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Phenols and Carbon Compounds as Efficient Organic Catalysts for Reversible Chain Transfer Catalyzed Living Radical Polymerization (RTCP)

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ABSTRACT: Simple phenols and hydrocarbons were used as novel and efficient organic catalysts for reversible chain transfer catalyzed living radical polymerization (RTCP). This is the first use of oxygen- and carbon-centered compounds as catalysts of living radical polymerization. The catalysts include such common compounds as phenol itself, phenol-based antioxidants for foods and resins (e.g., 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT)), phenol-based natural antioxidants (e.g., vitamin E), and dienes (e.g., 1,4-cyclohexadiene). Their cheapness, excellent environmental safety, and ease of handing may be quite attractive in practice. The catalysts were highly active and tolerant to functional groups. The required amounts of the catalysts were typically as small as 100−500 ppm, yielding low-polydispersity polymers ($M_w/M_n \sim 1.1-1.4$) at moderate temperatures (40−100 °C), where M_w and M_n are weight- and number-average molecular weights, respectively. A wide variety of functional monomers with alkyl, aryl, hydroxyl, poly(ethylene glycol), alkylamino, amino, and carboxylic acid groups were adopted to the homo- and copolymerizations. Kinetic studies supported that, mechanistically, the polymerization is based on reversible chain transfer (RT) for these catalysts.

Introduction

Organic (nonmetal) catalysts have extensively been studied for decades.[1] Many of them are cheap, relatively nontoxic, and stable to air and moisture (hence easily handled experimentally), offering attractive approaches for organic syntheses. Some organic catalysts exhibit higher reactivity and selectivity than the relevant metal catalysts and can even induce new reactions. The recent advent of organic catalysts for fine reactions such as asymmetric syntheses has promoted attention to organic catalysts and such catalysts are called organocatalysts.[1] In the field of polymer syntheses, living radical polymerization (LRP) has widely been utilized as an efficient method for preparing fine (well-defined, low-polydispersity) polymers.[2] We recently developed the first LRP using organic[4−9] (germanium (Ge),[4,5] phosphorus (P),[5] and nitrogen (N)[6,7] centered) catalysts and termed it reversible chain transfer catalyzed polymerization (RTCP) after the new reaction mechanism noted below.[5,8]

The basic concept of LRP is the reversible activation of the dormant species (Polymer-X) to the propagating radical (Polymer$^\bullet$) (Scheme 1a). A sufficiently large number of activation−deactivation cycles are requisite for good control of polydispersity.[10] RTCP (Scheme 1b) includes an alkyl iodide as a dormant species (X = I), a conventional radical initiator as a source of Polymer$^\bullet$, and a catalyst such as *N*-iodosuccinimide (NIS) (N-centered catalyst)[6] as a deactivator (IA). In this system, the conventional radical initiator gives Polymer$^\bullet$. It reacts with NIS, in situ producing the N-centered catalyst radical (NS$^\bullet$). NS$^\bullet$ works as an activator (A$^\bullet$) of Polymer-I, producing Polymer$^\bullet$ and NIS again. This reversible process allows a frequent activation of Polymer-I, attaining low polydispersity. Mechanistically, this process (Scheme 1b) is a reversible chain transfer (RT) of Polymer$^\bullet$ with NIS, and NIS works like a catalyst, and thus we termed the related polymerization RTCP.[5,8]

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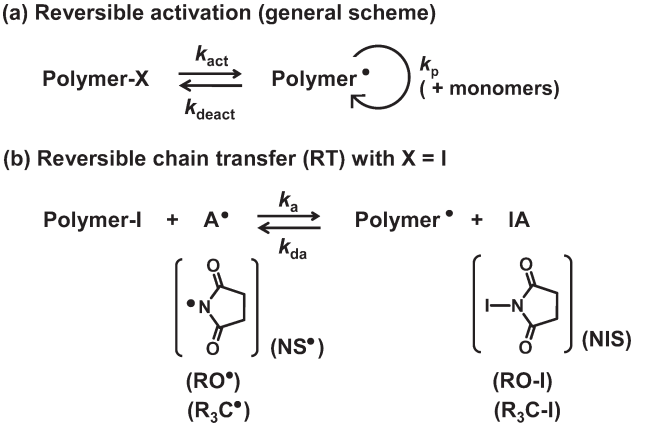
In this work, we extended the element of the catalyst to oxygen (O) and carbon (C) (Figure 1) from the previously studied Ge, P, and N. In RTCP, as requisites, (1) the activator radical A$^\bullet$ should be relatively stable and easily be formed, and (2) A$^\bullet$ should undergo no or little initiation (addition to monomer) but still be active enough to abstract iodine from Polymer-I. Phenoxyl radicals (Ph−O$^\bullet$) (O-centered radical) and conjugate C-centered radicals are relatively stable and do not initiate radical polymerization in many cases[11] and may be RTCP catalysts if they can activate Polymer-I. On the basis of this idea, we attempted to use phenol derivatives and conjugated carbon compounds as catalysts (Figure 1). Notably, the phenols include such common antioxidants for foods and resins as 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT) and 2,6-di-*tert*-butyl-4-hydroxyanisole (BHA) and natural compounds such as vitamins, and the carbon compounds include such common hydrocarbons as 1,4-cyclohexadiene (CHD). CHD has been used in organic syntheses

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



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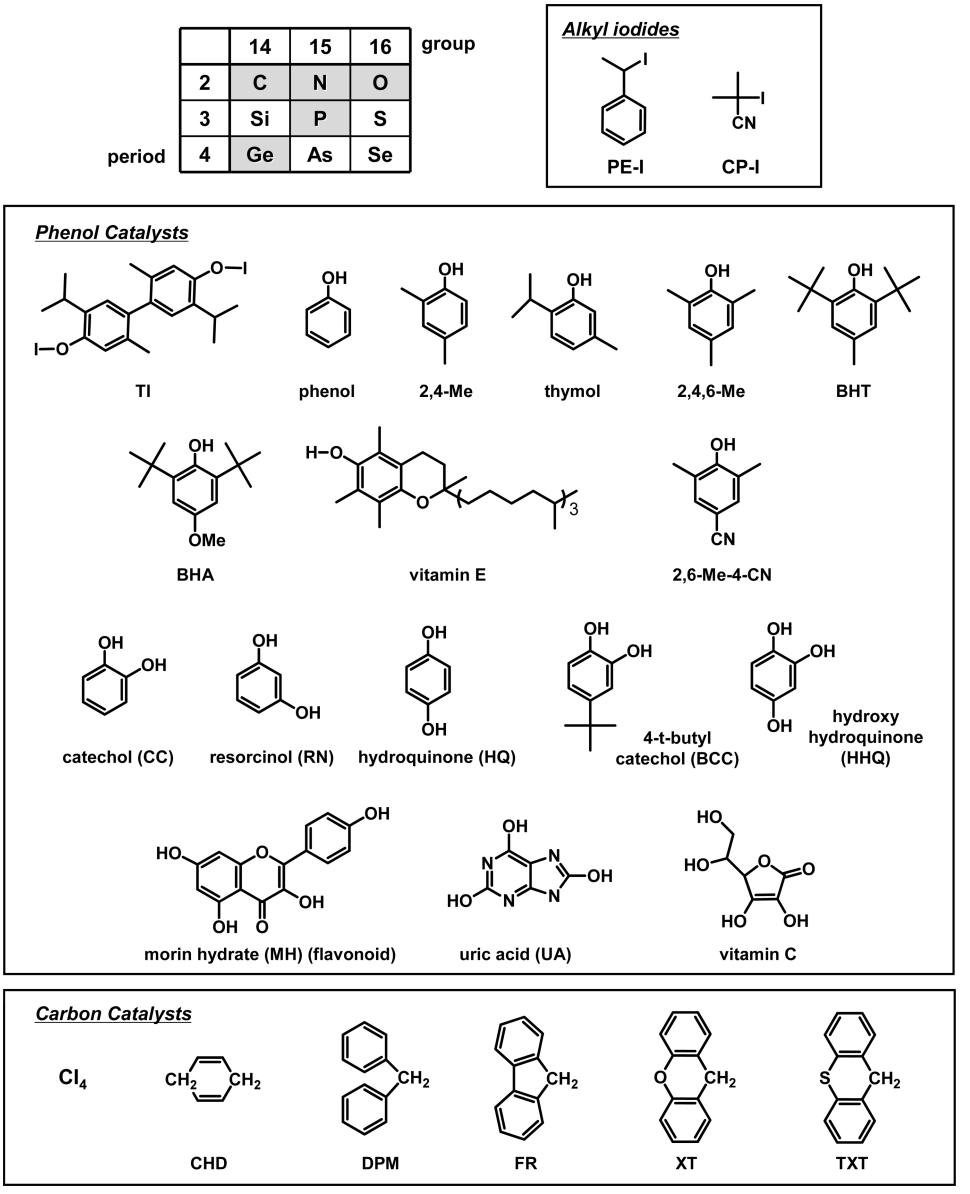


Figure 1. Table of elements and structures of alkyl iodides, phenol catalysts, and carbon catalysts studied in this work.

taking advantage of the easy generation of the CHD radical,[12] while it has not been used as a polymerization catalyst. The cheapness, low or no toxicity, and ease of handling of the O and C catalysts may be highly attractive for practical applications. Moreover, as shown below, the C catalysts exhibited higher reactivity and higher tolerance to functional groups over the previous RTCP catalysts, significantly improving the polydispersity control and the monomer versatility of RTCP. In this paper, we will present the results of the homo- and copolymerizations of several monomers (Figure 2) with the O and C catalysts (Figure 1) along with mechanistic studies. Some O catalysts were partly and briefly introduced in a conference proceeding.[13]

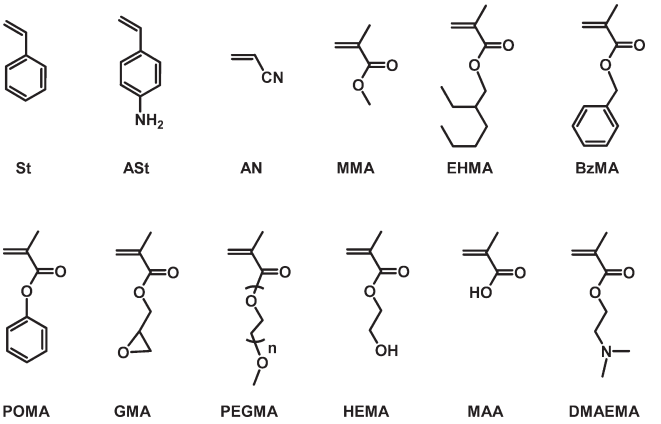


Figure 2. Structures of monomers studied in this work.

Results and Discussion

1. O Catalysts. *St with Thymol Iodide*. We first examined thymol iodide (TI) (Figure 1), a phenoxy iodide, as a catalyst (deactivator IA). TI is commercially available and used as a medicine, and thymol (with an OH group instead of an OI group) is a scent component of thyme (a natural compound). In the previous conference proceeding,[13] 1-phenylethyl iodide (PE-I) (Figure 1) was used as a low-mass alkyl iodide (dormant species) for St, while this paper reports the data using a more easily synthesized 2-cyanopropyl iodide (CP-I) (Figure 1). We examined the bulk polymerization of St (8000 mM) at 100 °C, using TI (5 mM), CP-I (80 mM), and 2,2′-azobis(2,4,4-trimethylpentane) (VR110) (80 mM) as a conventional radical

initiator (an azo-initiator). In this polymerization (Scheme 1b), Polymer•, which is originally supplied by VR110, is supposed to react with TI (R-OI), in situ producing the activator radical, the thymoxy radical (R−O•) (and Polymer-I). If R−O• effectively abstracts I from CP-I (or Polymer-I) to produce CP• (or Polymer•), cycles of activation and deactivation (RT) will be started.

Figure 3 (filled circle) shows the result. The first-order plot of the monomer concentration [M] showed a curvature in a long time range (for 24 h) due to a decrease of [VR110] with time t (Figure 3a). In a relatively short time range (for ~1 h), the polymerization rate was approximately constant. The number-average molecular weight M_n linearly increased with monomer conversion and well agreed with the theoretical value $M_{n,theo}$ (Figure 3b). The polydispersity index (PDI or M_w/M_n, where M_w is the weight-average molecular weight) reached a low value of about 1.3 from an early stage of polymerization, indicating a high frequency of the activation−deactivation cycle. The small amount (5 mM (~500 ppm)) of TI required to control the polydispersity suggests a high reactivity of TI. This amount is as small as those of the previously studied Ge, P, and N catalysts (5 mM, typically)[4−6,8] for St. The system without TI (iodide-mediated polymerization)[2d,14,15] (Figure 3 (open circle)) gave much larger PDIs than those with TI (filled circle) (with other conditions set the same), demonstrating the effectiveness of TI. For Figure 3b (filled circle), at a later stage of polymerization, M_n slightly deviated from $M_{n,theo}$ and PDI did not further decrease with conversion. These are ascribed to the increase in the number of chains by the decomposition of VR110. The system would also include the cross-termination between Polymer• and R−O• as a side reaction,[5] although the amount of catalyst is too small to have a large influence on PDI.

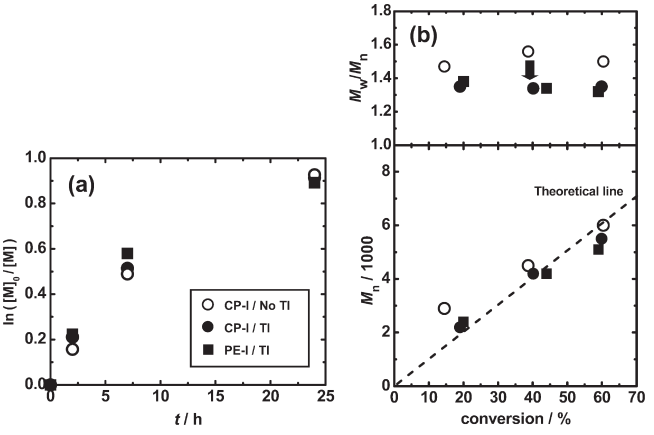
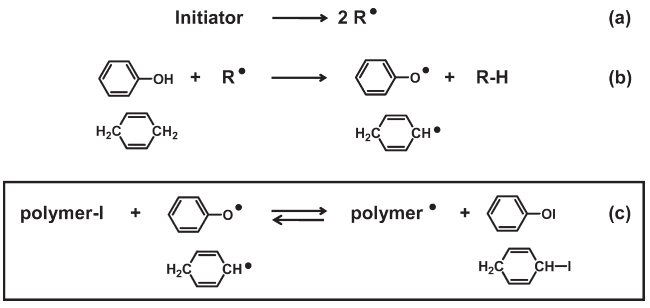


Figure 3. Plots of (a) $\ln([M]_0/[M])$ vs time t and (b) M_n and M_w/M_n vs conversion for the St/(CP-I or PE-I)/VR110/(TI) systems (100 °C): $[St]_0 = 8$ M (in bulk); $[CP\text{-}I \text{ or } PE\text{-}I]_0 = 80$ mM; $[VR110]_0 = 80$ mM; $[TI]_0 = 0$ or 5 mM, where St is styrene, CP-I is 2-cyanopropyl iodide (Figure 1), PE-I is 1-phenylethyl iodide (Figure 1), VR110 is 2,2′-azobis(2,4,4-trimethylpentane), and TI is thymol iodide (Figure 1). The symbols are indicated in the figure.

For the low-mass dormant species, CP-I (Figure 3 (filled circle)) was confirmed to be as effective as the previously studied PE-I (filled square). As a conventional radical initiator, the use of *tert*-butyl perbenzoate (BPB), which decomposes faster than VR110, led to a faster polymerization (Table 1 (entry 1)). In the examined case, the conversion reached 79% for 7 h, keeping a good polydispersity control (PDI = 1.35).

St with Phenol Catalyst. For a catalyst, instead of using a deactivator (R−OI) (TI in the above system), a precursor of a deactivator or an activator radical (R−O•), may be used as a starting compound. In this work, we used phenols R−OH as starting compounds (precursors), along with an alkyl

Scheme 2. Reaction Scheme for Precursor Catalyst[a]



[a] The system includes a conventional radical initiator, precursor catalyst (phenol and 1,4-cyclohexadine shown in the scheme), and alkyl iodide (shown as polymer-I in the scheme).

Table 1. Bulk Polymerizations of St (8 M) and MMA (8 M) with Phenol Catalysts

entry	monomer (equiv to $[CP\text{-}I]_0$)	catalyst	$[CP-I]_0/[I^a]_0/[OH \text{ group of catalyst}]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n[b] ($M_{n,theo}$)	PDI[b]
1	St (100 equiv)	TI	80/40/5[c]	100	7	79	7600 (7900)	1.35
2	St (100 equiv)	phenol	80/40/5	100	7	77	6700 (7700)	1.25
3	St (100 equiv)	thymol	80/40/5	100	7	74	6900 (7400)	1.26
4	St (100 equiv)	2,4,6-Me	80/40/5	100	7	76	6300 (7600)	1.16
5	St (100 equiv)	BHT	80/40/5	100	7	75	6900 (7500)	1.34
6	St (100 equiv)	vitamin E	80/40/5	100	7	76	6900 (7600)	1.18
7	St (100 equiv)	CC	80/40/5	100	7	73	6500 (7300)	1.21
8	St (100 equiv)	HHQ	80/40/5	100	7	82	7900 (8200)	1.18
9	St (100 equiv)	UA	80/40/5	100	7	85	7100 (8500)	1.18
10	St (100 equiv)	MH	80/40/5	100	7	78	6700 (7800)	1.18
11	St (100 equiv)	vitamin C	80/40/5	100	7	80	8300 (8000)	1.21
12	MMA (100 equiv)	phenol	80/80/10	80	0.5	81	6700 (8100)	1.39
13	MMA (100 equiv)	thymol	80/80/10	80	0.5	82	6900 (8200)	1.36
14	MMA (100 equiv)	2,4,6-Me	80/80/10	80	0.5	79	6900 (7900)	1.30
15	MMA (100 equiv)	BHT	80/80/10	80	0.5	81	6300 (8100)	1.36
16	MMA (100 equiv)	BHA	80/80/10	80	1	80	7000 (8000)	1.23
17	MMA (100 equiv)	vitamin E	80/80/10	80	0.5	69	6500 (6900)	1.23
18	MMA (100 equiv)	CC	80/80/10	80	0.5	89	6500 (8700)	1.35
19	MMA (100 equiv)	UA	80/80/10	80	0.5	84	6600 (8400)	1.41
20	MMA (100 equiv)	vitamin C	80/80/10	80	0.5	87	7200 (6700)	1.33

[a] I (conventional radical initiator) = BPB (*tert*-butyl perbenzoate) for St (entries 1−11) and PDX (di(4-*tert*-butylcyclohexyl) peroxydicarbonate) for MMA (entries 12−20). [b] M_n and M_w were determined by GPC calibrated by standard polystyrenes for entries 1−11 and standard poly(methyl methacrylate)s for entries 12−20. [c] The concentration of OI group was 5 mM.

iodide and a conventional radical initiator (as in the TI system). The initiator gives a radical (Scheme 2a), which abstracts a hydrogen from R−OH to in situ produce an activator R−O• (Scheme 2b). The R−O• leads to the reversible activation (Scheme 2c).

We carried out the polymerization of St (8000 mM) with CP-I (80 mM), VR110 (80 mM), and phenol at 100 °C (Figure 4 (filled square)). With 5 mM of phenol, relatively small PDIs (∼1.35) were achieved from an early stage to a later stage of polymerization, suggesting that the mentioned reactions (Scheme 2) effectively occurred. We then examined several phenols with different steric hindrance and different resonance stability in the same condition (Figures 4 and 5). As mentioned above, as a requisite, R−O• should easily be formed from R−OH (Scheme 2b), while it should be active enough as an activator (Scheme 2c). An increase of the steric hindrance and resonance stability can lead to (i) a faster formation of R−O• (Scheme 2b) but (ii) a slower activation (Scheme 2c).

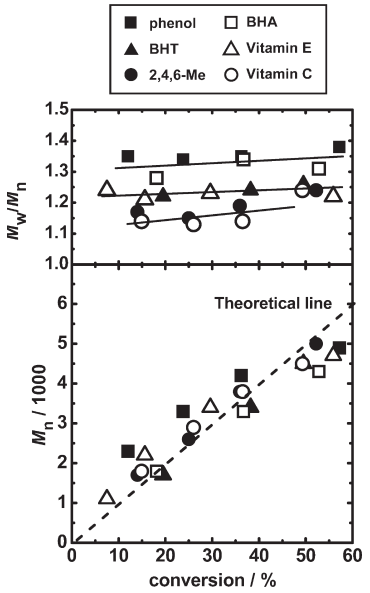


Figure 4. Plots of M_n and M_w/M_n vs conversion for the St/CP-I/VR110/phenol catalyst systems (100 °C): $[St]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[VR110]_0$ = 80 mM; $[catalyst]_0$ = 5 mM, where St is styrene, CP-I is 2-cyanopropyl iodide (Figure 1), VR110 is 2,2′-azobis-(2,4,4-trimethylpentane), and the structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

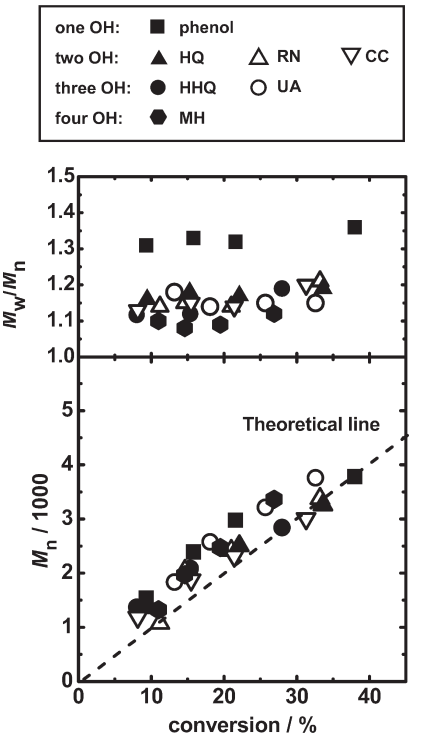


Figure 6. Plots of M_n and M_w/M_n vs conversion for the St/CP-I/VR110/phenol catalyst systems (100 °C): $[St]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[VR110]_0$ = 80 mM; $[OH\ of\ catalyst]_0$ = 2 mM, where St is styrene, CP-I is 2-cyanopropyl iodide (Figure 1), VR110 is 2,2′-azobis(2,4,4-trimethylpentane), and the structures of the catalysts are shown in Figure 1. The symbols are indicated in the figure.

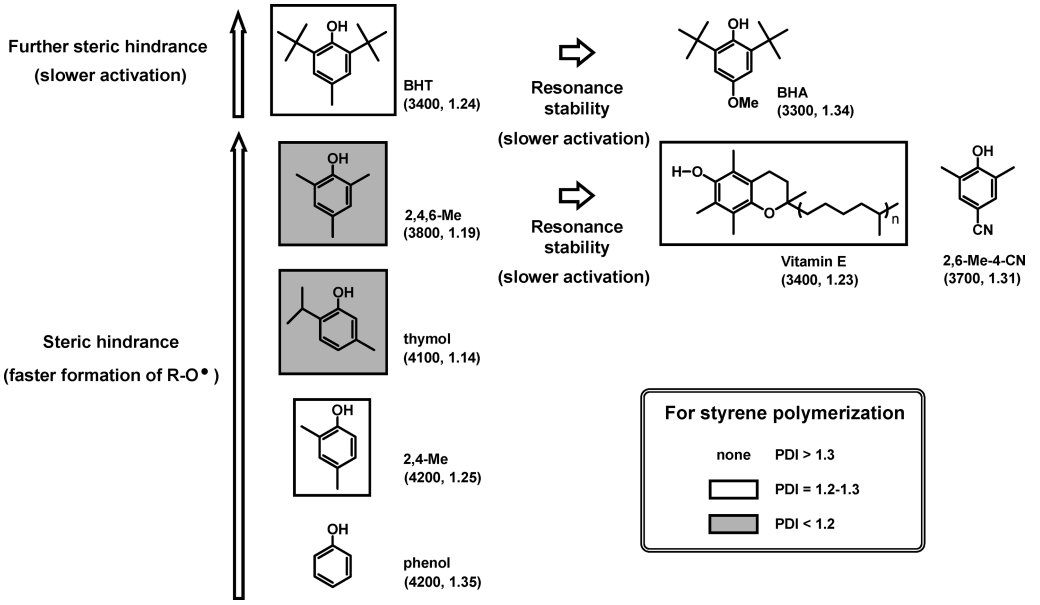


Figure 5. Comparison of the M_n and M_w/M_n (shown in the parentheses) of the polystyrenes produced in the St/CP-I/VR110/phenol catalyst systems (100 °C): $[St]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[VR110]_0$ = 80 mM; $[catalyst]_0$ = 5 mM, where St is styrene, CP-I is 2-cyanopropyl iodide (Figure 1), and VR110 is 2,2′-azobis(2,4,4-trimethylpentane).

Table 2. Polymerizations of Functional Methacrylates (8 M in Bulk) with CC (Catechol) Catalyst

entry	monomer (equiv to $[CP\text{-}I]_0$)	R−I	$[R-I]_0/[PDX]_0/[CC]_0$ (mM)	T (°C)	t (h)	conv (%)	M_n[a] ($M_{n,theo}$)	PDI[a]
1	BzMA (100 equiv)	CP−I	80/80/10[b]	80	0.17	83	11600 (14600)	1.32
2	GMA (100 equiv)	CP−I	80/80/10[b]	80	1.33	45	6700 (6400)	1.39
3	HEMA (100 equiv)	CP−I	40/40/15[c]	80	0.17	57	7000 (7400)	1.36
4	PEGMA[d] (100 equiv)	CP−I	80/80/10	80	0.17	45	10200 (11000)	1.18
5	HEMA/MMA (50/50 equiv)	CP−I	80/40/20	80	1	71	7900 (8200)	1.25
6	BzMA (100 equiv)	PMMA−I[e]	80/20/10[b]	80	0.17	84	12300 (15000)	1.33

[a] M_n and M_w were determined by GPC with a multiangle laser light-scattering (MALLS) detector for entries 1−4 and by poly(methyl methacrylate) calibration for entries 5 and 6. [b] Addition of I_2 ($[I_2]_0$ = 2 mM for entries 1 and 6 and 1 mM for entry 2). [c] In solution (methyl ethyl ketone (35 vol %) and ethanol (15 vol %)), hence $[HEMA]_0$ = 4 M. [d] Molecular weight = 246. [e] M_n = 2700 and PDI = 1.15.

Figure 5 compares the M_n and PDI values for 4 h (at about 35% conversion in the studied condition in all cases). An early stage of polymerization is focused on to clearly evaluate the catalyst activity. PDI was smaller with an increase of the steric hindrance, i.e., 1.35 for phenol, 1.25 for 2,4-dimethylphenol (2,4-Me), and 1.14−1.19 for thymol and 2,4,6-trimethylphenol (2,4,6-Me), due to (i) the faster formation of R−O• and its sufficiently fast activation. However, PDI was larger with a further increase of the steric hindrance, i.e., 1.24 for BHT with bulky alkyl substituents due to (ii) the slower activation of R−O•. For the resonance effect, the presence of resonance substituents (alkoxy and cyano groups) led to a larger PDI than their absence due to (ii) the slower activation of R−O• (too stable R−O•). The high stability of R−O• with the 4-methoxy substituent (BHA and vitamin E) was previously suggested by Ingold et al.[16] Figure 4 shows the whole (early to later) stages of polymerization for representative phenols, i.e., phenol, 2,4,6-Me, BHT, vitamin E, and BHA.

Phenols with two, three, and four OH groups exhibited better polydispersity control than phenol (with one OH group) with fixing the concentration of the OH group (Figure 6). With a fixed concentration (2 mM) of the OH group, PDI was < 1.2 for hydroquinone (HQ) (with two OH groups) (filled triangle) and hydroxylhydroquinone (HHQ) (with three OH groups) (filled circle), which is smaller than ∼1.35 for phenol (with one OH group) (filled square). The concentration of the OH group was set to be low (2 mM) to clearly see the catalyst activity. The position of the OH groups for the phenols with two OH groups (HQ, resorcinol (RN), and catechol (CC)) (triangles) did not significantly affect PDI. Uric acid (UA) (with three OH groups) (open circle) and morin hydrate (flavonoid) (with four OH groups) (filled pentagon) also exhibited good polydispersity control.

Besides phenols, a conjugated alcohol, vitamin C, was also effective and one of the most effective catalysts for St (Figure 4 (open circle)). Thus, the phenols and the conjugated alcohol (Figure 1) worked as effective catalysts of RTCP. The use of BPB (instead of VR110) led to a faster polymerization as in the TI system, as summarized in Table 1 (entries 2−11). 4-*tert*-Butylcatechol (BCC), which is included in commercially available St at 10−15 ppm, typically, can also work as an RTCP catalyst. We attempted to use the purchased and unpurified St (Aldrich) (including 10−15 ppm BCC) as a monomer and a catalyst (without additional BCC), along with CP-I and a peroxide. However, 10−15 ppm (0.1−0.15 mM) was too small to satisfactorily control the polydispersity, leading to a moderately low PDI of about 1.5 (e.g., M_n = 6900 and PDI = 1.49 at conversion = 49%). The addition of 500 ppm (5 mM) of BCC to this system led to a smaller PDI of about 1.3 (e.g., M_n = 4800 and PDI = 1.27 at conversion = 43%).

Methacrylates. The phenols and vitamin C also well controlled the MMA polymerization at 80 °C (PDI = 1.2−1.4) (Table 1 (entries 12−20)). In contrast to the St polymerization, BHA (entry 16) with a resonance substituent exhibited

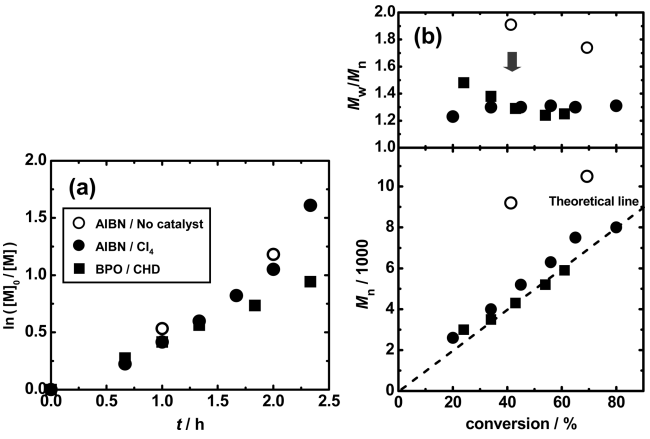


Figure 7. Plots of (a) $\ln([M]_0/[M])$ vs time t and (b) M_n and M_w/M_n vs conversion for the MMA/CP-I/(AIBN or BPO)/carbon catalyst systems (80 °C): $[MMA]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[AIBN]_0$ = 10 mM or $[BPO]_0$ = 20 mM; $[catalyst]_0$ = 0 or 1 mM for CI_4 or 3 mM for CHD, where MMA is methyl methacrylate, CP-I is 2-cyanopropyl iodide (Figure 1), AIBN is azobis(isobutyronitrile), BPO is benzoyl peroxide, and CHD is 1,4-cyclohexadiene (Figure 1). The symbols are indicated in the figure.

particularly good polydispersity control for the MMA polymerization (PDI ∼ 1.2). This would be because the C−I bond of PMMA−I is sufficiently weak, and thus even the stable R−O• from BHA can work as a good activator, where PMMA is poly(methyl methacrylate).

The phenols were applicable to functional methacrylates, i.e., benzyl (BzMA) (with a benzyl group), glycidyl (GMA) (with an epoxide), 2-hydroxyethyl (HEMA) (with a hydroxyl group), and poly(ethylene glycol) (PEGMA) (with a poly(ethylene glycol)) methacrylates, as the examples with CC as a catalyst (Table 2 (entries 1−4)) demonstrate. For BzMA and GMA, a small amount of molecular iodine (I_2) (0.1 and 0.2 equiv to CC, respectively) was added to aid the fast accumulation of Ph−OI (deactivator IA in Scheme 2c) via the reaction of I_2 and Ph−O•. The random and block copolymerizations were also successful (Table 2 (entries 5 and 6)).

2. C Catalysts. *MMA with CI_4*. Carbon tetraiodide (CI_4) was used as a C-centered deactivator catalyst (IA in Scheme 1b) (like TI as an O-centered one). The CI_3• in situ generated works as A• in Scheme 1b. Figure 7 (filled circle) shows the polymerization of MMA (8000 mM) with CP-I (80 mM), azobis(isobutyronitrile) (AIBN) (10 mM) as a conventional radical initiator, and CI_4 (1 mM) at 80 °C. A small PDI (∼1.2) was achieved with such a small amount (1 mM (100 ppm)) of CI_4. The amount is the smallest among the so far studied RTCP catalysts for MMA.[5,6,8] Without the catalyst (Figure 7 (open circle)), PDI was much larger (> 1.5).

MMA with Hydrocarbons. As C-centered precursor catalysts (Scheme 2), we used hydrocarbons (R_2CH_2) possessing conjugated R groups such as CHD. Because of the conjugation

Table 3. Polymerizations with CHD (1,4-Cyclohexadiene) Catalyst ([Monomer]$_0$ = 8 M in Bulk)

entry	monomer (equiv to [CP−I]$_0$)	R−I	I[a]	[R−I]$_0$/[I]$_0$/[CHD]$_0$ (mM)	T (°C)	t (h)	conv (%)	M_n[b] ($M_{n,theo}$)	PDI[b]
1	MMA (100 equiv)	CP−I	BPO	80/20/3	80	2.33	61	5900 (6100)	1.25
2	St (100 equiv)	CP−I	BPO	80/20/3	80	22	100	10300 (10400)	1.32
3	AN (200 equiv)	CP−I	BPO	20/20/2.5[c]	80	2	73	11800 (7800)	1.29
4	EHMA (100 equiv)	CP−I	BPO	80/20/3	80	2	87	13200 (17200)	1.20
5	POMA (100 equiv)	CP−I	V70	40/40/2.5[c]	40	2	100	12800 (16200)	1.24
6	BzMA (100 equiv)	CP−I	BPO	80/20/3	80	2	94	11000 (9300)	1.16
7	GMA (100 equiv)	CP−I	V70	60/15/2.25[c,d]	50	0.67	90	7300 (12800)	1.36
8	PEGMA[e] (100 equiv)	CP−I	V70	80/80/3[d]	50	2	49	11500 (22500)	1.29
9	DMAEMA (100 equiv)	CP−I	AIBN	80/40/10	80	1	90	12300 (14000)	1.40
10	ASt (100 equiv)	CP−I	none	80/0/30	50	1	78	8000 (9300)	1.32
11	HEMA/MMA (50/50 equiv)	CP−I	V70	40/10/10[c,d]	50	1	100	10300 (11900)	1.48
12	MAA/MMA (40/60 equiv)	CP−I	V70	80/80/10[c]	40	1.67	100	8300 (9400)	1.17
13	DMAEMA (100 equiv)	PMMA−I[f]	AIBN	80/40/10	80	0.5	95	18700 (15000)	1.32
14	MAA/MMA (16/24 equiv)	PMMA−I[f]	V70	80/80/5	40	2	80	6600 (5700)	1.31
15	MMA (100 equiv)	CP−I	AIBN	60/15/4[c]	80	1.5	60	6200 (6000)	1.29
	+ BzMA[g] (100 equiv)					+0.5	102	10100 (12500)	1.35
						+1.0	154	16300 (20500)	1.43

[a] I = conventional radical initiator, BPO = benzoyl peroxide, V70 = 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), and AIBN = azobis(isobutyronitrile). [b] Determined by GPC with poly(methyl methacrylate) calibration for entries 1 and 11−15, polystyrene calibration for entry 2, and a multiangle laser light-scattering (MALLS) detector for entries 3−10. [c] Solution polymerization with 50 vol % ethylene carbonate for entry 3, 50 vol % dipropylene glycol monomethyl ether for entries 5 and 12, 25 vol % toluene for entry 7, 15 vol % 1-propanol and 35 vol % methyl ethyl ketone for entry 11, and 25 vol % anisole for entry 15. [d] Addition of I_2 (0.75 mM for entry 7, 1 mM for entry 8, and 1.5 mM for entry 11). [e] Molecular weight = 246. [f] M_n = 2700 and PDI = 1.15. [g] The addition of 1 equiv of AIBN and 0.125 equiv of CHD along with BzMA (100 equiv).

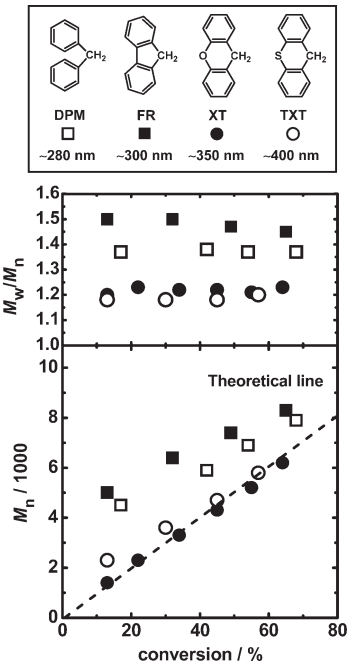


Figure 8. Plots of M_n and M_w/M_n vs conversion for the MMA/I_2/AIBN/BPO/hydrocarbon catalyst systems (80 °C): [MMA]$_0$ = 8 M (in bulk); [I_2]$_0$ = 40 mM; [AIBN]$_0$ = 80 mM; [BPO]$_0$ = 5 mM; [catalyst]$_0$ = 30 mM, where MMA is methyl methacrylate, AIBN is azobis(isobutyronitrile), and BPO is benzoyl peroxide. The symbols are indicated in the figure. The numbers (in the unit of nm) shown below the structures of the catalysts are their wavelengths of UV absorption.

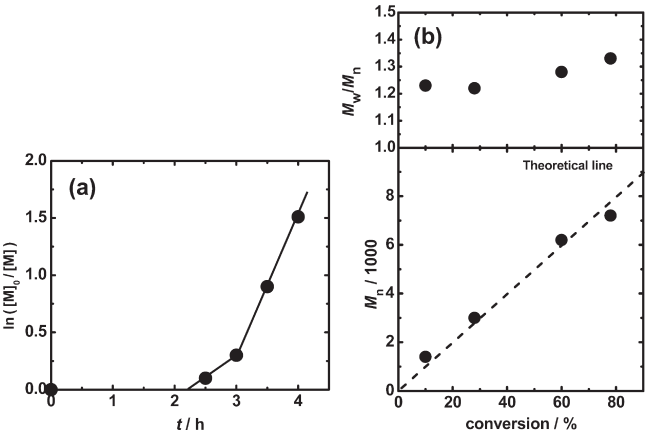


Figure 9. Plots of (a) ln([M]$_0$/[M]) vs time t and (b) M_n and M_w/M_n vs conversion for the MMA/I_2/AIBN/CHD systems (80 °C): [MMA]$_0$ = 8 M (in bulk); [I_2]$_0$ = 40 mM; [AIBN]$_0$ = 80 mM; [CHD]$_0$ = 5 mM, where MMA is methyl methacrylate, AIBN is azobis(isobutyronitrile), and CHD is 1,4-cyclohexadiene (Figure 1).

by the R groups, the C-centered radical $R_2C^{\bullet}H$ (activator A$^{\bullet}$) is readily generated. Figure 7 (filled square) and Table 3 (entry 1) show the polymerization of MMA (8000 mM) with CP−I (80 mM), benzoyl peroxide (BPO) (20 mM) as a conventional radical initiator, and CHD (3 mM) at 80 °C. A small PDI (~1.2) was achieved with a small amount (3 mM) of CHD, which is much smaller than those required for the so far studied precursor catalysts, i.e., 10 mM of diethyl phosphate (P precursor),[5] 30 mM of succinimide (N precursor),[7] and 10 mM of the mentioned phenols (O precursors), for MMA. CHD is thus the most active precursor catalyst for MMA.

We systematically studied hydrocarbons with two phenyl groups (Figure 8), i.e., fluorene (FR), xanthene (XT), and thioxanthene (TXT) with the two phenyl groups connected directly, via oxygen and via sulfur, respectively. The wavelength of the UV absorption of the three compounds is larger in the order of FR (~300 nm) < XT (~350 nm) < TXT (~400 nm), suggesting more effective conjugation in this order. Namely, the C-centered radical may be more easily formed and PDI may be smaller in this order. This was in fact observed, as Figure 8 compares the results at the same precursor concentration of 30 mM. In Figure 8, CP-I (as an alkyl iodide) was generated in situ in the polymerization, as the method will be explained later. Despite the less effective conjugation, diphenylmethane (DPM) (Figure 8) with no bond between the two phenyl groups exhibited fairly good polydispersity control possibly due to other factors. DPM is a common compound and structurally similar to toluene. The usefulness of such a common compound may be practically attractive.

Various Monomers. The C precursor catalysts were applicable to a variety of monomers. Table 3 shows the examples

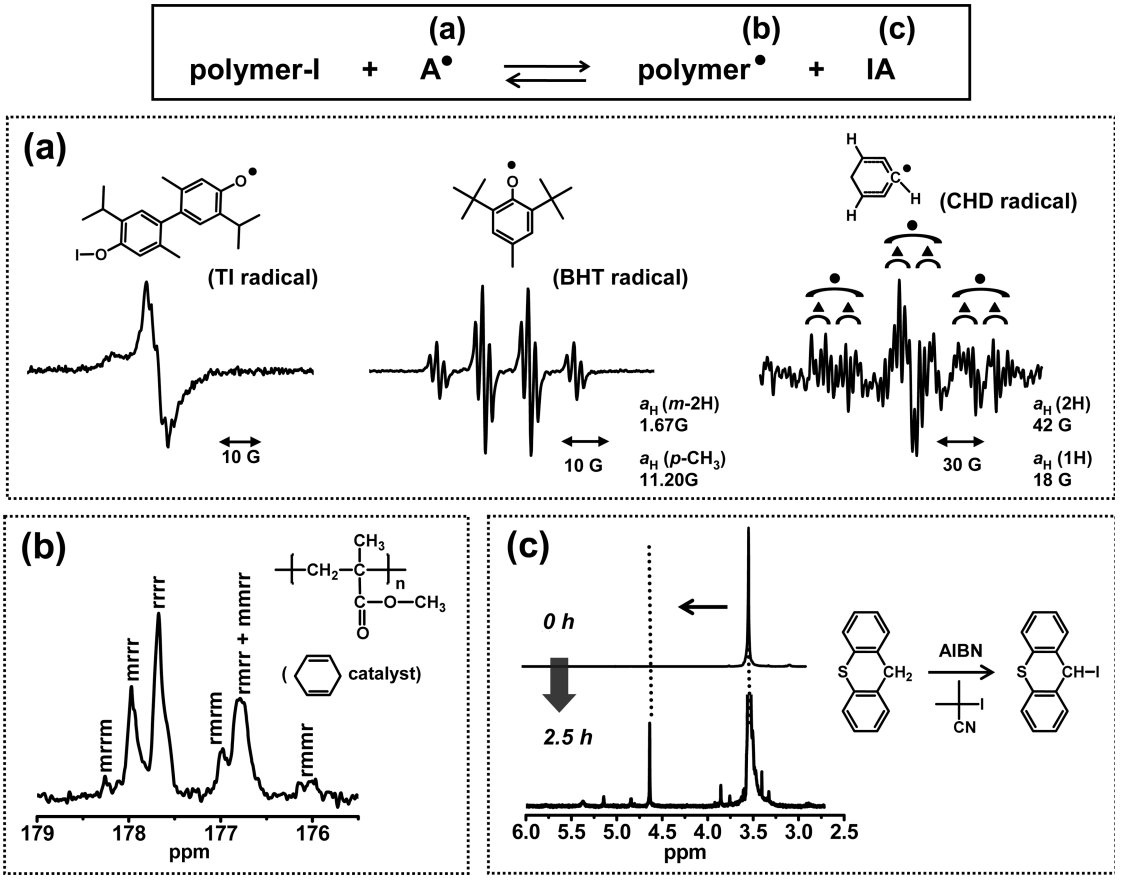


Figure 10. (a) Electron spin resonance (ESR) spectra for the St/PE-I/AIBN/TI system (85 °C), the St/PE-I/BPB/BHT system (100 °C), and the St/PE-I/PDX/CHD system (60 °C): $[St]_0$ = 8 M (in bulk); $[PE\text{-}I]_0$ = 400 mM; $[AIBN]_0$ = 200 mM; $[TI]_0$ = 150 mM for the TI system, $[St]_0$ = 8 M (in bulk); $[PE\text{-}I]_0$ = 400 mM; $[BPB]_0$ = 200 mM; $[BHT]_0$ = 100 mM for the BHT system, and $[St]_0$ = 8 M (in bulk); $[PE\text{-}I]_0$ = 200 mM; $[PDX]_0$ = 200 mM; $[CHD]_0$ = 400 mM for the CHD system, where St is styrene, PE-I is 1-phenylethyl iodide (Figure 1), AIBN is azobis(isobutyronitrile), TI is thymol iodide (Figure 1), BPB is *tert*-butyl perbenzoate, BHT is 3,5-di-*tert*-butyl-4-hydroxytoluene (Figure 1), PDX is di(4-*tert*-butylcyclohexyl)peroxydicarbonate, and CHD is 1,4-cyclohexadiene (Figure 1). (b) ^{13}C NMR spectrum (in the range of 175.5−179 ppm) of the poly(methyl methacrylate) produced in the MMA/CP-I/BPO/CHD system (60 °C): $[MMA]_0$ = 8 M (in bulk); $[CP\text{-}I]_0$ = 80 mM; $[BPO]_0$ = 20 mM; $[CHD]_0$ = 3 mM, where MMA is methyl methacrylate, CP−I is 2-cyanopropyl iodide (Figure 1), and BPO is benzoyl peroxide. (c) ^1H NMR spectra (in the range of 2.5−6.0 ppm) in the toluene-d_8/CP−I/AIBN/TXT system (80 °C) for 0 and 2.5 h: $[CP\text{-}I]_0$ = 80 mM; $[AIBN]_0$ = 80 mM; $[TXT]_0$ = 80 mM, where TXT is thioxanthene (Figure 1).

using CHD. The polymerizations of St (entry 2) and acrylonitrile (AN) (entry 3) were controlled with 3 and 2.5 mM of CHD, respectively. AN was for the first time controlled in RTCP. CHD was highly compatible to functional monomers (entries 4−15), being effective for the homopolymerizations of BzMA (entry 6), GMA (entry 7), and PEGMA (entry 8), as in the phenol systems, and also those of 2-ethylhexyl methacrylate (EHMA) (entry 4), phenyl methacrylate (POMA) (entry 5), (*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) (entry 9), and *p*-aminostyrene (ASt) (entry 10). The latter four were for the first time controlled in RTCP. The random copolymerizations of HEMA (entry 11) and methacrylic acid (MAA) (entry 12) were also successful. The composition of MAA (entry 12) increased from 15% previously achieved with NIS (N catalyst)[6] to 40% with CHD, yielding a water-soluble polymer. (The previous polymer is insoluble in water.) It is worth noting that the RTCP with CHD is applicable to both amino and acid functionalities (DMAEMA, ASt, and MAA) and even to unprotected amino and acid groups (ASt and MAA). Such dual compatibility to amino and acid functionalities is rare in LRP.

Exploiting the living character, we attempted the block copolymerizations using a PMMA−I macroinitiator as the first block (entries 13 and 14). Using DMAEMA (entry 13) and the mixture of MMA and MAA (entry 14) as the second block monomers, the PMMA chain successfully extended, yielding low-polydispersity block copolymers (PDI = 1.3−1.4). Instead of using an isolated macroinitiator, successive addition of two monomers was also attempted. To a polymerization of MMA (first monomer) with CP−I (low-mass alkyl iodide) at a conversion of 60%, the addition of BzMA (second monomer) yielded PMMA-*block*-(PMMA-*random*-PBzMA)s with relatively small PDIs (∼1.4) (entry 15), where PBzMA is poly(benzyl methacrylate).

Use of Alkyl Iodide in Situ Formed in the Polymerization. For the alkyl iodide, we may add molecular iodine I_2 and an azo compound (R−N=N−R) as starting compounds and use the alkyl iodide (R−I) in situ formed in the polymerization.[6−8] This method was originally invented by Lacroix-Desmazes et al. and used in the iodide-mediated LRP.[15] It may be practically useful due to the general lack of the long-term stability of alkyl iodides upon storage. We examined the polymerization of MMA with I_2 (40 mM), AIBN (80 mM), and CHD (5 mM) at 80 °C (Figure 9). AIBN gives 2-cyanopropyl radical CP•, and CP• reacts with I_2 to form CP−I. 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 throughout the polymerization.

Experimental Proof for RT Process. As noted above, RTCP is supposed to involve the RT process. If RT exists (Figure 10), (a) the catalyst radical A$^\bullet$ is mediated and (b) the propagating species is a free radical (Polymer$^\bullet$). Thus, we tried to detect A$^\bullet$ by electron spin resonance (ESR) in the St polymerizations with TI (phenol deactivator), BHT (phenol precursor), and CHD (carbon precursor) (three systems) and to confirm the free radical nature from the tacticity of the product polymer in the St and MMA polymerizations with the three catalysts (six systems). When a precursor is used, (c) the deactivator IA should be formed from the precursor. Thus, we tried to detect IA from TXT (carbon precursor).

A$^\bullet$ was in fact observed in the three systems (Figure 10a). The spectrum for TI was broad probably due to the aggregation (association) of TI in the St medium, and that for BHT clearly split into four peaks (1:3:3:1 ratio: hypersplitting constant a_H = 11.20 G) by the methyl group at the para position and further split into three peaks (1:2:1 ratio: a_H = 1.67 G) by the protons at the meta positions.[17] The spectrum for CHD was somewhat noisy due to the lower concentration of A$^\bullet$ than those for TI and BHT. The spectrum split into three peaks (1:2:1 ratio: a_H = 42 G) because of the protons at the meta positions and further split into two peaks (1: 1 ratio: a_H = 18 G) because of the proton at the central position. In these experiments, we used a large amount (100−400 mM) of the catalyst to facilitate the detection of A$^\bullet$. Nevertheless, the concentration of A$^\bullet$ was low, on the order of 10^{-6} M, in the three cases, indicating that in a typical polymerization condition (with 3−10 mM of the catalyst) it is very low, on the order of 10^{-8}−10^{-7} M, and the activation process (Scheme 1b) effectively occurs at such a low A$^\bullet$ concentration. In Figure 10a, Polymer$^\bullet$ (polystyrene radical) was not apparently detected due to its much lower concentration (10^{-8}−10^{-7} M estimated from the polymerization rate) than that of A$^\bullet$ (10^{-6} M).

The tacticity (pentad distribution) of the product polymer (after purification by reprecipitation) was analyzed by ^{13}C NMR for the six systems. Figure 10b shows an example of the NMR chart, i.e., that for the MMA/CHD system. The tacticity was virtually the same as that without the catalyst (iodide-mediated LRP), meaning that the propagating species is a free radical, in all cases.

The formation of the carbon−iodide adduct IA was confirmed by ^1H NMR (Figure 10c). TXT (precursor), AIBN, and CP−I were heated in toluene-d_8 at 80 °C for 2.5 h. This is a monomer-free (model) system to simplify the NMR analysis, in which all radical reactions except propagation occur as in the monomer-containing system. The carbon−iodide adduct IA was in fact observed (Figure 10c). Thus, the three experiments (Figure 10a−c) strongly indicate the existence of RT.

Conclusions

O- and C-centered organic catalysts were developed for RTCP. They exhibited higher reactivity and higher tolerance to functional groups over the previous RTCP catalysts, significantly improving the polydispersity control and the monomer versatility of RTCP. Thus, RTCP can now be used to a wide variety of applications. The organic catalysts include such common compounds as phenol itself, antioxidants for foods and resins (BHT and BHA) and even natural antioxidants (vitamins, thymol, and flavonoid), and simple dienes (CHD and DPM). Their markedly low cost, excellent environmental safety, and ease of handling may be highly attractive for practical applications, possibly solving some practically important problems of the current LRPs. Mechanistically, the existence of RT was supported by the three experiments.

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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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