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Homogeneous Reverse Atom Transfer Radical Polymerization of Styrene Initiated by Peroxides

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ABSTRACT: The homogeneous reverse atom transfer radical polymerization (ATRP) of styrene was initiated by benzoyl peroxide (BPO) in the presence of CuBr or $CuBr_2$ complexed by 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy). In contrast to the successful reverse ATRP initiated by azobis(isobutyronitrile) (AIBN) and $CuBr_2$/2dNbpy, no control of polymerization was observed for the BPO/$CuBr_2$/2dNbpy system. However, controlled/“living” polymerization was observed when BPO was used together with CuBr/2dNbpy. The differences between the BPO and AIBN systems are ascribed to the electron transfer and the formation of copper benzoate species.

Atom transfer radical polymerization (ATRP) is among the most promising approaches to controlled radical polymerization.[1−3] Copper-mediated ATRP has been successfully used to prepare polymers with predetermined molecular weights, low polydispersities, and precise end functionalities as well as a variety of (co)polymers with controlled topologies and compositions.[4,5] ATRP can be realized using two different initiating systems: either an alkyl halide and transition-metal compound in its lower oxidation state (e.g., CuBr complexed by two molecules of 4,4′-di(alkyl)-2,2′-bipyridine[6] or one molecule of *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine[7]) or a conventional radical initiator such as azobis(isobutyronitrile) (AIBN) with the transition-metal compound in its higher oxidation state (e.g., $CuBr_2$ complexed by an appropriate ligand). The latter approach has been named reverse ATRP and was successfully used for copper-based heterogeneous[8,9] and homogeneous[10] systems in solution and in emulsion[11] as well as for iron complexes.[12]

In reverse ATRP, it is important to use metal halides (e.g., cupric dibromide), since salts with anions that cannot be efficiently transferred by a radical mechanism, such as cupric ditriflate or cupric diacetate, cannot reversibly deactivate the growing radicals. For example, the polymerization of methyl acrylate was not affected by $Cu(OTf)_2$/2dNbpy (dNbpy = 4,4′-di(5-nonyl)-2,2′-bipyridine), and the polymerization of styrene showed some reduction of rates and molecular weights only when a large excess of cupric ditriflate over AIBN was used.[13] The latter behavior was ascribed to a slow outer-sphere electron-transfer (OSET) process[14] with the oxidation of growing styryl radicals to carbocations. It should be noted that conventional ATRP initiated by alkyl halides and catalyzed by copper carboxylates[15−17] or triflates[13] proceeds faster than that catalyzed by copper halides. In this paper, we report the unusual behavior of reverse ATRP initiated by peroxides rather than by azo initiators.[18]

Table 1 compares the results of the bulk styrene polymerization initiated by AIBN and benzoyl peroxide (BPO) in the presence of $CuBr_2$ or CuBr complexed by dNbpy. With $[AIBN]_0 = 0.09$ mol/L alone as the initiator, i.e., without copper halide, polystyrene of $M_n = 9700$ and $M_w/M_n = 2.6$ was obtained in 66% yield after 1 h at 110 °C. A similar result was obtained in the presence of CuBr/2dNbpy, indicating no appreciable interaction of the salt with either the radicals or AIBN. When the reaction was carried out in the presence of $CuBr_2$/2dNbpy, the color of the initially green solution of cupric complex changed to red, typical for cuprous species. Moreover, a controlled reverse ATRP process occurred, as reported previously.[10]

However, the peroxide-initiated system behaved very differently. Using $[BPO]_0 = 0.09$ mol/L in a blank experiment carried out at 110 °C in bulk without copper halide, polystyrene of $M_n = 11\,300$ and $M_w/M_n = 2.19$ was obtained in 86% yield after 30 min. In the presence of $CuBr_2$/2dNbpy, the solution remained green even when an excess of BPO was used. The reactions were very slow, and polymers with relatively high polydispersities ($M_w/M_n > 2.0$) were obtained.

Surprisingly, control of the polymerization was obtained in the presence of CuBr/2dNbpy (vide infra). After 1.5 h, polystyrene with $M_n = 10\,700$ and $M_w/M_n = 1.14$ was obtained in 61% yield (entry 8). In the presence of CuBr but without the complexing ligand, only oligomers were obtained with low conversion after 30 min. The reaction carried out in the presence of ligand alone behaved similarly to the blank experiment. When a large excess of BPO with regard to CuBr/2dNbpy was used, the color remained green and control was lost, resulting in a polymer with bimodal molecular weight distribution (entry 12). When the reaction was carried out in the presence of salts whose anions cannot reversibly deactivate the growing radicals, uncontrolled polymerizations, similar to BPO alone, were obtained (entries 13 and 14).

It is known that cuprous salts act as very efficient accelerators in the decomposition of peroxides.[19,20] The resulting radical anions decompose to radicals and anions (e.g., carboxylate) which can initiate polymerization and coordinate to the salt in the higher oxidation state, respectively. Scheme 1 presents the reactions involved in the ATRP process initiated by BPO/CuBr/2dNbpy (dNbpy ligand was omitted to simplify the scheme).

The benzoyloxy primary radicals are generated from the BPO initiator either by the thermal decomposition

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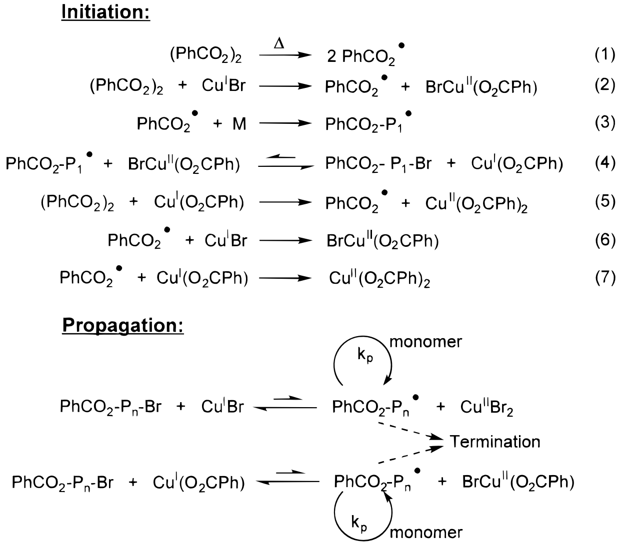
Table 1. Polymerizations of Styrene in Bulk at 110 °C Initiated by AIBN and BPO in the Presence of Copper Complexes

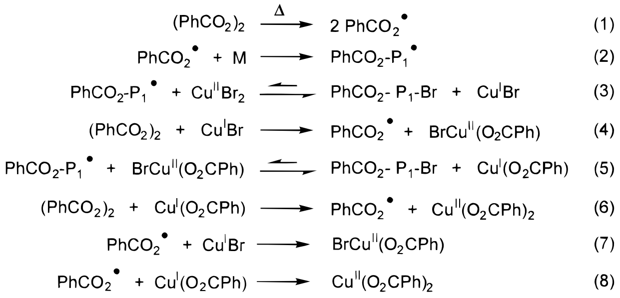
entry	M_tX	In	$[In]_0/[M_tX]_0/[dNbpy]_0$	time (h)	conv (%)	$M_{n,SEC}$	M_w/M_n
1[a]		AIBN	1/0/0	1.0	66	9 700	2.60
2[a]	CuBr	AIBN	1/1/2	1.0	64	9 200	2.90
3[b]	$CuBr_2$	AIBN	0.6/1/2	4.6	69	5 500	1.11
4[c]		BPO	1/0/0	0.5	86	11 300	2.19
5[d]	$CuBr_2$	BPO	0.6/1/2	39.0	19	*i*	*i*
6[e]	$CuBr_2$	BPO	1.5/1/2	93.0	45	2 900	1.58
7[f]	$CuBr_2$	BPO	2.5/1/2	13.0	67	3 700	1.70
8[c]	CuBr	BPO	1/1/2	1.5	61	10 700	1.14
9[c]	CuBr	BPO	1/1/0	0.5	10	*i*	*i*
10[c]	CuBr	BPO	1/0/2	0.5	93	13 500	2.23
11[e]	CuBr	BPO	1.5/1/2	1.0	77	8 400	1.21
12[g]	CuBr	BPO	2/1/2	1.0	87	7 300	1.68[h]
13[c]	CuAc	BPO	1/1/2	0.5	51	18 800	1.92
14[c]	$CuAc_2$	BPO	1/1/2	0.5	82	11 900	2.21

[a] Conditions: initiator (In) = AIBN; $[styrene]_0 = 8.7$ M (bulk); $[styrene]_0/[AIBN]_0 = 96$. [b] $[Styrene]_0/[AIBN]_0 = 160$. [c] $[Styrene]_0/[BPO]_0 = 96$. [d] $[Styrene]_0/[BPO]_0 = 160$. [e] $[Styrene]_0/[BPO]_0 = 64$. [f] $[Styrene]_0/[BPO]_0 = 38$. [g] $[Styrene]_0/[BPO]_0 = 48$. [h] Bimodal distribution. [i] Oligomer.

Scheme 1. Mechanism of Reverse ATRP Initiated by BPO/CuBr



Scheme 2. Mechanism of Initiation Using $BPO/CuBr_2$



(step 1) or by the induced decomposition through the OSET process (steps 2 and 5). The significantly faster OSET process makes it the dominant pathway to generate the benzoyloxy primary radicals. In addition to the formation of oligomers with benzoate tail groups (some phenyl tail groups from decarboxylation can also be formed) and bromine headgroups, the initiation process generates $Cu(O_2CPh)$, which can participate in the induced decomposition of the BPO initiator and result in the formation $Cu(O_2CPh)_2$. Since $Cu(O_2CPh)_2$/2dNbpy does not reversibly deactivate the growing radicals, the benzoyloxy radicals generated in step 5 cannot form oligomers with bromine headgroups. As a result, initiator efficiency[21] is reduced. The benzoyloxy radicals may also oxidize CuBr and $Cu(O_2CPh)$ to the corresponding Cu(II) speces (steps 6 and 7), resulting in the decrease of initiator efficiency and the consumption of active catalyst. Propagation proceeds similarly to conventional ATRP, with the produced $Cu(O_2CPh)$/2dNbpy and the remaining CuBr/2dNbpy acting as the catalyst to generate radicals and reversibly form $CuBr_2$/2dNbpy and $BrCu(O_2CPh)$/2dNbpy as deactivators. Radicals propagate by adding monomer, are reversibly deactivated, and can also terminate. In the absence of the ligand, only bromine-terminated oligomers are obtained as they cannot be activated for propagation (Table 1, entry 9). When a sufficient excess of BPO over CuBr is used, the copper species are completely and irreversibly converted to $Cu(O_2CPh)_2$, which can no longer participate in the ATRP process (Table 1, entry 12).

In contrast, $CuBr_2$/2dNbpy does not accelerate the decomposition of BPO (Scheme 2). However, it deactivates the growing radicals and generates in situ, in addition to bromine-terminated oligomers, CuBr/2dNbpy which then induces the decomposition of BPO by OSET. After deactivation of the growing radicals by $BrCu(O_2CPh)$/2dNbpy, the newly formed $Cu(O_2CPh)$/2dNbpy also participates in the induced decomposition of BPO. As a result, the intermediate Cu(I) species, both CuBr and $Cu(O_2CPh)$, are reoxidized to Cu(II) species by BPO. In other words, for the BPO/$CuBr_2$/2dNbpy system, there are almost no Cu(I) species for activation, and only $CuBr_2$, $BrCu(O_2CPh)$, and $Cu(O_2CPh)_2$ are present. Thus, ATRP cannot occur. From Scheme 2, it can be seen that 1 equiv of $CuBr_2$/2dNbpy can react with 2 equiv of BPO and generate 2 equiv of bromine-terminated oligomers.

It is known that the aromatic substitution reaction of the benzoyloxy radical is strongly reversible,[19] but the intermediate radical can be trapped by an oxidizing reagent such as $CuCl_2$.[22] This possible pathway as a side reaction to the initiation process is shown in Scheme 3. In our studies, a ligand such as dNbpy is used to complex the copper species, and this should decrease the Cu(II) redox potential. Nevertheless, the pathway shown in Scheme 3 may be additionally responsible for the inefficient reverse ATRP for the BPO/$CuBr_2$/2dNbpy system.

Figures 1, 2, and 3 present the results of the kinetic studies of the polymerization of styrene in a 50 vol % anisole solution at 110 °C using the BPO/CuBr/2dNbpy initiating system. When the concentration of BPO was

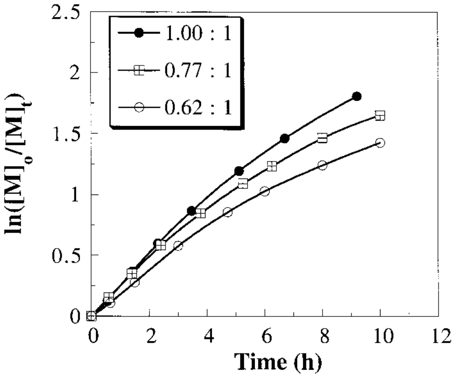


Figure 1. Kinetic plots for the ATRP of styrene initiated by BPO/CuBr/2dNbpy at 110 °C, varying $[BPO]_0$. $[Styrene]_0 = 4.3$ M (50 vol % anisole); $[CuBr]_0 = [dNbpy]_0/2 = 0.045$ M; $[BPO]_0 = 0.045$ M (1:1), 0.035 M (0.77:1), and 0.028 M (0.62:1).

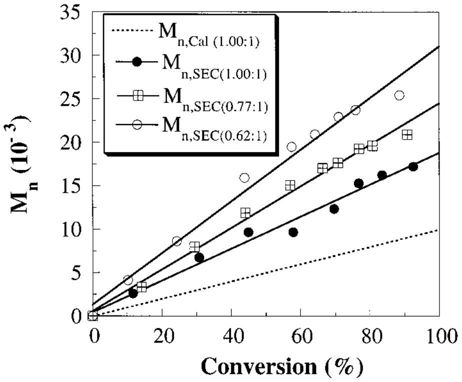
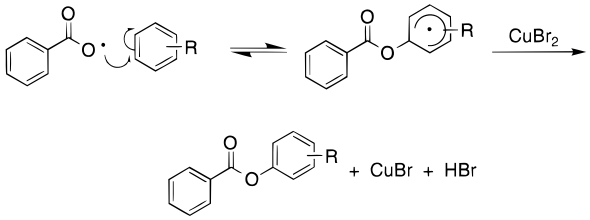


Figure 2. Dependence of molecular weight ($M_{n,SEC}$) on monomer conversion for the ATRP of styrene initiated by BPO/CuBr/2dNbpy at 110 °C, varying $[BPO]_0$. See Figure 1 for conditions.

Scheme 3. Aromatic Substitution Reaction of the Benzoyloxy Radical



progressively increased from $[BPO]_0 = 0.028$ to 0.035 and 0.045 mol/L with a constant concentration of $[CuBr/2dNbpy]_0 = 0.045$ mol/L, the rate of polymerization increased only slightly. Apparently, rate was not strongly affected by $[BPO]_0$, probably due to both a relatively low efficiency of initiation and short half-lifetime of BPO at 110 °C. All the kinetic plots showed some curvature with the increase of reaction time. This can partially be ascribed to the side reaction of anion exchange of Br^- on the polymer chain ends with O_2CPh^- of the copper complex, similar to what was reported previously for styrene polymerization carried out in the presence of copper carboxylates.[15] It can also be ascribed to the slow termination reaction of the macromolecular alkyl halide or growing polymeric radicals with the Cu(II) species which becomes more pronounced when the polymerization is carried out in a polar solvent such as anisole.[23]

Figure 2 shows the evolution of molecular weights (M_n) with conversion for the three discussed systems. In all cases, the number of chains roughly corresponds to an apparent initiator efficiency of 50% based on $[BPO]_0$. This means that not all bromines were transferred from CuBr/2dNbpy to polymer headgroups and may indicate the presence of both CuBr/2dNbpy and $Cu(O_2CPh)$/2dNbpy as activators. The low initiator efficiency may also be ascribed to the aromatic substitution reaction as shown in Scheme 3.

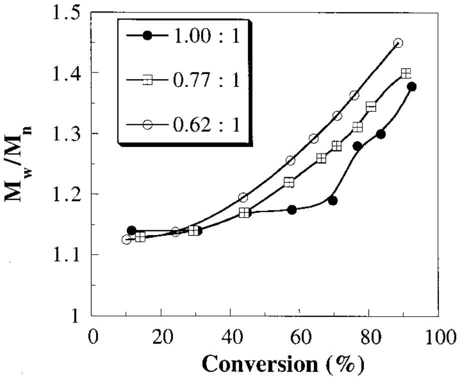


Figure 3. Dependence of polydispersity (M_w/M_n) on monomer conversion for the ATRP of styrene initiated by BPO/CuBr/2dNbpy at 110 °C, varying $[BPO]_0$. See Figure 1 for conditions.

Figure 3 illustrates the evolution of polydispersities (M_w/M_n) with conversion. For all three systems, the polydispersities were initially quite low ($M_w/M_n < 1.15$) but progressively increased with conversion. The increase of polydispersity corresponds to the kinetic curvature and is attributed to the side reactions discussed before.

Other peroxides have also be studied in conjunction with CuBr/2dNbpy. In general, peroxides that undergo facile induced decomposion by cuprous salts yielded polystyrenes with low polydispersities ($M_w/M_n < 1.20$). Therefore, diakyl peroxides and hydroperoxides are less efficient initiators in the presence of CuBr/2dNbpy (Supporting Information, Table S1). Moreover, the BPO/$CuBr_2$/2dNbpy system can be improved by the addition of Cu(0) powder (Supporting Information, Table S2). This approach yielded similar results as the BPO/CuBr/2dNbpy system, since the presence of Cu(0) enables the reduction of $CuBr_2$, $BrCu(O_2CPh)$, or $Cu(O_2CPh)_2$ to the corresponding cuprous species which can catalyze ATRP.[24]

In summary, we would like to emphasize the differences in the homogeneous reverse ATRP initiated by azo compounds and peroxides. In the former process, reverse ATRP occurs efficiently in the presence of $CuBr_2$/2dNbpy, which can scavenge initiating/growing radicals and form CuBr/2dNbpy and RBr species. In addition, initiating/growing radicals do not interact with CuBr/2dNbpy species. In contrast, $CuBr_2$/2dNbpy is an inefficient component of reverse ATRP initiated by BPO. This is due to electron transfer from Cu(I) to BPO and coordination of benzoate anions to copper. Such an induced decomposition reoxidizes Cu(I) back to Cu(II) species and disables the catalytic reaction. However, the polymerization initiated by BPO can be controlled in the presence of a sufficient amount of CuBr. After the induced decomposition of BPO, the growing radicals are deactivated by Cu(II) species to produce bromine-terminated oligomers and Cu(I) species. Both $Cu(O_2CPh)$ and CuBr complexed by the ligand can then successfully catalyze ATRP.

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Supporting Information Available: Tables showing polymerizations of styrene initiated by CuBr/2dNbpy and different peroxides and by BPO/$CuBr_2$/Cu(0)/2dNbpy. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Typical polymerizations are as follows. *Solution*: A dry round-bottom flask was charged with CuBr and dNbpy. The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed monomer and solvent were added using degassed syringes. The flask was immersed in an oil bath held by a thermostat at the desired temperature and allowed to stir until the mixture became homogeneous. Then, BPO, dissolved in a small amount of monomer, was added dropwise. At timed intervals, samples were withdrawn from the flask using a degassed syringe and added to THF. *Bulk*: To a dry glass tube with copper halide and dNbpy under argon was added a solution of BPO dissolved in the monomer. Three freeze–pump–thaw cycles were performed, and the tube was sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature. The polymerization was stopped by cooling the tube in ice–water. Afterward, the tube was opened and the contents were dissolved in THF.
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(21) The calculated molecular weight $M_{n,Cal} = ([M]_0/[BPO]_0) \times (MW)_0 \times$ conversion, where $[M]_0$ and $[BPO]_0$ represent the initial concentrations of monomer and BPO and $(MW)_0$ is the molecular weight of the monomer. The apparent initiator efficiency = $M_{n,Cal}/M_{n,SEC}$, includes both the intrinsic initiator efficiency and any contribution from termination of the growing chains.
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