). [d] M_n = number-average molecular weight. [e] $M_{n,theo}$ = theoretical number-average molecular weight. [f] PDI = polydispersity index. [g] Determined by gel permeation chromatography with polystyrene (PSt) calibration for entry 1, poly(methyl methacrylate) (PMMA) calibration for entries 2, 3, and 9−14, and a multiangle laser light scattering detector for entries 4−8. [h] Solution polymerization in 25 vol % anisole for entries 3 and 5, 15 vol % 1-propanol and 35 vol % methyl ethyl ketone for entry 7, and 50 vol % anisole for entry 13 for the first block. [i] Molecular weight = 246. [j] M_n = 3900 and PDI = 1.14.

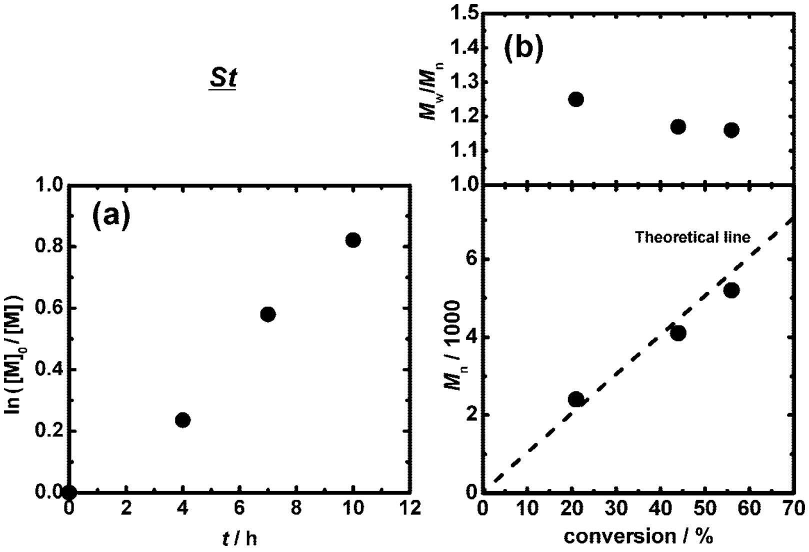


Figure 1. Plots of (a) $\ln([M]_0/[M])$ vs time t and (b) M_n and M_w/M_n vs conversion for the polymerization of styrene (St) for entry 1 in Table 1, where [M] is the monomer concentration and M_n and M_w are the number- and weight-average molecular weights, respectively.

by DCP, is supposed to react with NIS, in situ producing the activator radical, *N*-succinimide radical NS$^\bullet$ (and Polymer−I). If NS$^\bullet$ 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 1 (entry 1) and Figure 1 show the result. The polymerization rate was approximately constant in the studied time range (∼10 h) (Figure 1a). The number-average molecular weight M_n linearly increased with conversion and well agreed with the theoretical value $M_{n,theo}$ (Figure 1b). 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 DCP. 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, indicating a high frequency of the activation−deactivation cycle. The small amount (5 mM (∼500 ppm)) of NIS required to control the polydispersity suggests a high reactivity of NIS. This amount is as small as those of the previously studied catalysts (Sn, Ge, and P catalysts) (5 mM, typically).[5−7] (See ref 6 for reference experiments without the catalyst.)

NIS exhibited particularly good performance for MMA (entries 2 and 3 in Table 1 and Figure 2). For MMA, as in the previous studies (Ge and P catalysts),[5−7] we used a tertiary alkyl iodide, 2-cyanopropyl iodide (CP-I: Table 1), instead of the secondary one, PE-I, to ensure a fast initiation from the alkyl iodide. Remarkably, even with 1 mM (∼100 ppm) of NIS, which is among the lowest concentrations of the so far studied catalysts, PDI was small (1.15−1.4) from an early stage to a later stage of polymerization (Figure 2b), both in bulk (filled circles) and in anisole solution (open circle). Notably, the temper-

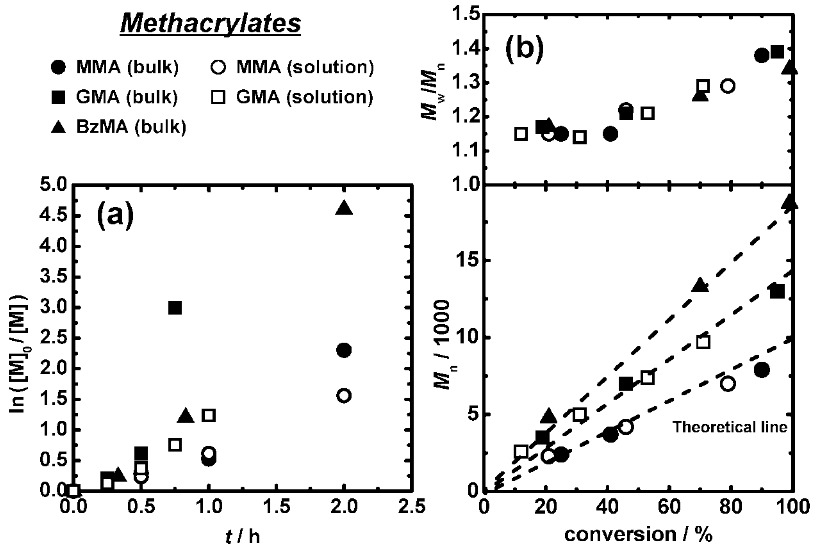


Figure 2. Plots of (a) ln([M]$_0$/[M]) vs time t and (b) M_n and M_w/M_n vs conversion for the polymerizations of methacrylates for entries 2−6 in Table 1, where [M] is the monomer concentration and M_n and M_w are the number- and weight-average molecular weights, respectively. MMA, GMA, and BzMA are methyl, glycidyl, and benzyl methacrylates, respectively.

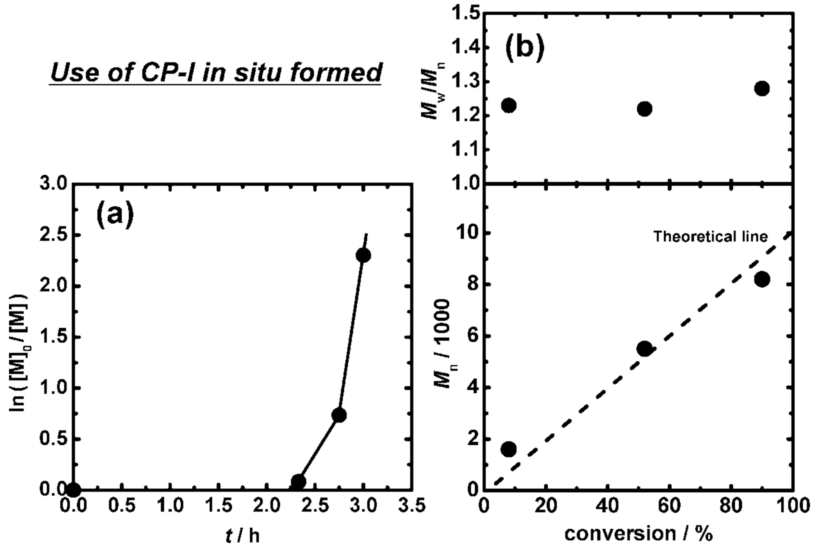


Figure 3. Plots of (a) ln([M]$_0$/[M]) vs time t and (b) M_n and M_w/M_n vs conversion for the polymerization of methyl methacrylate (MMA) for entry 14 in Table 1, where [M] is the monomer concentration and M_n and M_w are the number- and weight-average molecular weights, respectively. CP-I is 2-cyanopropyl iodide.

ature for MMA (80 °C) was lower than that for St (100 °C).

The good tolerance to functional groups allowed the control in the polymerizations of functional methacrylates, BzMA (with a benzyl group), GMA (with an epoxide), HEMA (with a hydroxy group), and PEGMA (with ethylene oxide units) (molecular weight = 246) (entries 4−8 in Table 1 and Figure 2). The M_n well agreed with $M_{n,theo}$, and PDI was about 1.1−1.4 from a low conversion to a high conversion, suggesting that the high catalytic function of NIS for these monomers. The polymerizations of GMA and BzMA were about twice faster than that of MMA, reflecting about that much of larger propagation rate constants k_p for GMA (2500 M^{-1} s^{-1})[8] and BzMA (2800)[8] than that for MMA (1300).[9] BzMA and GMA are widely applied to photoresists (electronic materials) and HEMA and PEGMA are to biomaterials. No conductivity and low toxicity of NIS may particularly be attractive for those applications.

The random copolymerizations of functional methacrylates, i.e., BzMA with MAA (with a carboxylic acid), with DMAEMA (with a dimethylamino group), and with HEMA were also successful (entries 9−11 in Table 1). 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), fairly low-polydispersity polymers (PDI = 1.21−1.37) were obtained up to high conversions (60−90%). For all examined homopolymerizations (see above) and copolymerizations, the polymerization was fairly fast; i.e., the conversion reached 60−90% in 1−10 h, in the studied conditions (Table 1).

Exploiting the living character, we attempted the block copolymerization using a PMMA-I macroinitiator (first block), where PMMA is poly(methyl methacrylate). With BzMA as the second block monomer (entry 12 in Table 1), the PMMA chain successfully extended, yielding a block copolymer with a fairly small PDI (=1.2). Instead of using an isolated macroinitiator (see above), successive addition of two monomers was also applicable. 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 13 in Table 1), where PBzMA is poly(benzyl methacrylate).

For the alkyl iodide, we may add molecular iodine I_2 and an azo compound 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 to the iodide-mediated LRP.[10] We examined the polymerization of MMA with I_2 (40 mM), AIBN (80 mM), and NIS (5 mM) at 80 °C (entry 14 in Table 1 and Figure 3). AIBN gives 2-cyanopropyl radical $CP^•$, and $CP^•$ reacts with I_2 to form CP-I.[11] 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 $CP^•$, we used an excess of it (2 equiv to I_2). Virtually no polymerization occurred for 2.25 h, during which time $CP^•$ 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 to a high conversion regions. Besides the robustness, this method may also be promising for easy introduction of a functional group at the initiating chain end by using a functional azo compound. This topic is currently studied in our laboratory.

In summary, we have demonstrated that a common nitrogen compound, NIS, works as an excellent catalyst in RTCP. The good controllability, good tolerance to functional groups, and prominent robustness may be great advantages for this polymerization to serve as a useful synthetic tool for well-defined polymers. The method using the in situ formed alkyl iodide would enhance the convenience of RTCP, particularly attractive for practical applications.

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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