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Reversible Complexation Mediated Living Radical Polymerization (RCMP) Using Organic Catalysts

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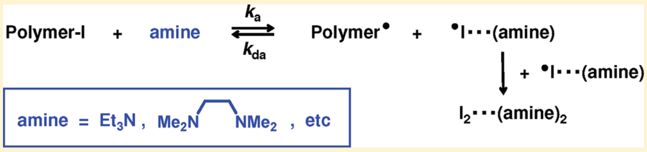
Supporting Information



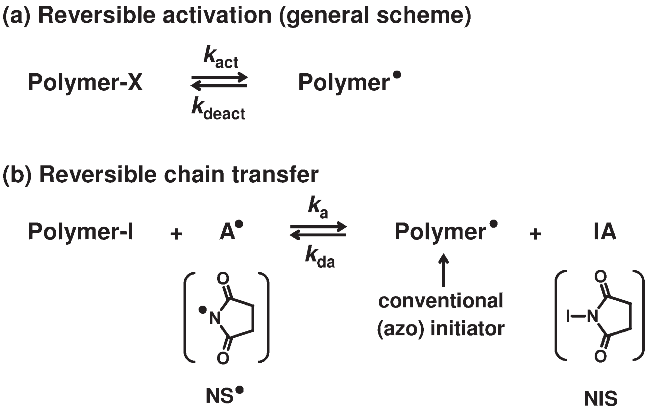
ABSTRACT: A novel class of living radical polymerization using amines as organic catalysts was developed. It is based on a new reversible activation mechanism, *reversible complexation* (*RC*). The polymer molecular weight and its distribution (M_w/M_n = 1.1−1.4) were well controlled in the polymerizations of methyl methacrylate (MMA), styrene, acrylonitrile, and some functional methacrylates with a fairly high conversion in hours in many cases. The catalysts include such common amines as triethylamine and tetramethylethylenediamine (TMEDA). Their low cost, good environmental safety, and ease of handling may be attractive for possible applications. Kinetic studies supported the RC mechanism. The activation rate constant for the MMA/TMEDA system was large enough to explain why the system provides low-polydispersity polymers from an early stage of polymerization.

INTRODUCTION

Living radical polymerization (LRP) has attracted growing attention as an efficient method for preparing well-defined, low-polydispersity polymers.[1−3] The basic concept of LRP (Scheme 1a) is the reversible activation of the dormant species (Polymer-X) to the propagating radical (Polymer$^\bullet$). A sufficiently large number of the activation−deactivation cycles are requisite for good control of polydispersity.[4] We recently developed an LRP using organic molecules as catalysts, which we have proposed to term reversible chain transfer catalyzed polymerization (RTCP) (Scheme 1b).[5] It is the first LRP using organic catalysts. The catalysts are reversible chain transfer agents such as *N*-iodosuccinimide (NIS) (Scheme 1b). RTCP consists of an alkyl iodide as a dormant species (X = iodine), a conventional radical initiator as a source of radical, and a catalyst (NIS in Scheme 1b). In this polymerization, Polymer$^\bullet$, which is originally supplied by the conventional initiator, reacts with NIS, in situ producing the *N*-centered radical (NS$^\bullet$). NS$^\bullet$ works as an activator of polymer-iodide (Polymer-I) to produce Polymer$^\bullet$ and NIS. This cycle, i.e., the *reversible chain transfer* to the catalyst, allows a frequent activation of Polymer-I.

In the present paper, we report a new class of LRP using organic catalysts, which is mechanistically different from RTCP. The background of the new LRP is atom transfer radical polymerization (ATRP) (Scheme 2a) that uses a halogen as X and a transition metal compound such as Cu^{I}X as an activator catalyst.[2] Cu^{I}X reversibly activates Polymer-X to generate Polymer$^\bullet$ and Cu^{II}X$_2$. This is a redox reaction of copper. As an initial motivation, we got an idea that even organic compounds may work as catalysts, if they have redox ability. To test this concept, we used an alkyl iodide as an initiator (low-mass dormant species with iodine as X) and a well-known organic reducing agent tetra(dimethylamino)ethylene (TDAE) (Figure 1) as an activator catalyst instead of Cu^{I}X. This in fact worked well, as will be shown below. After this initial study and some mechanistic study, we found that even a simple amine, triethylamine (TEA), which has little or a much weaker redox ability, also well worked as a catalyst.

Scheme 1. Reversible Activation Processes: (a) General Scheme and (b) Reversible Chain Transfer



As a possible mechanism (Scheme 2b), the amine abstracts an iodine from Polymer-I to generate Polymer$^\bullet$ and a complex of the

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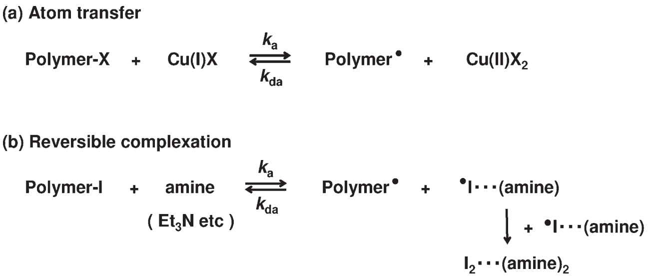
Scheme 2. Reversible Activation Processes: (a) Atom Transfer and (b) Reversible Complexation



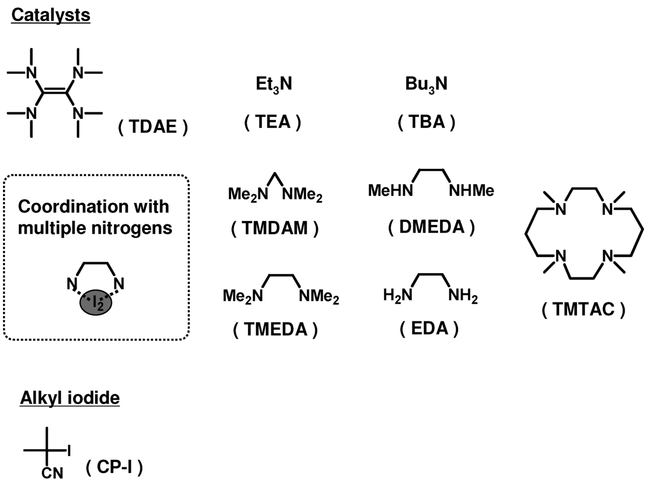


Figure 1. Structures of catalysts and an alkyl iodide studied in this work. Me, Et, and Bu mean methyl, ethyl, and butyl groups, respectively.

iodine radical and amine (I•/amine complex). Since the iodine radical is not a stable radical, it recombines with another iodine radical to form a complex of the iodine molecule and amine (I_2/amine complex).[6] Polymer• reacts with these complexes (deactivators) to form Polymer-I and the amine. In this process, electron transfer from the amine to iodine would occur to a range of different degrees including full (redox), partial (coordination) and nearly no transfer, depending on the kind of amines. The process is *reversible complexation* (*RC*) of iodine and catalyst, and we propose to term the LRP mediated by this process reversible complexation mediated polymerization (RCMP). Clearly, it is mechanistically distinguished from both ATRP and RTCP.

Technically, RCMP is like ATRP[2] in that they both include only a dormant species and an activator catalyst. Unlike RTCP, it requires no conventional radical initiator, even though a conventional radical initiator would, as in other LRPs, work to decrease the concentration of deactivator and thus increase the polymerization rate R_p.[4] A small amount of the deactivator $Cu^{II}X_2$ is sometimes added in ATRP. In the same way, the deactivator I_2/amine complex is sometimes added in RCMP. In the literature, the formation of an alkyl radical from an alkyl halide with an amine was studied in organic chemistry[7] and employed as a conventional radical initiation in polymer chemistry.[8] However, in all cases, the reaction was irreversible. We found the reversible reaction, which is new in chemistry.

In this paper, we present the polymerizations of methyl methacrylate (MMA) with a variety of amine catalysts (Figure 1), mechanistic and kinetic studies, and application to the polymerizations of some monomers.

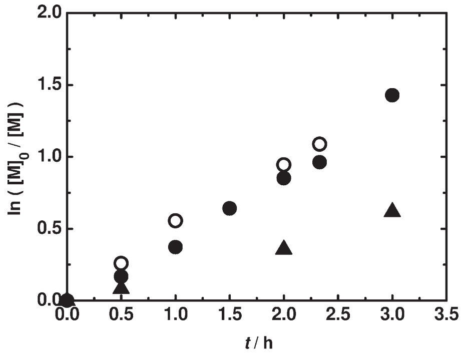


Figure 2. Plot of $\ln([M]_0/[M])$ vs time t for the MMA/CP-I/catalyst/(I_2) systems (90 °C): $[MMA]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[catalyst]_0$ = 40 mM; $[I_2]_0$ = 0 (open circle) or 1 mM (filled circle and triangle), where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), and the catalyst is TEA or TDAE. The structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

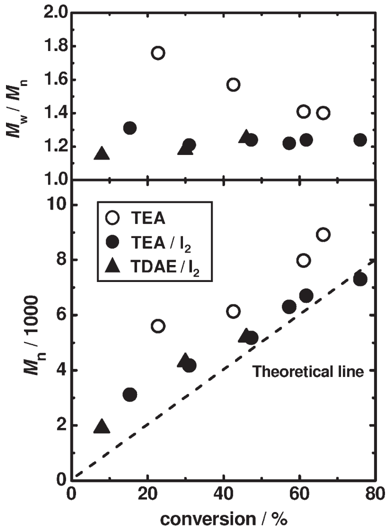


Figure 3. Plots of M_n and M_w/M_n vs conversion for the MMA/CP-I/catalyst/(I_2) systems (90 °C): $[MMA]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[catalyst]_0$ = 40 mM; $[I_2]_0$ = 0 (open circle) or 1 mM (filled circle and triangle), where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), and the catalyst is TEA or TDAE. The structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

■ RESULTS AND DISCUSSION

1. Polymerizations of MMA with a Variety of Catalysts. Figures 2 and 3 (open circles) and Table 1 (entry 1) show the bulk polymerization of MMA (8 M) (100 equiv) with 2-cyanopropyl iodide (CP-I (Figure 1)) (80 mM) (1 equiv) as a low-mass dormant species and TEA (40 mM) (0.5 equiv) as an activator catalyst at 90 °C. The polymerization proceeded up to, e.g., a 66% monomer conversion in 2.3 h (Figure 2 (open circle)), confirming the generation of the carbon-centered radical (the propagating radical) from CP-I and TEA. Without CP-I or TEA, no polymerization proceeded, again confirming that the radical

Table 1. Polymerizations of Several Monomers ($[\text{Monomer}]_0$ = 8 M in Bulk)

entry	monomer[a] (eq to $[\text{CP-I}]_0$)	catalyst[b]	$[\text{CP-I}]_0/[\text{catalyst}]_0/[I_2]_0$ (mM)	T (°C)	t (h)	convn (%)	M_n[c] ($M_{n,theo}$)[d]	PDI[c]
1	MMA (100 equiv)	TEA	80/40/0	90	2.3	66	8900 (6600)	1.40
2	MMA (100 equiv)	TEA	80/40/1	90	3	76	7300 (7600)	1.24
3	MMA (100 equiv)	TMTAC	80/40/2	90	0.75	67	7800 (6700)	1.30
4	St (100 equiv)	TMTAC	80/40/20	120	24	74	10000 (7700)	1.45
5	AN (200 equiv)	TMTAC	20/10/5[e]	75	4	100	14900 (11400)	1.49
6	BzMA (100 equiv)	TMTAC	80/40/5	90	1	84	13400 (14800)	1.35
7	HEMA (100 equiv)	TBA	80/80/20	90	1	70	6700 (9100)	1.28
8	DMAEMA/MMA (5/95 equiv)	none	80/0/20	90	24	37	5300 (5800)	1.39

[a] MMA = methyl methacrylate, St = styrene, AN = acrylonitrile, BzMA = benzyl methacrylate, HEMA = 2-hydoxyethyl methacrylate, and DMAEMA = 2-dimethylaminoethyl methacrylate. [b] Structures of the catalysts are shown in Figure 1. [c] Determined by GPC with poly(methyl methacrylate) calibration for entries 1−3 and 8, polystyrene calibration for entry 4, and a multiangle laser light-scattering (MALLS) detector for entries 5−7. [d] $M_{n,theo}$ = (molecular weight of monomer) × ($[\text{monomer}]_0/[\text{CP-I}]_0$) × (conversion/100). [e] Solution polymerization in 50 wt % ethylene carbonate (hence $[M]_0$ = 4 M).

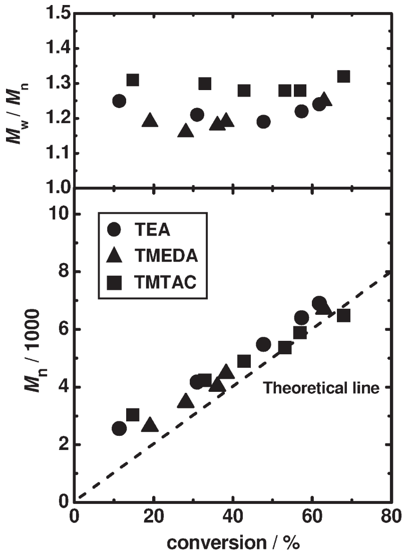


Figure 4. Plots of M_n and M_w/M_n vs conversion for the MMA/CP-I/catalyst/I_2 systems (90 °C): $[\text{MMA}]_0$ = 6 M (in 25 wt % toluene (solution polymerization)); $[\text{CP-I}]_0$ = 60 mM; [nitrogen atom of catalyst]$_0$ = 30 mM; $[I_2]_0$ = 0.75 mM, where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), and the catalyst is TEA, TMEDA, or TMTAC. The structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

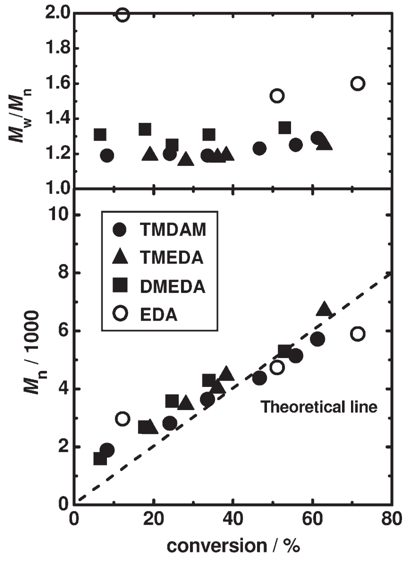


Figure 5. Plots of M_n and M_w/M_n vs conversion for the MMA/CP-I/catalyst/I_2 systems (90 °C): $[\text{MMA}]_0$ = 6 M (in 25 wt % toluene (solution polymerization)); $[\text{CP-I}]_0$ = 60 mM; $[\text{catalyst}]_0$ = 15 mM; $[I_2]_0$ = 0.75 mM, where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), and the catalyst is TMDAM, TMEDA, DMEDA, or EDA. The structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

was generated by the combination of CP-I and TEA. The first order plot of the monomer concentration [M] was linear in the studied range of time t (Figure 2 (open circle)). However, M_n deviated from the theoretical value $M_{n,theo}$ and the polydispersity index (PDI) (=M_w/M_n) was larger than 1.5 at an early stage of polymerization (Figure 3 (open circles)). This is because a sufficient amount of deactivator (I_2/amine complex) was not accumulated at an early stage of polymerization, at which many monomers added to Polymer$^\bullet$. Thus, we added a small amount of iodine molecule (I_2) as a stating compound, which will form the I_2/amine complex[9−11] with TEA (Scheme 2b). In fact (Figures 2 and 3 (filled circles) and Table 1 (entry 2)), with the addition of 1 mM of I_2 (as small as 1/40 equiv to TEA), M_n agreed with $M_{n,theo}$ and PDI was about 1.3 from an early stage of polymerization. Also importantly, PDI kept small (about 1.2) up to high conversions, e.g., 80% (Figure 3 (filled circles)), demonstrating the success of RCMP. The R_p with I_2 was slightly lower than that without it (Figure 2), as expected from the equilibrium in Scheme 2b. As mentioned in Introduction, TDAE (an organic reducing agent) also well worked as a catalyst in the presence of I_2 (Figure 2 and 3 (triangles)). (CP-I and Polymer-I can thermally dissociate to generate the alkyl radical (CP$^\bullet$ or polymer$^\bullet$) and I$^\bullet$ at elevated temperatures, which can be a possible activation mechanism. However, at the studied temperature (90 °C), as mentioned above, no polymerization occurred with CP-I only (without TEA), suggesting the unimportance of the thermal dissociation.)

For the catalyst, compounds which can wrap iodine with multiple nitrogens can stabilize iodine (Figure 1) and may work as highly active catalysts. The amines thus examined and their abbreviated names are shown in Figure 1. In fact (Figure 4), with fixing the concentration of the nitrogen atom, compared with

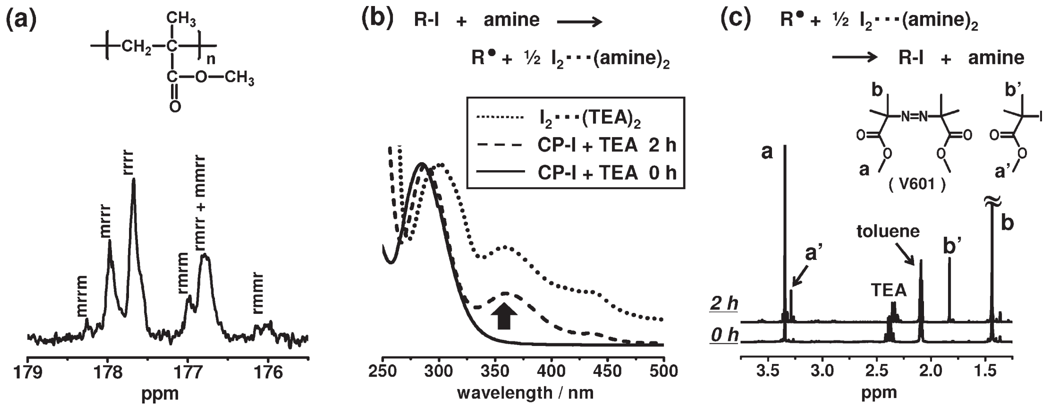


Figure 6. (a) ^{13}C NMR spectrum (in the range 175.5−179 ppm) of the poly(methyl methacrylate) produced in the MMA/CP-I/TEA/I_2 system (90 °C) for entry 2 in Table 1, where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), and TEA is triethylamine. (b) UV spectra of the toluene solution of CP-I (20 mM) and TEA (20 mM) heated at 70 °C for 0 h (solid line) and 2 h (broken line) and a toluene solution of the I_2/TEA complex (dotted line). (c) ^{1}H NMR spectra (in the range of 1.25−3.75 ppm) of the toluene-d_8 solution of V601 (20 mM), I_2 (20 mM), and TEA (40 mM) heated at 70 °C for 0 and 2 h, where V601 is dimethyl-2,2′-azobis(2-methylpropionate). The I_2/TEA complex was in situ formed by mixing I_2 and TEA.

TEA with one nitrogen (circles), TMEDA with two nitrogens (triangles) afforded lower polydispersity at an early stage of polymerization (and the PDI kept small (about 1.2) up to a high conversion (about 60%)). TMTAC with four nitrogens (squares) was also a good catalyst, although it did not further lower polydispersity, possibly because the coordination is divalent and thus the remaining two nitrogens did not effectively work (other factors can also be involved).

For the amines with two nitrogens (Figure 5), the length of the spacer (one carbon or two carbons) between the nitrogens did not clearly affect the polydispersity (TMDAM (filled circles) vs TMEDA (triangles)). The number of the alkyl group attached to nitrogen was important, as PDI became larger in the order of tertiary amine TMEDA (triangles) < secondary one DMEDA (squares) < primary one EDA (open circles). Thus, tertiary amines are the most effective. This would be due to a higher electron density on the nitrogen with a more number of alkyl groups and hence a higher coordination ability. EDA (primary amine) also causes a side reaction particularly significant for primary amines NH_2−R, i.e., a chain-end transformation of Polymer-I (dormant species) to Polymer−NH−R (inactive species).[12] This side reaction is much faster for primary amines than secondary and tertiary amines.[12]

The studied amines such as TEA, TMEDA, and TMDAM are among the simplest and cheapest amines. The use of such common amines as catalysts may be attractive for possible applications. The small PDI values achievable even at high conversions may also be an attractive feature.

2. Mechanisms and Kinetics. *Mechanisms.* The RC mechanism assumed in Scheme 2b was experimentally tested for TEA. If the mechanism is valid, (a) the propagating species is a free radical, (b) the I_2/amine complex is formed from an alkyl iodide and TEA (as the activation process), and (c) the I_2/amine complex reacts with an alkyl radical ($R^{\bullet}$) to form the alkyl iodide (R-I) (as the deactivation process).

(a) The free radical nature of the propagating species was confirmed from the tacticity of the polymer obtained in the MMA/CP-I/TEA/I_2 system for entry 2 in Table 1. The ^{13}C NMR spectrum (Figure 6a) showed that the pentad distribution (for the carbonyl carbon) is virtually the same as that for a conventional free radical polymerization.[13] The present polymerization was also completely inhibited in the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO), supporting the radical mechanism.

(b) The formation of the I_2/amine complex was tested in a model experiment (Figure 6b). We heated a toluene solution of CP-I (20 mM) and TEA (20 mM) at 70 °C. After 2 h (broken line), the characteristic UV absorptions of the I_2/TEA complex at 360 and 302 nm were in fact observed. (The system at 2 h included not only the complex (with a peak top at 302 nm) but also the unreacted CP-I (with a peak top at 284 nm), and their overlapped absorption appeared with a peak top at 289 nm. The dotted line shows the spectrum of the complex independently prepared with I_2 and TEA.) The absorptions at 360 and 302 nm correspond to the blue-shifted band of iodine molecule and the charge-transfer band of the complex, respectively, as assigned in the literature.[9] Thus, the formation of the complex was demonstrated. (The complex can take a 1:1 form (I_2/amine form) at a low amine concentration and a 1:2 form (I_2/(amine)$_2$) at a high amine concentration.[9,10] In this paper, we do not distinguish the two forms but write them as the I_2/amine complex, unless it is specifically noted.)

(c) The work of the I_2/amine complex as a deactivator was tested in a model experiment. We heated a toluene-d_8 solution of the I_2/TEA complex (20 mM) and an azo compound (V601) (20 mM) which produces a model unimer radical of MMA at 70 °C. Figure 6c shows the ^{1}H NMR spectra of the solution at time zero and 2 h. At 2 h, the adduct of the unimer radical and iodine (MMA-I) was observed, demonstrating the work of the I_2/TEA complex as a deactivator. The result should also hold for the polymer radical (poly(methyl methacrylate) (PMMA) radical) as well as the unimer radical. (The I_2/TEA complex is in an equilibrium with the free molecules (I_2 and TEA). Since the equilibrium is predominantly shifted to the complex,[9−11] the complex would play a main role in deactivation, while a small amount of free I_2, which is a

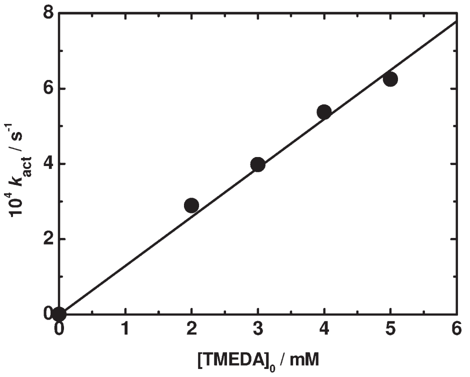


Figure 7. Plot of k_{act} vs [TMEDA] for the MMA/PMMA-I/TMEDA system (90 °C), where MMA is methyl methacrylate, and PMMA-I is poly(methyl methacrylate) iodide. The structure of TMEDA is shown in Figure 1.

good deactivator,[11] possibly plays a role in deactivation as well.)

Thus, the three experiments (Figure 6, parts a, b, and c) strongly support the assumed RC mechanism (Scheme 2b).

Determination of Activation Rate Constant. In the following three kinetic studies, we studied TMEDA with two nitrogens, which is a representative good catalyst. We determined the pseudo-first-order activation rate constant k_{act} (Scheme 1a) of a PMMA-I (M_n = 3700; PDI = 1.12) under various concentrations of TMEDA in the MMA polymerization at 90 °C by the gel permeation chromatography (GPC) peak resolution method[14] (Supporting Information). We focused on the polymer dormant species PMMA-I, i.e., the k_{act} in the polymer region. According to Schemes 1a and 2b, k_{act} takes the form

$$k_{act} = k_a[\mathrm{TMEDA}] \tag{1}$$

where k_a is the activation rate constant in Scheme 2b. Figure 7 shows the plot of k_{act} vs $[\mathrm{TMEDA}]_0$. The plot was linear, as expected from eq 1, and the slope of the line gave k_a to be 0.13 M^{-1} s^{-1}. (In more detail, the system also includes degenerative chain transfer (activation of Polymer-I by Polymer$^\bullet$),[3,11,15] but its rate constant k_{ex} (4200 M^{-1} s^{-1}) and the [Polymer$^\bullet$] (10^{-9} M) in this study were small enough to neglect the contribution of degenerative chain transfer (k_{ex}[Polymer$^\bullet$] < 10^{-5} s^{-1}) in the obtained k_{act} (on the order of 10^{-4} s^{-1} in the vertical axis in Figure 7) (Supporting Information).) This k_a value (0.13 M^{-1} s^{-1}) is similar in magnitude to that (0.45 M^{-1} s^{-1})[16] in a representative ATRP system of styrene with PSt-Br and CuBr/dHbipy catalyst (110 °C), where PSt is polystyrene and dHbipy is 4,4′-di-*n*-heptyl-2,2′-bipyridine. Of course, since monomer, halogen, and temperature are different for the two systems, this does not directly compare the catalytic activities of TMEDA and CuBr/dHbipy, but this suggests that our system is virtually as effective as this good ATRP system as a system. (The PDI in our system kept almost constant (about 1.2−1.3) and does not become even lower in the course of polymerization (Figures 3-5). This is possibly due to a side reaction of the iodine capping agent, i.e., a chain-end self-decomposition of Polymer-I (dormant species) to form an inactive polymer species, depending on the kind of polymer and temperature.)

Determination of Equilibrium Constant. We determined the equilibrium constant K defined as $K = [\mathrm{PMMA}^\bullet][\mathrm{I_2/TMEDA}]/([\mathrm{PMMA\text{-}I}][\mathrm{TMEDA}])$ in the MMA polymerization with CP-I (60 mM), TMEDA (9 mM), and an excess amount of I_2/TMEDA (deactivator) (6 mM) at 90 °C.[4,17,18] The first order plot of [M] (Figure 8) was linear in the studied range of *t*, and the slope of the line gave [Polymer$^\bullet$] = 1.7 × 10^{-8} M with the known propagation rate constant k_p (2600 M^{-1} s^{-1}).[19] With $[\mathrm{CP\text{-}I}]_0$, $[\mathrm{TMEDA}]_0$, and $[\mathrm{I_2/TMEDA}]_0$, K was obtained to be 1.8 × 10^{-7}. The obtained K and k_a give the deactivation rate constant k_{da} = 7.2 × 10^5 M^{-1} s^{-1} (Scheme 2b) according to $K = k_a/k_{da}$. This k_{da} value is about 20 times smaller than that (1.1 × 10^7 M^{-1} s^{-1})[16,17] in the mentioned ATRP system, explaining why our system requires a small amount of deactivator added at the beginning of polymerization while the ATRP system does not. (The first-order deactivation rate constant k_{deact} (Scheme 1) is related as $k_{deact} = k_{da}[\mathrm{I_2/TMEDA}]$ (Scheme 2b).)

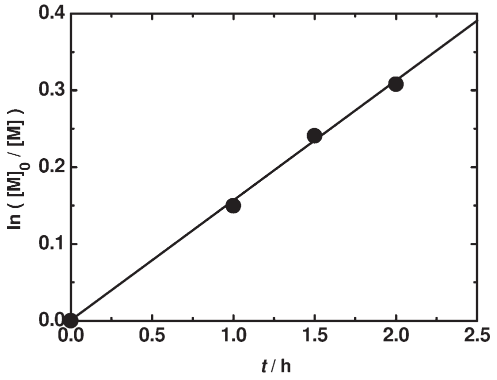


Figure 8. Plot of ln($[M]_0$/[M]) vs time *t* for the MMA/CP-I/TMEDA/I_2 system (90 °C): $[\mathrm{MMA}]_0$ = 8 M (in bulk); $[\mathrm{CP\text{-}I}]_0$ = 60 mM; $[\mathrm{TMEDA}]_0$ = 9 mM; $[\mathrm{I_2/TMEDA}]_0$ = 6 mM, where MMA is methyl methacrylate, and CP-I is 2-cyanopropyl iodide (Figure 1). The structure of TMEDA is shown in Figure 1. The I_2/TMEDA complex (6 mM) was in situ formed by mixing I_2 (6 mM) and TMEDA (6 mM).

Polymerization Rate. The R_p was studied in the MMA polymerizations with CP-I (60 mM), TMEDA (15 mM), and I_2/TMEDA (1 mM) at 90 °C by varying the concentration of one component. The R_p should follow the relation

$$\begin{aligned} R_p/[\mathrm{M}] &= k_p[\mathrm{polymer}^\bullet] \\ &= k_pK([\mathrm{polymer\text{-}I}][\mathrm{amine}])/[\mathrm{I_2/amine}] \end{aligned} \tag{2}$$

As shown in Figure 8, R_p was approximately stationary in the studied cases. We confirmed that R_p is proportional to $[\mathrm{CP\text{-}I}]_0$ (Figure 9a) and $[\mathrm{TMEDA}]_0$ (Figure 9b) and reciprocal to $[\mathrm{I_2/TMEDA}]_0$ (Figure 9c), as expected from the equilibrium (eq 2). (For Figure 9c, at a low $[\mathrm{I_2/TMEDA}]_0$, R_p was somewhat smaller than expected, probably because a small amount of I_2/TMEDA was accumulated in the course of polymerization by the persistent radical effect[4] and it was not negligible at a low $[\mathrm{I_2/TMEDA}]_0$.)

3. Polymerizations of Some Other Monomers. Besides MMA, we attempted the homopolymerizations of some monomers (Table 1 (entries 4−7)) such as styrene (St), acrylonitrile (AN), and functional methacrylates with a benzyl group (BzMA) and a hydroxyl group (HEMA), obtaining relatively low-polydispersity polymers (PDI = 1.28−1.49) even at high conversions (>70%). (The St system at the studied high temperature (120 °C) included thermal self-initiation by monomer as an additional radical source to run the polymerization.) Interestingly, *N*,*N*-dimethylanimoethyl methacrylate (DMAEMA) monomer possesses a tertiary amine on the side chain and hence may be used as a catalyst at the same time. In fact, the random copolymerization

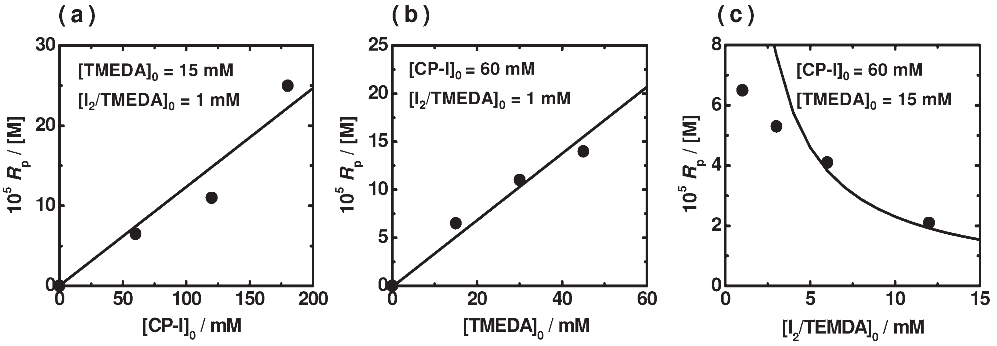


Figure 9. Plots of R_p/[M] vs (a) [CP-I]$_0$, (b) [TMEDA]$_0$, and (c) [I$_2$/TMEDA]$_0$ for the MMA/CP-I/TMEDA/I$_2$ system (90 °C): [MMA]$_0$ = 8 M (in bulk) and the other conditions are indicated in the figure, where MMA is methyl methacrylate, and CP-I is 2-cyanopropyl iodide (Figure 1). The structure of TMEDA is shown in Figure 1. The I$_2$/TMEDA complex was in situ formed by mixing equimolar I$_2$ and TMEDA.

of DMAEMA (5 mol %) and MMA (95 mol %) proceeded in a controlled manner without the addition of a catalyst (Table 1 (entry 8)). On the basis of the initial success in these monomers, we are currently exploring the higher polydispersity control and wider monomer versatility.

CONCLUSIONS

RCMP was developed as a new class of LRP using amines as organic catalysts. The molecular weights and its distribution were well controlled in the polymerizations of MMA, St, AN, and some functional methacrylates. The PDI kept small up to a high conversion in many cases. RCMP is based on reversible complexation as a new reversible activation mechanism of LRP, which was supported by the three experiments. The k_a for the PMMA-I/TMEDA system was large enough to explain why the system yields low-polydispersity polymers from an early stage of polymerization. The k_{da} for PMMA-I/TMEDA system was relatively small, explaining why the system requires a small amount of deactivator added at the beginning of polymerization. The catalysts include such common amines as TEA, TMEDA, and TMDAM. Their cheapness, good environmental safety, and ease of handling may be highly attractive for practical applications. RCMP includes no metal (being different from ATRP) and no conventional radical initiator (being different from RTCP and reversible addition−fragmentation chain transfer (RAFT) polymerization), which may also be advantageous for some applications. RCMP may possibly be applicable to a wider variety of monomers for higher molecular weight polymers, and a wider variety of organic compounds may possibly be used as catalysts. These issues are currently examined in our laboratory.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental section and the determination of k_{act}. This material is available free of charge via the Internet at http://pubs.acs.org.

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