A Reverse ATRP Process with a Hexasubstituted Ethane Thermal Iniferter Diethyl 2,3-Dicyano-2,3-di(*p*-tolyl)succinate as the Initiator

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Received March 21, 2000; Revised Manuscript Received July 3, 2000

ABSTRACT: "Living"/controlled radical polymerization of methyl methacrylate (MMA) was successfully carried out using the diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS)/$CuCl_2$/bipy initiation system, in which DCDTS is a hexasubstituted ethane thermal iniferter. The polymerization mechanism belongs to a new reverse atom transfer radical polymerization (ATRP) process with the initiator DCDTS reversibly decomposed to primary radicals in the initiation step. The molecular weights of the resulting PMMA increased with conversion, the molecular weight distributions of PMMA were quite narrow (M_w/M_n < 1.30), and the first-order plots of $\ln([M]_0/[M])$ versus time were linear. ^{1}H NMR analysis of PMMA revealed the presence of an α-(carbethoxy−cyano−tolyl)methyl end group from DCDTS fragments and an *ω*-chlorine group from catalyst. Since polymer is end-functionalized with a chlorine atom, it can then proceed the chain extension reaction with fresh MMA or the block copolymerization with the second monomer styrene (St) in the presence of CuCl/bipy catalyst.

Introduction

Since Szwarc first reported the concept of living polymerization in 1956,[1] some living polymerization systems such as anionic (including group transfer polymerization) and cationic have been reported for preparing well-defined polymers.[2] In recent years, "living"/controlled radical polymerization has also become reality. The metal-catalyzed system, i.e., atom transfer radical polymerization (ATRP), is an efficient method to prepare polymers with low polydispersities and controlled architectures.[3,4]

Two kinds of ATRP methods have been reported, i.e., conventional ATRP and reverse ATRP.[5] In conventional ATRP, the organic halides (e.g., arenesulfonyl halides, haloalkanes, haloketones, halonitriles, haloesters) are used as initiators, and transition metals in their lower oxidation state complexed with suitable ligands are used as catalysts.[6−9] Various monomers, such as St,[10] MMA,[11] methyl acrylate (MA),[12] acrylonitrile,[13] and *n*-butyl acrylate,[14] have been successfully polymerized. It also provides a functional end group to prepare well-defined block and graft copolymers, star polymers, and hybrid polymers.[15−18] Many recent studies have combined conventional ATRP with other polymerization methods, such as ring-opening metathesis polymerization (ROMP), anionic polymerization, and cationic polymerization, to prepare novel block copolymers.[19−22]

To avoid the toxicity of the initiator and the easy oxidation of the catalyst in the conventional ATRP initiation system, Matyjaszewski et al.[23,24] and Teyssié et al.[25] reported the "reverse" or "alternative" ATRP system, respectively. In the reverse ATRP system, conventional initiators such as AIBN[23−26] and BPO[27,28] are used in place of halide initiators, and the transition metal catalysts are in their higher oxidation state instead of the lower oxidation state. Several monomers, including St,[23,24,27,28,30] MMA,[24,25,29,31,32] and MA,[24,26] were successfully polymerized by reverse ATRP in a "living"/controlled manner. The "living"/controlled radical polymerization of MMA has been extensively investigated using reverse ATRP, such as AIBN/$FeCl_3$/PPh_3,[25] tetraphenyl 1,2-ethanediol/$FeCl_3$/PPh_3,[29] or AIBN/$CuBr_2$/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy)[24] initiation systems. The polymerization of MMA is not a "living"/controlled polymerization with copper-based heterogeneous initiation system, i.e., AIBN/$CuCl_2$/bipy.[23]

In the past, only azo- and peroxide compounds were employed as the initiator in the reverse ATRP system. Since the decomposition of those conventional initiators is irreversible, the concentration of primary radicals is high even in the presence of a strong inhibitor such as $CuCl_2$, especially at the early stage of polymerization. It is therefore difficult to realize the "living"/controlled radical polymerization for some monomers having high rate constants of propagation such as MMA and MA. 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 using a large amount of deactivator (10 equiv of $CuCl_2$ to AIBN) but was uncontrolled for (meth)acrylate monomers.[23,24] Although using AIBN/$CuBr_2$/dNbpy homogeneous copper-based initiation system the "living"/controlled radical polymerization of MMA has been reported,[24] the initiation efficiencies were low at 110 and 90 °C, respectively.

To develop new types of the initiator that reversibly decompose in reverse ATRP, we first introduced the carbon−carbon bond thermal iniferter into the reverse ATRP system to produce a new initiation system and obtained some exciting results.[30−32] In this article, we employed diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS) iniferter to replace AIBN as the initiator in conjunction with $CuCl_2$/bipy catalyst for a new reverse ATRP initiation system (Scheme 1). Because of the reversible cleavage of the iniferter, the concentrations of primary radicals in the initiation step are low as in conventional ATRP. In this heterogeneous system, only small amounts of deactivator ($CuCl_2$) are needed to inhibit the propagating radicals ($CuCl_2$/DCDTS = 2 molar ratio) efficiently. The lower molar ratio of $CuCl_2$

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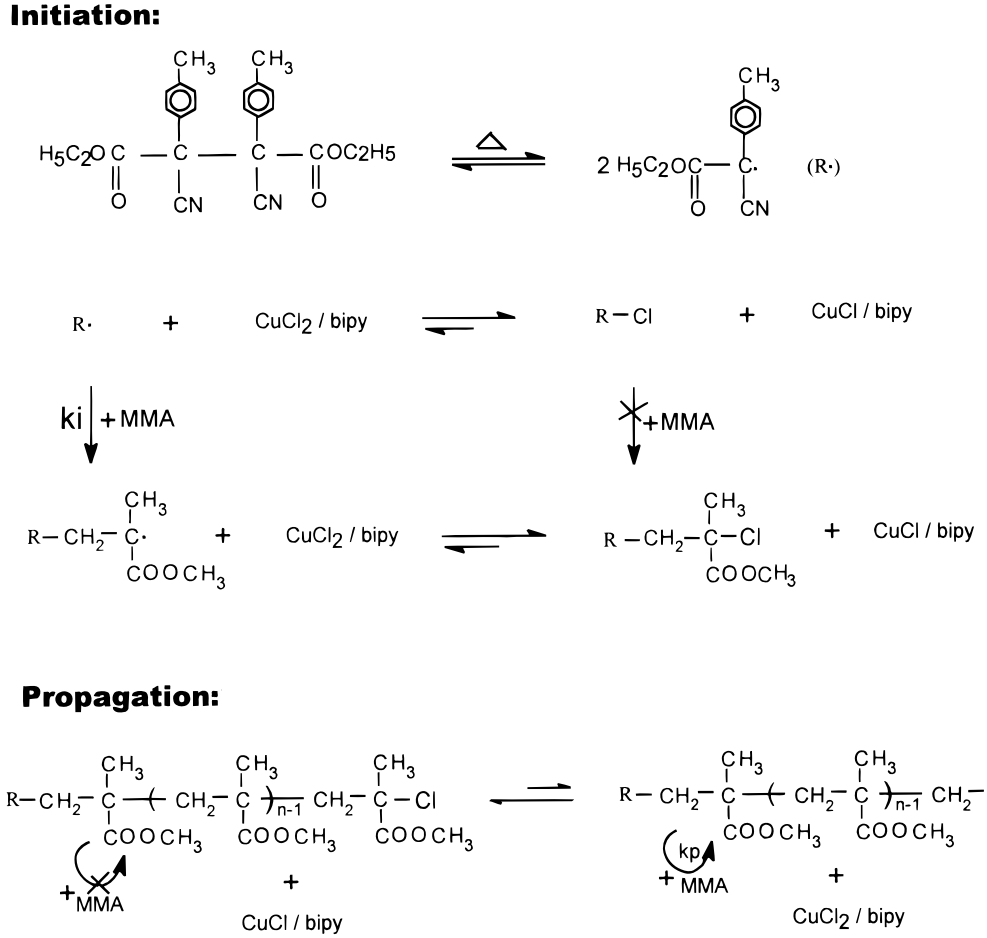
10.1021/ma000512y CCC: $19.00
Published on Web 08/22/2000

Scheme 1



to DCDTS gave a well-controlled radical polymerization of MMA, to produce a well-defined PMMA with high molecular weight and quite low polydispersity. The resulting PMMA with a chlorine end group can be used as a macroinitiator to prepare block copolymers.

Experimental Section

Materials. $CuCl_2$ (99.0%) was used as received from Aldrich. CuCl (local product, 98.0%) was purified by stirring in acetic acid, filtered, washed with ethanol, and dried. 2,2′-Bipyridine (bipy, Acros, 99+%) was recrystallized from acetone. Methyl methacrylate (Beijing Chemical Co., AR) was dried over CaH_2 and then distilled under vacuum. DCDTS was prepared according to the method reported in the literature.[33,34] Tetrahydrofuran (THF) and toluene were distilled over CaH_2. Petroleum ether was used as received.

Measurements. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymer samples were measured at 35 °C by gel permeation chromatography (GPC) on a Waters 2410 instrument with HT2+HT3+HT4 μ-Styragel columns (pore sizes: 10^2, 10^3, and 10^4 Å, respectively) and calibrated with standard polystyrene. THF is used as eluent with a flow rate of 1.0 mL/min. The ^{1}H NMR spectrum was taken at 25 °C on a Bruker ARX400 (400 MHz) spectrometer in dimethyl-d_6 sulfoxide (DMSO-d_6) using tetramethylsilane (TMS) as internal reference.

Polymerization and Block Copolymerization. In a typical run, MMA (1.87 g, 18.7 mmol) was added in a dry glass tube with DCDTS (3.8 mg, 9.40×10^{-3} mmol), $CuCl_2$ (3.2 mg, 18.8×10^{-3} mmol), and bipy (8.8 mg, 56.8×10^{-3} mmol). The mixture was immediately degassed by the three pump−thaw cycles and sealed under vacuum. Then it was immersed into an oil bath thermostated at 85 °C. After 2 h, the polymerization was stopped by cooling the tube in ice water. Then the resultant polymers were dissolved in 5 mL of THF; the PMMA was precipitated with 75 mL of petroleum ether and dried. The conversion (0.18 g of PMMA, 9.6%) of polymerization was determined gravimetrically. The molecular weight and molecular weight distribution of the resulting PMMA measured by GPC were 15 700 and 1.30, respectively.

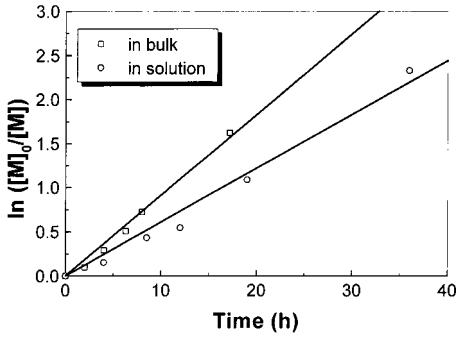


Figure 1. Time dependence of $\ln([M]_0/[M])$ and conversion at 85 °C in bulk polymerization of MMA. Conditions: in bulk, $[MMA]_0 = 9.38$ M, $[CuCl_2]_0 = 9.38$ mM, $[bipy]_0 = 28.4$ mM, $[DCDTS]_0 = 4.69$ mM; in toluene, $[MMA]_0 = 6.25$ M, $[CuCl_2]_0 = 6.26$ mM, $[bipy]_0 = 18.5$ mM, $[DCDTS]_0 = 3.13$ mM.

Results and Discussion

"Living"/Controlled Radical Polymerization of MMA. Radical polymerization of MMA was carried out in bulk and in solution with the DCDTS/$CuCl_2$/bipy initiation system ($[MMA]_0$:$[DCDTS]_0$:$[CuCl_2]_0$:$[bipy]_0$ = 2000:1:2:6) at 85 °C. Figure 1 shows the relationships

Table 1. Kinetic Data and Estimated Concentrations of Growing Radicals in Bulk[a] and Solution[b] Polymerization of MMA at 85 °C with DCDTS/$CuCl_2$/bipy Initiation System

	bulk	solution
$[M]_0$, M	9.38	6.25
k_p^{app}, 10^5 s^{-1}	2.54	1.70
$k_{p\bullet}$,[c] 10^{-3} L mol^{-1} s^{-1}	1.34	1.34
$[P^\bullet]$, 10^8 M	1.90	1.27

[a] Conditions: $[CuCl_2]_0 = 9.38$ mM, $[bipy]_0 = 28.4$ mM, $[DCDTS]_0 = 4.69$ mM. [b] Conditions: (in toluene): $[CuCl_2]_0 = 6.26$ mM, $[bipy]_0 = 18.5$ mM, $[DCDTS]_0 = 3.13$ mM. [c] Values extrapolated from the 60 to 90 °C; see ref 35.

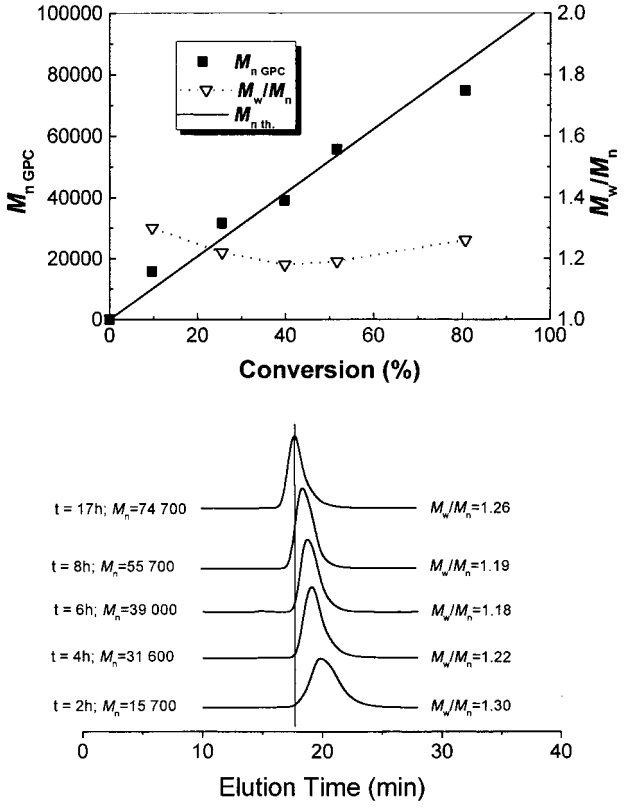


Figure 2. Dependence of number-average molecular weights and molecular weight distributions of PMMA on conversion in bulk polymerization at 85 °C and the corresponding GPC traces of resulting PMMA. Conditions: $[MMA]_0 = 9.38$ M, $[CuCl_2]_0 = 9.38$ mM, $[bipy]_0 = 28.4$ mM, $[DCDTS]_0 = 4.69$ mM.

of $\ln([M]_0/[M])$ versus time. The relationships between $\ln([M]_0/[M])$ versus time in bulk and in solution polymerization are linear and pass through the origin. This means that the concentration of growing radicals is constant during the polymerization, indicating that the kinetics is first order in monomer concentration in both reaction conditions. Comparison of the kinetic plot of PMMA in bulk with that in solution polymerization at the same molar ratio shows that the rate of the bulk polymerization is much faster than that in solution polymerization. The apparent propagation rate constants (k_p^{app}) in bulk and solution polymerization were calculated from the slops of the straight lines plotted in Figure 1. The stationary concentration of radicals $[P^\bullet]$ then can be estimated from the ratio of the apparent rate constant and the rate constants of radical propagation available,[35] i.e., $[P^\bullet] = k_p^{app}/k_{p\bullet}$.The kinetic data and the estimated concentrations of growing radicals are compiled in Table 1.

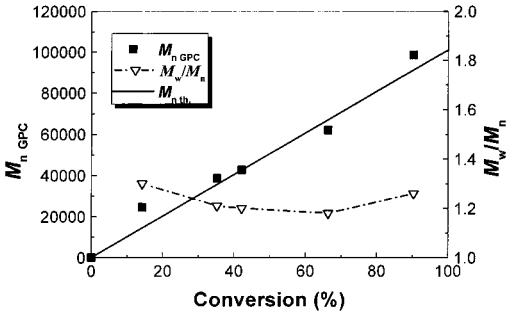


Figure 3. Dependence of number-average molecular weights and molecular weight distributions of PMMA on conversion at 85 °C in toluene solution polymerization. Conditions: $[MMA]_0 = 6.25$ M, $[CuCl_2]_0 = 6.26$ mM, $[bipy]_0 = 18.5$ mM, $[DCDTS]_0 = 3.13$ mM.

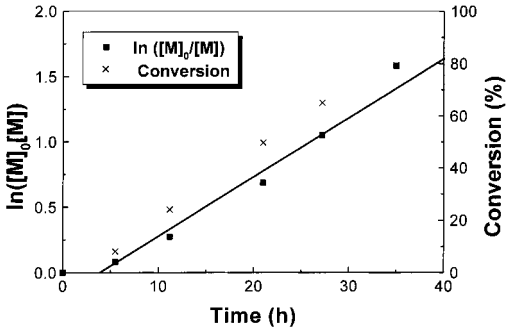


Figure 4. Time dependence of $\ln([M]_0/[M])$ and conversion at 75 °C in bulk polymerization of MMA. Conditions: $[MMA]_0 = 9.38$ M, $[CuCl_2]_0 = 9.38$ mM, $[bipy]_0 = 28.4$ mM, $[DCDTS]_0 = 4.69$ mM

Figure 2 shows that the number-average molecular weights of PMMA produced in bulk (measured by GPC) increase with increasing conversion. Molecular weights determined from GPC were similar to the theoretical predictions ($M_{n(th)} = ([MMA]_0/2[DCDTS]_0 \times MW_{MMA} \times$ conversion). The slight deviation of the $M_{n(GPC)}$ from the $M_{n(th)}$ is presumably due to irreversible termination, especially at the early stage of the polymerization. The disparity may be also caused by hydrodynamic differences between PMMA polymers and PSt standards. The GPC curves of PMMA shown in Figure 2 were sharp peaks, and the molecular weight distributions ($M_w/M_n = 1.18-1.30$) were narrow throughout the polymerization, indicating a controlled polymerization. While in a comparison experiment MMA was polymerized with DCDTS alone in bulk (DCDTS/$CuCl_2$/bipy/MMA = 1/0/0/2000, at 85 °C); the conversion reached 34.7% after 1 h, the molecular weight ($M_{n(GPC)}$) was 183 400, and the polydispersity is broad ($M_w/M_n = 1.62$). From these results we can see that the conversion, $M_{n(GPC)}$, and MWD in the comparison experiment are much higher than those produced by the ATRP method. Therefore, in the reverse ATRP initiation system, DCDTS acts as an initiator rather than an iniferter. Similarly, $M_{n(GPC)}$ increased with conversion in the solution polymerization with this new initiation system at 85 °C (Figure 3). All these data convincingly reveal that the bulk and solution radical polymerization of MMA is therefore "living"/controlled at 85 °C with the DCDTS/$CuCl_2$/bipy initiation system.

The polymerization of MMA can also be carried out at lower temperature such as 75 °C with the heterogeneous copper-based catalyst, and the first-order plot of the bulk polymerization is shown in Figure 4. The linear correlation of $\ln([M]_0/[M])$ versus time at 75 °C indicates

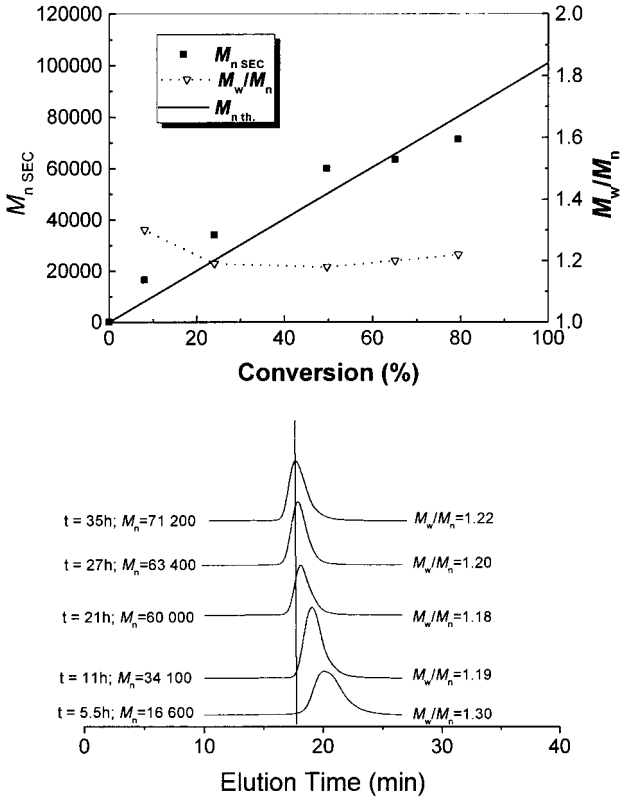


Figure 5. Dependence of molecular weights and molecular weight distributions of PMMA on conversion in bulk polymerization of MMA at 75 °C and the corresponding GPC traces of resulting PMMA. Same conditions as Figure 4.

that the concentration of growing radicals is almost unchanged throughout the polymerization, although there is an induction period (unlike the plot at 85 °C). The reason might be that the initiator DCDTS decomposed slower at 75 °C than at 85 °C, and under the same conditions $CuCl_2$ was in great excess compared to the radical generated. Therefore, the polymerization was inhibited at the early stage.

The molecular weights increased with conversion at 75 °C, and the molecular weight distributions remained narrow (reached as low as 1.18) throughout the reaction (Figure 5). The GPC traces with sharp peaks of PMMA obtained showed a well-controlled bulk polymerization of MMA with the DCDTS/$CuCl_2$/bipy initiation system at 75 °C.

Although $M_{n(GPC)}$ did not fit well with the $M_{n(th)}$, well-defined PMMA with low polydispersities and high conversions can be synthesized from the MMA polymerization using the DCDTS/$CuCl_2$/bipy heterogeneous initiation system in bulk or in solution at 75 or 85 °C.

End Group Analysis and Block Copolymerization. Figure 6 shows a representative ^{1}H NMR spectrum of the resulting PMMA produced with the DCDTS/$CuCl_2$/bipy initiation system in bulk at 85 °C. In addition to the characteristic chemical shifts of the MMA repeat units, there are characteristic signals originating from a fragment of DCDTS iniferter. The signals at 1.24, 4.18, 2.29, and 7.18−7.26 ppm are assigned to the methyl (f) and the methylene (e) protons of the ethyl ester group, the methyl (h) protons of the tolyl group, and the protons of the phenyl (g) group. The signal at 3.72 ppm (d) is assigned to the protons of the terminal methyl ester unit, which is resolved from other methyl protons (c) of the repeated methyl esters (ca. 3.65 ppm). Similar spectra of PMMA obtained from the reverse ATRP were reported in the literature, such as the signal at 3.79 ppm reported by Chen and Qiu[29] and at 3.79 ppm by Moineau et al.[25] This was ascribed to the effect of the ω-chlorine end group. Both of these results indicate that the PMMA was end functionalized with an α-(carbethoxy−cyano−tolyl)methyl group from DCDTS fragments and an ω-chlorine group from catalyst. The molecular weight determined from the ^{1}H NMR spectrum ($M_{n(NMR)} \approx 28\,200$) is not exactly the same as the one obtained from GPC ($M_{n(GPC)} \approx 33\,200$) but is close to the theoretical molecule weight ($M_{n(th)} = 27\,800$). This is evidently because the $M_{n(GPC)}$ of PMMA was obtained from a polystyrene standard.

The PMMA with an ω-chlorine end group can be used as a macroinitiator for chain extension or block copolymerization via conventional ATRP. The chain extension reaction of PMMA was carried out in toluene at 100 °C with a PMMA ($M_n = 16\,800$, $M_w/M_n = 1.30$) in the

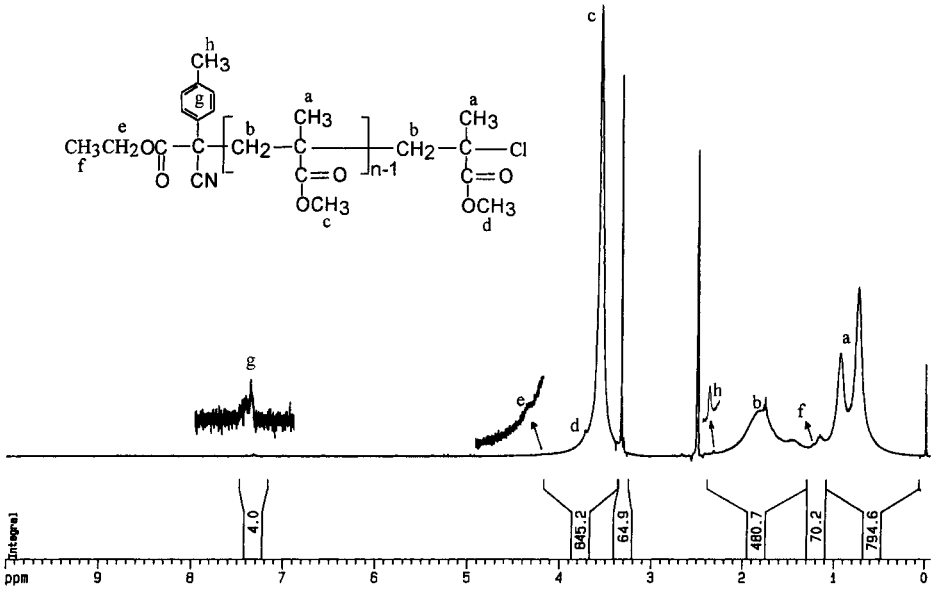


Figure 6. ^{1}H NMR spectrum of resultant PMMA initiated with DCDTS/$CuCl_2$/bipy in bulk at 75 °C; $M_n = 33\,200$, $M_w/M_n = 1.27$ (in DMSO-d_6, 400 MHz).

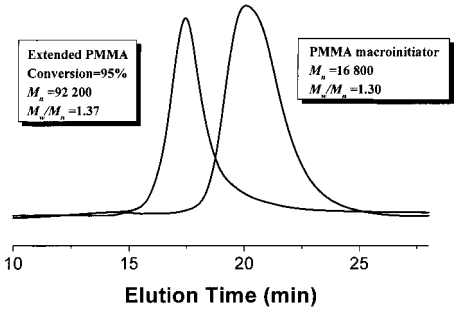


Figure 7. GPC curves of PMMA before and after chain extension reaction in the presence of CuCl/bipy system at 100 °C. Conditions: $t = 12$ h, $[MMA]_0 = 6.25$ M, $[PMMA]_0 = 7.76$ mM, $[CuCl] = 7.25$ mM, $[bipy]_0 = 19.8$ mM.

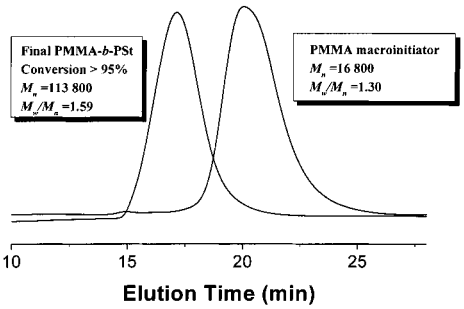


Figure 8. GPC curves of PMMA before and after copolymerization with St in the presence of CuCl/bipy system at 100 °C. Conditions: $t = 19$ h, $[St]_0 = 5.8$ M, $[PMMA]_0 = 6.18$ mM, $[CuCl] = 5.58$ mM, $[bipy]_0 = 13.5$ mM.

presence of CuCl/bipy. The GPC traces of the extended PMMA (Figure 7) show that chain extension from a PMMA macroinitiator with fresh MMA was efficient, yielding a final polymer with $M_n = 92\ 200$ ($M_w/M_n = 1.37$). PMMA-*b*-PSt block copolymer ($M_n = 113\ 800$; $M_w/M_n = 1.59$) was obtained using the same ω-chlorine-terminated PMMA as the macroinitiator for the atom transfer radical copolymerization of St. The GPC curve of the copolymer in Figure 8 shifted entirely to higher molecular weight, which indicated that the PMMA-*b*-PSt block copolymer has been essentially formed. These results revealed that the DCDTS/$CuCl_2$/bipy initiation system induces "living"/controlled polymerization via a reverse ATRP process.

Polymerization Mechanism. As reported by Matyjaszewski and co-workers, control of the polymerization depends on the concentration of propagating radicals.[5] In the reported reverse ATRP system using a conventional initiator such as AIBN, decomposition of the initiator is irreversible, which makes the concentration of primary radicals rather high, especially at high temperature (>90 °C) and at the early stage of polymerization. In contrast, DCDTS decomposes to primary radicals reversibly. As a result, primary radicals are produced in a suitable concentration or in much lower so that they can be efficiently deactivated by copper-based catalyst in this heterogeneous system.

We proposed a modified reverse ATRP mechanism with DCDTS/$CuCl_2$/bipy initiation system, as depicted in Scheme 1. In the initiation step, the thermal iniferter DCDTS first reversibly cleaves to the primary radicals (R•). Then the primary radical or the activated monomer radical abstracts a chlorine atom from the highly oxidized transition-metal species, $CuCl_2$/bipy complex, to create the reduced transition-metal species, CuCl/bipy complex, and the dormant organic chloride compounds. Later, the polymer propagates via a conventional ATRP process.

Conclusions

Well-defined PMMA with high conversion, high molecular weight, and narrow polydispersity ($M_n = 15\ 700-98\ 600$, $M_w/M_n = 1.18-1.30$) has been synthesized by radical polymerization of MMA with the DCDTS/$CuCl_2$/bipy initiation system. The polymerization was successful in both bulk and toluene at 85 °C. The radical polymerization of MMA with the DCDTS/$CuCl_2$/bipy initiation system is a "living"/controlled polymerization process. The polymerization mechanism belongs to a new reverse ATRP process, in which the decomposition of DCDTS is reversible in the initiation step. The polymer obtained is α-functionalized by a (carbethoxy−cyano−tolyl)methyl group from DCDTS fragments and ω-functionalized by a chlorine atom from the $CuCl_2$/bipy catalyst. The PMMA with a chlorine atom at the chain end can be used as a macroinitiator to generate higher molecular weight polymer or block polymer in the presence of CuCl/bipy catalyst system via a conventional ATRP process.

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