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Notes

Copper(II) Compound Catalyzed Living Radical Polymerization of Methyl Methacrylate in the Presence of Benzoyl Peroxide

Peng Li and Kun-Yuan Qiu*

Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Introduction

Benzoyl peroxide (BPO) is a widely used radical initiator. In the presence of copper(I) halides, the polymerization of vinyl monomers with BPO can be well controlled, namely reverse atom transfer radical polymerization (ATRP).[1−4] Copper(II) species are reportedly incapable of inducing a controlled course.[5,6] For instance, in the presence of CuBr$_2$/2dNbpy [dNbpy = 4,4′-di(5-nonyl)-2,2′-bipyridine] and BPO, the polymerization of styrene (St) produced oligomers at $[\mathrm{BPO}]_0/[\mathrm{CuBr}_2/2\mathrm{dNbpy}]_0 = 2/1$ ratio, presumably because no activator but only deactivators were present. However, we first report here that the polymerization of methyl methacrylate (MMA) with BPO is controlled in conjunction with Cu(S$_2$CNEt$_2$)Cl, a mixed-ligand copper(II) compound (so-called in the field of inorganic chemistry), and 2,2′-bipyridine (bpy).

Experimental Section

Materials. MMA and St (Beijing Chemical Factory, 98%) were dried over CaH$_2$ and vacuum-distilled. BPO (Beijing Chemical Factory, 95%) was purified by precipitation from chloroform to petroleum ether (distillation range 60−90 °C). Bpy (Acros, 99%) was recrystallized from ethanol. Chloride mixed-ligand diethyldithiocarbamate complex of copper(II), Cu(S$_2$CNEt$_2$)Cl, and cuprous *N*,*N*-diethyldithiocarbamate, Cu(S$_2$CNEt$_2$), were synthesized as reported previously.[7,8] Cuprous chloride (CuCl) was synthesized from CuCl$_2$·2H$_2$O (Beijing Chemical Factory, 99%) and purified according to the literature.[9]

ATRP Procedure. In a typical run, the dry glass tube containing MMA (2.00 g, 0.02 mol), BPO (4.8 mg, 0.02 mmol), Cu(S$_2$CNEt$_2$)Cl (9.8 mg, 0.04 mmol), and bpy (18.7 mg, 0.12 mmol) was degassed by three vacuum−nitrogen cycles and sealed under vacuum. Then the tube was placed in an oil bath thermostat at 100 °C. After 62 h, the polymerization was stopped by cooling the tube in liquid nitrogen. The tube was opened, and the reaction mixture was dissolved in 20 mL of tetrahydrofuran (THF). The solution was filtered and precipitated with 200 mL of petroleum ether to obtain the polymer, which weighed 1.22 g after being vacuum-dried. Monomer conversion (61%) was determined gravimetrically. The number-average molecular weight ($M_{\mathrm{n(GPC)}}$) and molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) of the resulting PMMA analyzed by gel permeation chromatography (GPC) were 91 000 and 1.24, respectively.

Photopolymerization. The polymerization was carried out under UV irradiation when monomer (St or MMA) was added to the resulting PMMA. For example, St (2.10 g, 0.02 mol) was added to PMMA (97.2 mg, 0.011 mmol) in a baked glass tube. After degassing three times, the tube was sealed and irradiated with a 250 W high-pressure mercury lamp from a distance of 20 cm at ambient temperature. After 34 h, the tube was removed and opened. The reaction mixture was treated as stated above. St conversion was gravimetrically measured to be 81%. $M_{\mathrm{n(GPC)}}$ and $M_\mathrm{w}/M_\mathrm{n}$ of the block copolymer PMMA-*b*-PSt analyzed by GPC were 107 100 and 1.70.

Characterization. GPC analysis was carried out on a Waters 515 pump equipped with μ-Styragel columns (10^1, 10^2, and 10^3 nm pore sizes) at 35 °C. THF was used as eluent at a rate of 1.0 mL min^{-1}. The gel columns were calibrated using PSt standard samples (M_n ranging from 600 000 to 1000). Data were processed by Waters Millennium 32 software. The ultraviolet spectrum of the polymer was measured in acetonitrile with an Ultraviolet Cary-1E instrument.[10]

Results and Discussion

Table 1 exhibits the results of MMA polymerization initiated with BPO and catalyzed by Cu(S$_2$CNEt$_2$)Cl or Cu(S$_2$CNEt$_2$). The polymerization is ill controlled with BPO initiator alone (entries 1 and 2). Cu(S$_2$CNEt$_2$)Cl inhibited the reaction (entries 3 and 4), with only 9% monomer conversion after 120 h. The polymerization proceeded smoothly in the presence of Cu(S$_2$CNEt$_2$)Cl/bpy (entries 5 and 6) or Cu(S$_2$CNEt$_2$)/bpy (entries 7 and 8). The rate was slower with Cu(S$_2$CNEt$_2$)Cl/bpy, 19% conversion in 14 h, than that with Cu(S$_2$CNEt$_2$)/bpy, which had become a solid after 10 h and reached a higher conversion, 54%, because of the rapid redox reaction between BPO and Cu(S$_2$CNEt$_2$).

The kinetic and molecular weight characteristics of PMMA produced using $[\mathrm{MMA}]_0/[\mathrm{BPO}]_0/[\mathrm{Cu(S_2CNEt_2)Cl}]_0/[\mathrm{bpy}]_0 = 1000/1/2/6$ in bulk at 100 °C are presented in Figures 1 and 2. The first-order kinetics with respect to reaction time indicates that no termination occurs. The monomer conversion increased with time up to 68% until the system became a solid in 75 h. $M_{\mathrm{n(GPC)}}$ was revised (eq 1), considering the different hydrodynamic volumes between PMMA and PSt.[11] $M_{\mathrm{n(Rev)}}$ values were higher than the calculated ones, $M_{\mathrm{n(Cal)}}$, assuming that one initiating molecule produces one polymer chain (eq 2). The initiator efficiency, *f*, calculated from $M_{\mathrm{n(Cal)}}/M_{\mathrm{n(Rev)}}$, is 0.5, which indicates that side reactions occur.

$$M_{\mathrm{n(Rev)}} = 0.644 M_{\mathrm{n(GPC)}}^{\ 1.019} \qquad (1)$$

$$M_{\mathrm{n(Cal)}} = ([\mathrm{MMA}]_0/2[\mathrm{BPO}]_0) \times \mathrm{MW}_{\mathrm{MMA}} \times \mathrm{conversion} \qquad (2)$$

UV spectroscopic analysis of the resulting PMMA demonstrates that the polymer chain contains a S$_2$CNEt$_2$ group by its characteristic absorption at 282

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* Corresponding author: Tel +86-10-6275-4187; Fax +86-10-62751708; e-mail kyqiu@chem.pku.edu.cn.

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Scheme 1. Elementary Reactions of Radical Polymerization Using the BPO/Cu(S_2CNEt_2)Cl/bpy Initiation System

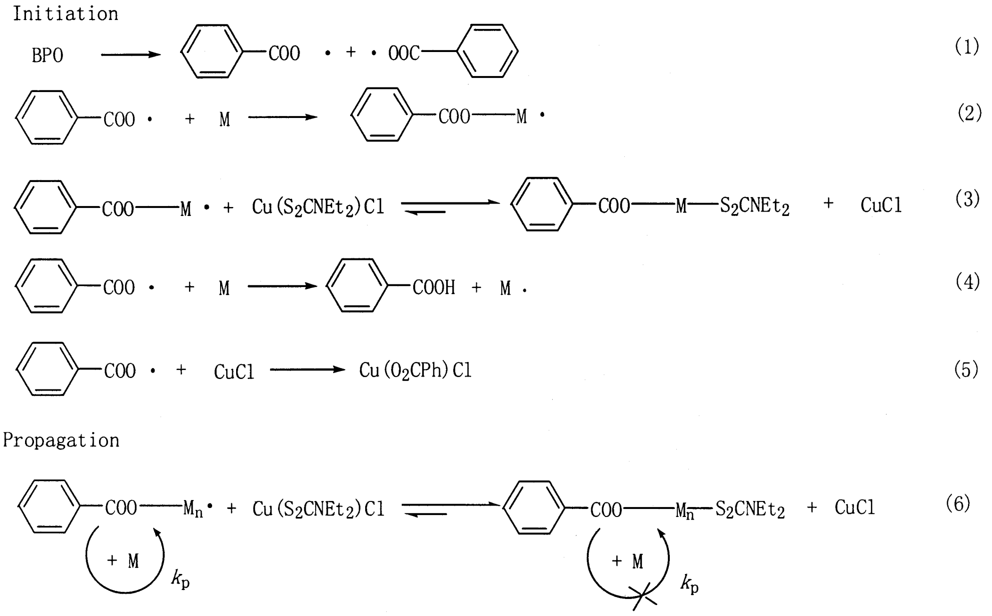

Table 1. Bulk Radical Polymerization of Methyl Methacrylate Initiated with BPO at 100 °C in the Presence of Different Copper Catalysts

entry	catalyst	$[BPO]_0/[catalyst]_0/[bpy]_0$[a]	time	conversion (%)	$M_{n(Cal)}$	$M_{n(Rev)}$[d]	M_w/M_n
1		1/0/0	15 min	22		105 500	1.50
2		1/0/0	26 min	43		143 100	1.51
3	Cu(S_2CNEt_2)Cl	1/2/0	60 h	2			
4	Cu(S_2CNEt_2)Cl	1/2/0	120 h	9			
5	Cu(S_2CNEt_2)Cl	1/2/6	14 h	19	9500[b]	21 000	1.17
6	Cu(S_2CNEt_2)Cl	1/2/6	62 h	61	30 600[b]	73 000	1.24
7	Cu(S_2CNEt_2)	1/1/3	5.3 h	34	34 000[c]	75 000	1.16
8	Cu(S_2CNEt_2)	1/1/3	10 h	54	54 000[c]	117 900	1.32

[a] $[MMA]_0 = 9.4$ mol L^{-1}, $[MMA]_0/[BPO]_0 = 1000/1$. [b] $M_{n(Cal)} = ([MMA]_0/2[BPO]_0) \times MW_{MMA} \times$ conversion, where MW_{MMA} is the molecular weight of MMA. [c] $M_{n(Cal)} = ([MMA]_0/[BPO]_0) \times MW_{MMA} \times$ conversion. [d] $M_{n(Rev)} = 0.644M_{n(GPC)}^{1.019}$.

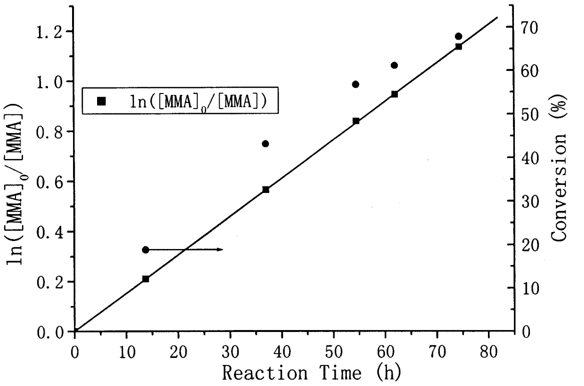

Figure 1. Kinetic plot of bulk MMA polymerization at 100 °C initiated by BPO/Cu(S_2CNEt_2)Cl/bpy. Conditions: $[MMA]_0 = 9.4$ mol L^{-1}, $[MMA]_0/[BPO]_0/[Cu(S_2CNEt_2)Cl]_0/[bpy]_0 = 1000/1/2/6$.

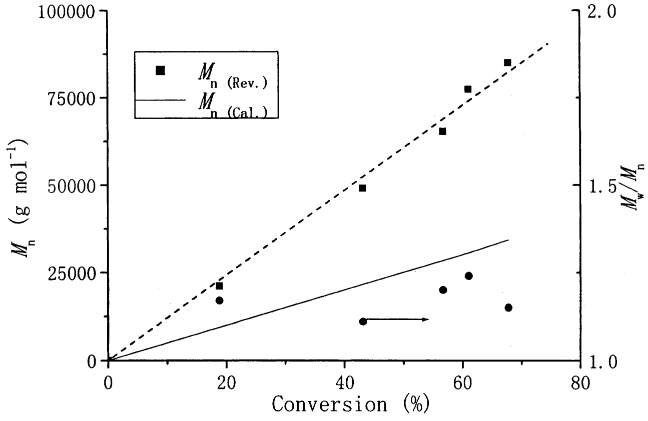

Figure 2. Dependence of M_n and M_w/M_n on monomer conversion during the bulk polymerization of MMA at 100 °C with BPO/Cu(S_2CNEt_2)Cl/bpy initiation system. Conditions identical to Figure 1. Notes: $M_{n(Cal)} = ([MMA]_0/2[BPO]_0) \times MW_{MMA} \times$ conversion, $M_{n(Rev)} = 0.644M_{n(GPC)}^{1.019}$.

nm.[10] When a fresh feed of St was added to a pre-PMMA ($M_{n(GPC)} = 8500$, $M_w/M_n = 1.28$), 81% of St reacted after 34 h under UV irradiation at ambient temperature, producing PMMA-*b*-PSt of $M_{n(GPC)} = 107\,100$ and $M_w/M_n = 1.70$. Similarly, post-PMMA of $M_{n(GPC)} = 74\,000$ and $M_w/M_n = 1.64$ was produced after 20 h and 78% MMA conversion (Figure 3). Otherwise, polymerizations of St or MMA alone without initiators under UV irradiation resulted in only 13% conversion after 34 h and 12% after 20 h, respectively. Therefore, pre-PMMA initiated the photopolymerization of St and MMA, demonstrating that the polymer did contain the photolabile group.

Pre-PMMA can also serve as a macroinitiator for a fresh feed of MMA when normal ATRP is performed in bulk with CuCl/bpy or Cu(S_2CNEt_2)/bpy catalyst. The chain extension of MMA (2.00 g, 0.02 mol) with CuCl/bpy catalyst at 100 °C ($[MMA]_0/[pre\text{-}PMMA]_0/[CuCl]_0/[bpy]_0 = 1920/1/1/3$) generated post-PMMA ($M_{n(GPC)} = 122\,000$, $M_w/M_n = 1.11$). The same polymerization catalyzed by Cu(S_2CNEt_2)/bpy at 125 °C produced post-

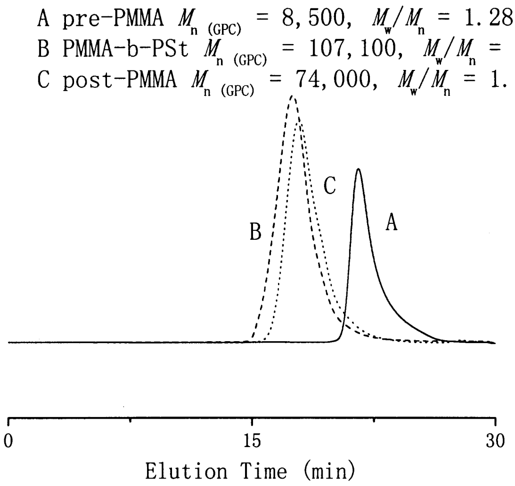

Figure 3. GPC traces of polymers before and after chain extensions using UV irradiation at ambient temperature. Conditions: $[\text{pre-PMMA}]_0 = 4.9 \times 10^{-3}$ mol L^{-1}, before irradiation (A), $[\text{St}]_0 = 8.7$ mol L^{-1} (B), $[\text{MMA}]_0 = 9.4$ mol L^{-1} (C).

PMMA of $M_{n(GPC)} = 132\,000$ and $M_w/M_n = 1.49$. The change of M_w/M_n is consistent with the literature.[12-14]

The primary radical is generated by the redox reaction between the initiator and catalyst in the living polymerization of MMA with BPO/Cu(S_2CNEt_2)/bpy.[8] However, the polymerization with BPO/Cu(S_2CNEt_2)-Cl/bpy requires the thermolysis of the initiator as displayed in Scheme 1 (bpy omitted for simplification). Two benzoyloxy radicals $PhCOO^{\bullet}$ are generated, initiating the polymerization by reacting with MMA to form a monomer radical, which either combines reversibly with Cu(S_2CNEt_2)Cl or reacts with additional monomer molecules to form a growing carbon-centered radical that subsequently combines reversibly with Cu(II) (reactions 1−3). The propagating reaction (6) is similar to an ATRP procedure. The generated monomer radical or growing carbon-centered radical preferentially captures S_2CNEt_2, provided that the bond energy of Cu−S is weaker than that of Cu−Cl.[8,15,16] Thus, the resulting polymer should be functionalized with α-OOCPh and ω-S_2CNEt_2 groups.

Side reactions accounted for the decreasing initiator efficiency. MMA can donate an active hydrogen atom to the primary radical, producing benzoic acid and a more stable allytic type radical (reaction 4).[8,17] The generated copper(I) species, CuCl, is capable of abstracting the benzoyloxy radical (reaction 5).[1] The cage effect on the primary radical will also lower the *f* value. Therefore, only parts of primary radicals attend the propagation.

Conclusions

Reverse ATRP with BPO initiator can be catalyzed by a copper(II) compound, Cu(S_2CNEt_2)Cl. The polymerization of MMA initiated with BPO/Cu(S_2CNEt_2)Cl/bpy was successfully performed. Polymers with narrow M_w/M_n were synthesized under heterogeneous conditions. Chain extensions indicate that the resulting polymer is functionalized with a photosensitive group, $-S_2CNEt_2$. In comparison to the reverse process with BPO/Cu(S_2CNEt_2)/bpy initiation system, the primary radical was generated via the homolysis of the initiator, not the redox reaction between the initiator and catalyst.

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Note Added after ASAP Posting

This note was released ASAP on 10/21/2002 with an error on page 3, left-hand column, paragraph 1, sentence 5. The correct version was posted on 10/29/2002.

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