A Copper-Based Reverse ATRP Process for the Living Radical Polymerization of Methyl Methacrylate

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ABSTRACT: The reverse atom transfer radical polymerization (RATRP) technique using $CuCl_2$/bipyridine (bipy) complex as a catalyst was applied to the living radical polymerization of methyl methacrylate (MMA). A hexa-substituted ethane thermal iniferter, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), was used as the initiator in this copper-based reverse ATRP initiation system. The reversible dissociation nature of DCDPS gives a more suitable amount of primary radical than formerly used conventional initiators, such as AIBN. High molecular weight and narrow molecular weight distribution ($M_w/M_n \approx 1.20$) of the resulting PMMA was obtained in bulk and in solution polymerization at 85°C. End-group analysis result by ^{1}H-NMR spectroscopy shows that the polymer obtained is ω-functionalized by a chlorine group, which can be used as macroinitiator for chain extension and block copolymerization with a conventional ATRP catalyst. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2237–2245, 2001

Key words: living radical polymerization; reverse ATRP; iniferter; methyl methacrylate

INTRODUCTION

Since Szwarc first reported on anionic living polymerization and defined the living polymerization as a chain-growth process without chain-breaking reactions (transfer and termination),[1] much effort has been made to find a living radical polymerization system. Due to the facile coupling and disproportionation reactions between the propagating radicals during polymerization, it is very difficult to reach true living radical polymerization.[2] However, in recent years several methods, such as nitroxide-mediated stable free radical polymerization (SFRP),[3,4] atom transfer radical polymerization (ATRP),[5–7] reversible addition fragmentation chain transfer (RAFT), etc.,[8] have been developed in the living radical polymerization process.[9]

ATRP is based on transition metal-catalyzed atom transfer radical addition including the reversible formation of carbon-centered radicals via homolytic cleavage of carbon–halogen bonds by transition metals in a low oxidation state, such as copper(I),[6,7,10] iron(II),[11,12] and ruthenium(II).[5,13,14] Conventionally, in the ATRP system the organic halides (e.g., haloalkanes, haloketones, halonitriles, haloesters, arenesulfonyl chloride) are used as the initiators to reversibly generate initiating radicals in the presence of complexes of transition metals in their lower oxidation states. The ATRP method was successfully applied to the living radical polymerization of St,[6,7,15] MMA,[11] methyl acrylate (MA),[16] acrylonitrile,[17] and n-butyl acrylate etc.[18] It also provides controlled chain end structure to prepare

functional polymers, such as block, graft, and star polymers.[6,19–21]

Among all of the transition metals, copper appears to be the most robust because of its versatility, for example, a variety of monomers can be readily polymerized in a well-controlled manner.[6,7,10] Initially, Xia and Matyjaszewski reported the use of 2,2′-bipyridine (bipy) as the ligand in copper-based ATRP to promote the controlled radical polymerization of St and (meth)acrylic monomers. Later, they succeeded in improving the synthesis of poly(St) with a narrow molecular weight distribution (M_w/M_n), as low as 1.05 and comparable to living anionic polymerization, by employing more solubilizing 4,4′-di-n-heptyl-2,2′dipyridyl (dHbpy) and 4,4′-di-(5-nonyl)-2,2′dipyridyl (dNbpy) ligands.[15]

Although the above-mentioned conventional ATRP method is an efficient way to maintain living radical polymerization of various vinyl monomers, it has two major problems: the halide species RX are toxic, and the catalysts M_t^n/L_X are easily oxidized by air.[22] To overcome the drawbacks, the use of conventional radical initiators, such as 2,2′-azobisisobutyronitrile (AIBN) in the presence of complexes of transition metals in their higher oxidation state, have been reported and referred to as "reverse" or "alternative" ATRP by Matyjaszewski et al.[23,24] and Teyssié et al.,[22] respectively. This type of ATRP approaches the same type of equilibrium as a conventional ATRP starting from conventional radical initiators such as peroxides or diazo compounds.[10] Several monomers, including St, MMA, and MA, were successfully polymerized via this process.[22–31]

In the past, only two kinds of initiators, such as azo- and peroxide compounds, were employed as the initiator in the reverse ATRP system. It is well known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature, and it is also difficult to realize living radical polymerization for some high reactivity monomers. For example, the AIBN/CuCl$_2$/bipy initiation system was successfully used for the living/controlled radical polymerization of St via a reverse ATRP process, but it was uncontrolled for (meth)acrylate monomers.[23,24]

The development of new type initiators for reverse ATRP, using carbon–carbon bond initiator instead of azo or peroxide ones, is of interest. At the same time this new type initiator (an iniferter) could provide the initiation step of reverse ATRP, in which the iniferter reversibly decomposes to primary radicals, unlike other conventional initiators (AIBN or BPO) having an irreversible decomposition step, resulting in suitable amounts of primary radicals being generated. In our lab, we first introduced a carbon–carbon bond thermal iniferter instead of AIBN into the iron-based reverse ATRP system for St polymerization.[27,29] In this article we describe the living polymerization of MMA with a new copper-based ATRP process, by using a DCDPS/CuCl$_2$/bipy initiation system. The reversible decomposition equilibrium of the iniferter DCDPS provides a suitable concentration of radicals for the living polymerization system. A well-defined PMMA with high molecular weight and quite narrow polydispersity was obtained through this process. The resulting PMMA with a chlorine end-capped group can be used as a macroinitiator to induce a chain extension reaction with fresh MMA and a block copolymerization with an St monomer.

EXPERIMENTAL

Materials

CuCl$_2$ was purchased from Aldrich Chemical Company, and used as received. CuCl was purified by stirring in acetic acid, filtered, washed with ethanol, and dried. 2,2′-Bipyridine (bipy) was recrystallized from acetone. Methyl methacrylate was dried over CaH$_2$, then distilled under vacuum. DCDPS was prepared according to the method reported previously.[32] Solvent and other reagents were purified by usual methods.

Polymerization and Block Copolymerization

The polymerization was carried out in a sealed tube charged with a predetermined amount of a mixture of the reaction components. For an example, in the bulk polymerization of MMA, a mixture of 3.5 mg DCDPS, 1.88 g MMA, 3.2 mg CuCl$_2$, and 5.9 mg bipy were charged into a glass tube. The mixture was immediately degassed by three pump–thaw cycles, sealed under vacuum, then immersed into an oil bath thermostat at 85°C. After polymerization for 6.5 h the tube was quenched with ice water to stop the reaction, and the resultant polymers were dissolved in 4 mL tetrahydrofuran (THF), then precipitated with 40 mL petroleum ether and dried. The resultant PMMA was weighted as 0.094 g, and the polymer-
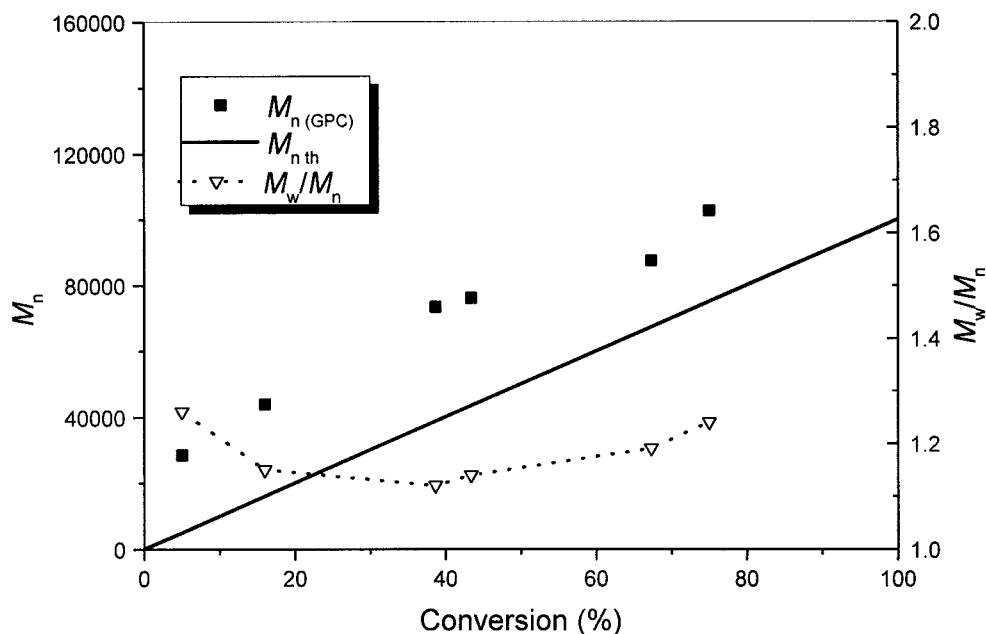
Figure 1 Dependence of number-average molecular weight and molecular weight distribution of PMMA on conversion at 85°C in bulk polymerization of MMA. Conditions: $[MMA]_0 = 9.38$ mol L^{-1}, $[CuCl_2]_0 = 9.38 \times 10^{-3}$ mol L^{-1}, $[bipy]_0 = 18.8 \times 10^{-3}$ mol L^{-1}, $[DCDPS]_0 = 4.69 \times 10^{-3}$ mol L^{-1}.

ization conversion was calculated as 5%. The other polymerization conversions for a given time were obtained similarly. Block copolymerization was performed in the same manner as the typical homopolymerization.

Characterization

Molecular weights and molecular weight distributions of polymer samples were measured at 35°C by Gel Permeation Chromatography (GPC) on a Waters 2410 instrument using THF as the eluent (1.0 mL/min), calibration with polystyrene standards, and Waters Millenium 32 as the data-processing software. ^{1}H-NMR spectra were taken at 25°C on a Brucker ARX400 (400 MHz) spectrometer in DMSO-d_6 using tetramethylsilane (TMS) as internal reference.

RESULTS AND DISCUSSION

Matyjaszewski and coworker reported that control of the ATRP process to some degree depends on the concentration of propagating radicals. In the reverse ATRP system, using a conventional initiator such as AIBN, the decomposition of initiator is irreversible, which makes the concentration of primary radicals rather high, especially at

the early stage of polymerization at high temperature, even in the presence of a strong inhibitor such as $CuCl_2$. So it is difficult to realize a living/controlled radical polymerization for some monomers having high rate constants for radical propagation such as MMA and MA.[23] In fact, the living/controlled radical polymerization of St monomer was achieved with AIBN/$CuCl_2$/bipy system by use of a large excess amount of deactivator (10 equiv $CuCl_2$ to AIBN).[23]

While introducing iniferter DCDPS to replace AIBN in the copper-based system, due to the reversible cleavage nature of the iniferter, the concentrations of primary radicals, (carbethoxycyanophenyl)methyl radicals (R ·), in the initiating step are more suitable just like the reversible-initiating step in a conventional ATRP process. In addition, in this system only a lower amount of catalyst ($CuCl_2$) was needed to inhibit the propagating radicals ($CuCl_2$/DCDPS =2 molar ratio). The lower molar ratio of $CuCl_2$ to DCDPS, used in this work, resulted in a living radical polymerization for a high reactivity monomer, i.e., MMA.

Living Radical Polymerization of MMA

Figure 1 shows that the experimental molecular weight increased, with monomer conversion, from
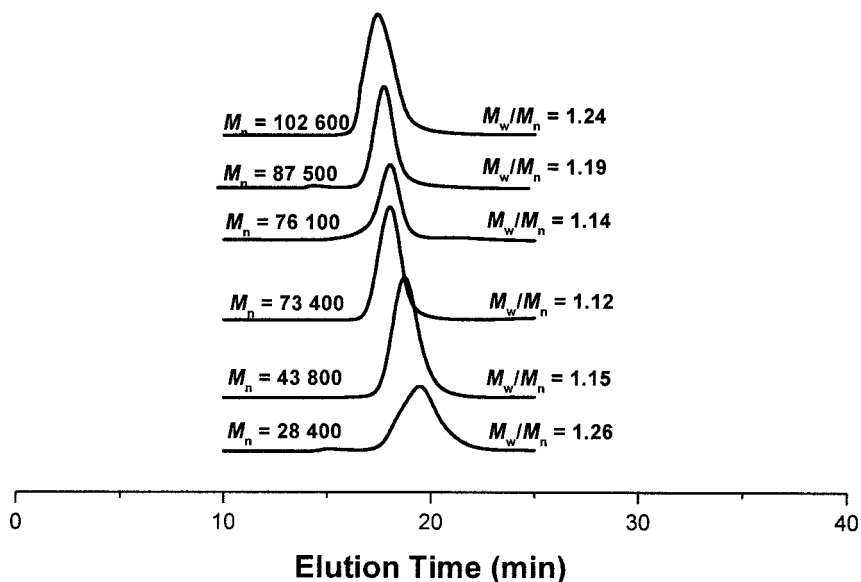
Figure 2   GPC traces of bulk polymerization of MMA at 85°C using DCDPS/CuCl$_2$/bipy initiating system. Same conditions as Figure 1.

28,400 up to 102,600 for the bulk polymerization of MMA initiated with the DCDPS/CuCl$_2$/bipy system at 85°C. The molecular weight distributions remained narrow during the whole polymerization (M_w/M_n = 1.12–1.26). The GPC curves of the resulting PMMA are shown in Figure 2. They appear to be exactly unimodal peaks as in living polymerization. However, the efficiencies of the initiator (f), as calculated from $M_{n\ \text{(th)}}/M_{n\ \text{(GPC)}}$, are generally low ($f < 0.8$). $M_{n\ \text{(th)}}$ is the theoretical number-average molecular weight ($M_{n\ \text{(th)}}$ = ([MMA]$_0$/2[DCDPS]$_0$) × MW$_{\text{MMA}}$ × Conversion). The low efficiency (f) is presumably due to the irreversible termination reaction that might happen especially at the early stage of the polymerization. The $M_{n\ \text{(GPC)}}$ of the resulting PMMA was measured with a PSt standard. In a comparison experiment, the bulk polymerization of MMA was carried out with DCDPS alone at 85°C (DCDPS/CuCl$_2$/bipy/MMA = 1/0/0/2000). The conversion reached 19.1% after 0.5 h. The molecular weight of PMMA, measured by GPC ($M_{n\ \text{(GPC)}}$ =108,000), gave a much higher value than calculated according to the former equation ($M_{n\ \text{(th)}}$ = 19,100), and the polydispersity is rather broad (M_w/M_n = 1.70). From these results we can see that the polymerization initiated with DCDPS alone cannot be well controlled due to the terminations between the propagating active species. The logarithmic conversion data ln([M]$_0$/[M]) plotted against time t as shown in Figure 3, gave

a straight line passing through the origin, which shows the kinetics is first order in the monomer, and the concentrations of growing species keep constant during the polymerization. All these mentioned above convincingly show that the living radical polymerization of MMA was efficiently carried out in bulk at 85°C with the DCDPS/CuCl$_2$/bipy initiation system.

The solution polymerization of MMA with the initiation system was carried out in toluene at 85°C. From Figure 4 we can see that, as the conversion increased, the $M_{n\ \text{(GPC)}}$ values also increased keeping the low M_w/M_n values (M_w/M_n < 1.25), indicating a well-controlled polymerization process. In a plot of ln([M]$_0$/[M]) vs. time t, as shown in Figure 5, a straight line was observed that indicated that the kinetics is also first order in the monomer. This means that the concentrations of propagating radicals are constant during the solution polymerization. By comparing the slopes of the kinetic plots of PMMA in bulk and in solution polymerization, shown in Figures 3 and 5, it is evident that, at the same experiment conditions, the bulk polymerization is much faster than the solution polymerization. These kinetic data allow us to calculate the apparent propagation rate constants (k_p^{app}). Then the stationary concentration of radicals, [P·], can be estimated from the ratio of the apparent rate constants, k_p^{app}, and the rate constants of radical propagation k_p. available,[33] i.e., [P·] = k_p^{app}/k_p. Table I
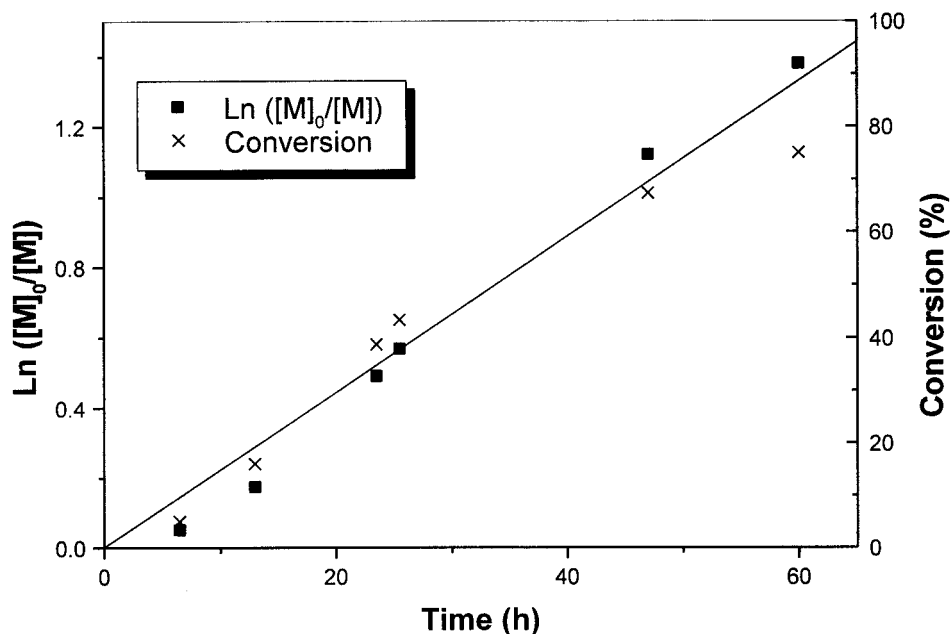
Figure 3 Time dependence of $\ln([M]_0/[M])$ and conversion at 85°C in bulk polymerization of MMA. Same conditions as Figure 1.

compiles the kinetic data with estimated concentrations of growing radicals in the polymerization of MMA using the DCDPS/CuCl$_2$/bipy initiation system. It shows that the concentrations of propagating radicals in both cases are rather low, and the low concentrations of active radicals lead to narrow polydispersity, as shown in Figures 2 and 4. We also can see that the concentration of prop-
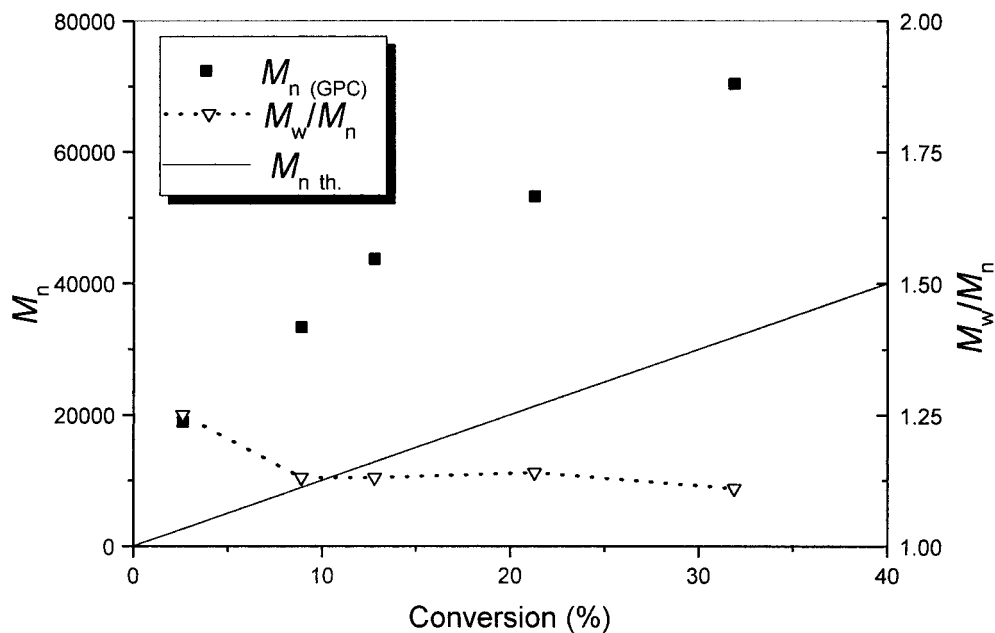
Figure 4 Dependence of number-average molecular weight and molecular weight distribution of PMMA on conversion at 85°C in toluene solution polymerization of MMA. Conditions: $[MMA]_0 = 6.25$ mol L^{-1}, $[CuCl_2]_0 = 6.26 \times 10^{-3}$ mol L^{-1}, $[bipy]_0 = 12.5 \times 10^{-3}$ mol L^{-1}, $[DCDPS]_0 = 3.13 \times 10^{-3}$ mol L^{-1}.
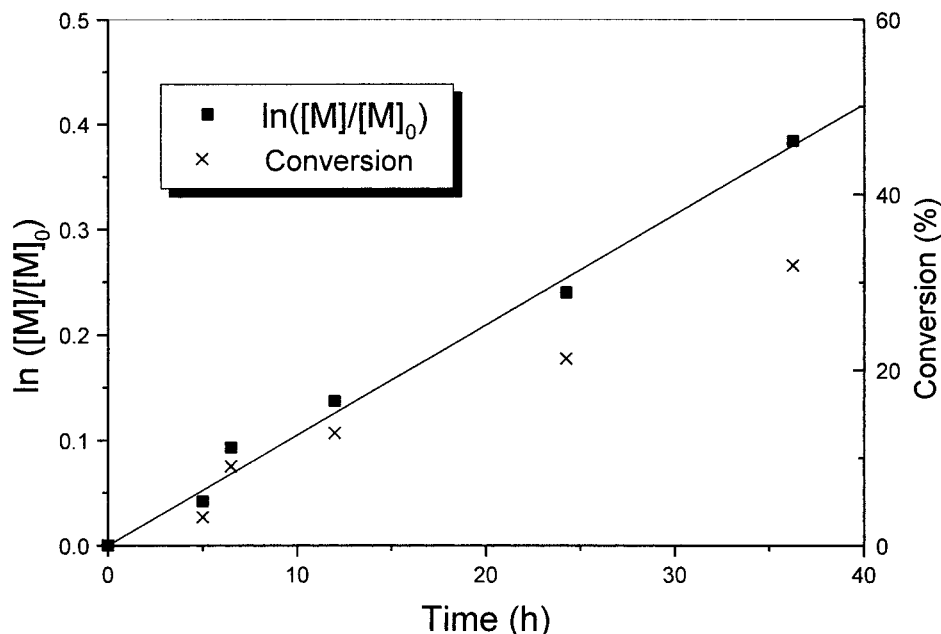
Figure 5   Time dependence of $\ln([M]_0/[M])$ and conversion at 85°C in toluene solution polymerization of MMA. Same conditions as Figure 4.

agating radicals in solution is much lower than that in bulk, which may result in the slower polymerization rate, as indicated in the slopes of kinetic plots.

End-Group Analysis and Block Copolymerization

End-group analysis of the resulting PMMA was carried out by ^{1}H-NMR spectroscopy, as shown in Figure 6. The methyl protons (d) of the terminal

Table I   Kinetic Data and Estimated Concentrations of Growing Radicals for Bulk^a and Solution^b Polymerization of MMA with DCDPS/CuCl$_2$/bipy Initiation System

	Bulk	Solution
Temperature (°C)	85	85
$[M]_0$, mol L^{-1}	9.38	6.25
k_p^{app}, $10^6 s^{-1}$	6.16	2.91
$k_p.^c$, 10^{-3}L mol^{-1} s^{-1}	1.34	1.34
$[P\cdot]$, 10^9 mol L^{-1}	4.59	2.17

^{a} Conditions: $[MMA]_0 = 9.38$ mol L^{-1}, $[CuCl_2]_0 = 9.38 \times 10^{-3}$ mol L^{-1}, $[bipy]_0 = 18.8 \times 10^{-3}$ mol L^{-1}, $[DCDPS]_0 = 4.69 \times 10^{-3}$ mol L^{-1}.

^{b} Conditions: (in toluene) $[MMA]_0 = 6.25$ mol L^{-1}, $[CuCl_2]_0 = 6.26 \times 10^{-3}$ mol L^{-1}, $[bipy]_0 = 12.5 \times 10^{-3}$ mol L^{-1}, $[DCDPS]_0 = 3.13 \times 10^{-3}$ mol L^{-1}.

^{c} Values extrapolated from the 60 to 90°C, see: ref. 33.

methyl ester unit, seen at 3.72 ppm, departed from other methyl protons (c) of the repeated methyl esters (ca. 3.65 ppm) because they are affected by an ω-chlorine atom in the PMMA chain end. The protons (g) of the phenyl group that derived from DCDPS are seen at 7.45–7.55 ppm. Both of these results indicate that end functionalized PMMA with an α-(carbethoxy-cyanophenyl)-methyl group from DCDPS fragments and an ω-chlorine group from catalyst was obtained by this initiation system. The molecular weight, determined from the ^{1}H-NMR spectrum ($M_{n\,(NMR)} \approx 9800$), is not close to the one obtained from GPC ($M_{n\,(GPC)} \approx 13,200$), but it is close to the $M_{n\,(th)} = 9600$. This may be because the molecular weight of PMMA measured by GPC was calibrated with polystyrene standard, but not PMMA standard, which results in some deviation from the $M_{n\,(NMR)}$.

The resulting PMMA, with an ω-chlorine atom in the chain end, can be used as a macroinitiator for chain extension or block copolymerization using a conventional ATRP process. The chain extension reaction of PMMA was carried out in bulk at 100°C with a chlorine-terminated PMMA ($M_n = 25,600$, $M_w/M_n = 1.26$) in the presence of a conventional ATRP catalyst, i.e., CuCl/bipy. The M_n of the resulting PMMA increases up to 146,600 ($M_w/M_n = 1.49$), which can be essentially
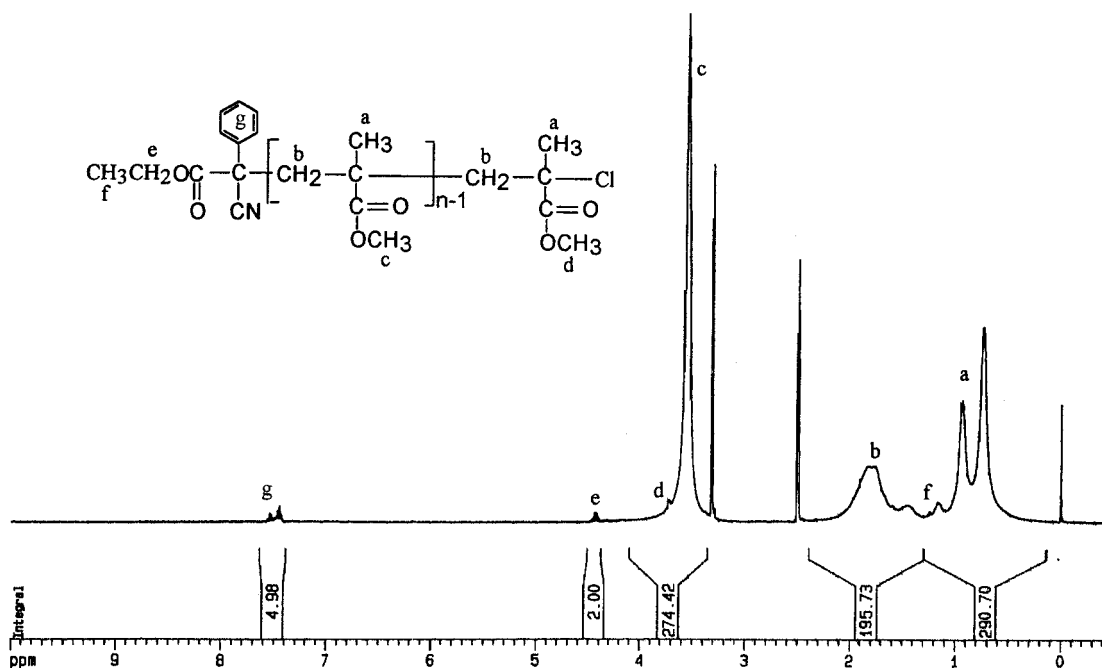
Figure 6 ^{1}H-NMR spectrum of resultant PMMA initiated with DCDPS/CuCl$_2$/bipy (1/2/4) in bulk at 85°C, M_n = 13,200; M_w/M_n = 1.29 (in DMSO-d$_6$, 400 MHz).

demonstrated by the GPC curves shown in Figure 7. By using the chlorine-terminated PMMA as the macroinitiator for the atom transfer radical copolymerization of St, PMMA-*b*-PSt block copolymer could be obtained. Figure 8 displays the GPC trace of the copolymer, and it shows no additional peak, confirming that essentially block copolymer has been formed. These results indicate that the DCDPS/CuCl$_2$/bipy initiation system induces living polymerization via a reverse ATRP process.
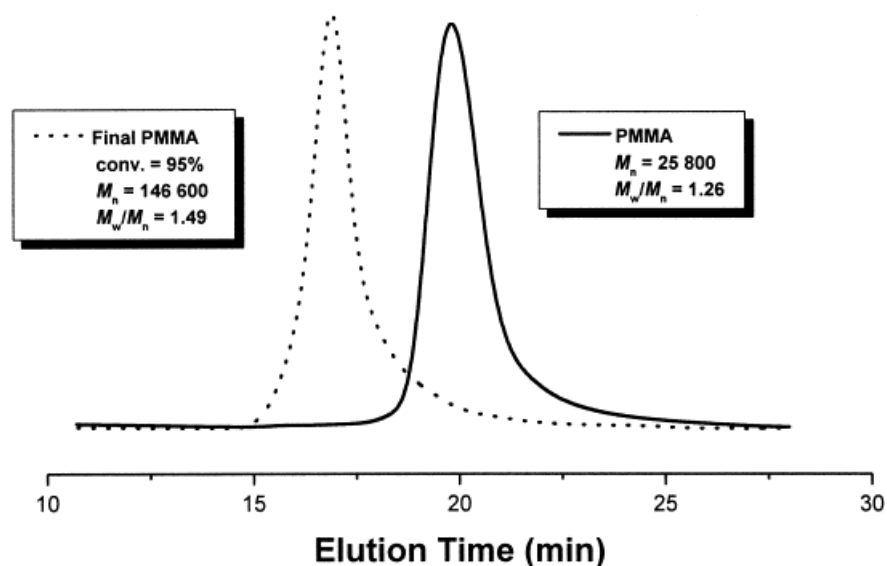

Figure 7 GPC curves of PMMA before and after chain extension reaction in the presence of CuCl/bipy catalyst at 100°C. Conditions: t = 36 h, [MMA]$_0$ = 9.38mol L^{-1}, [PMMA]$_0$ = 7.35 × 10^{-3} mol L^{-1}, [CuCl]$_0$ = 9.38 × 10^{-3} mol L^{-1}, [bipy]$_0$ = 18.8 × 10^{-3} mol L^{-1}.

Figure 8 GPC curves of PMMA before and after copolymerization with St in the presence of CuCl/bipy system at 100°C. Conditions: $t = 40$ h, $[St]_0 = 8.75$mol L^{-1}, $[PMMA]_0 = 7.35 \times 10^{-3}$ mol L^{-1}, $[CuCl]_0 = 9.38 \times 10^{-3}$ mol L^{-1}, $[bipy]_0 = 18.8 \times 10^{-3}$ mol L^{-1}.

Polymerization Mechanism

The polymerization mechanism is proposed according to the end group analysis, as depicted in Scheme 1. In the initiation step, the DCDPS iniferter first reversibly cleaves to the primary radicals R · , which is different from the irrevers-ible process of the conventional initiators (such as AIBN) in the reverse ATRP system reported before. Then the primary radicals combine with monomer to form activated monomer radicals. The monomer radicals can react with monomers to create propagating chains or directly react with CuCl$_2$/bipy complex by abstracting the chlorine

Scheme 1

atom to generate an organic chloride and a lower oxidation state metal complex CuCl/bipy. Then the polymer propagates via a conventional ATRP process.

CONCLUSION

A heterogenous reverse ATRP using the DCDPS/CuCl$_2$/bipy as the initiation system has been successfully carried out for MMA at 85°C. A well-defined PMMA with α-(carbethoxy-cyano-phenyl)-methyl and ω-chlorine end groups, high molecular weight (up to 102,600) and quite narrow polydispersity index ($M_w/M_n \approx 1.20$) was obtained using this system. The number-average molecular weights of polymers increased with increasing monomer conversion and first-order plots were developed from which the concentrations of growing radicals were estimated. Furthermore, the chain extension and block copolymerization reactions confirmed that the PMMA obtained with that ω-chlorine group could act as a macroinitiator.

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