

Living/controlled radical polymerization of methyl methacrylate by reverse ATRP with DCDPS/FeCl₃/PPh₃ initiating system

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Abstract

Living/controlled radical polymerization of methyl methacrylate (MMA) was investigated using a new initiating system, i.e. DCDPS/FeCl₃/PPh₃, in which diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) is a hexa-substituted ethane thermal iniferter. The polymerization mechanism belongs to a reverse ATRP process. The polymerization was closely controlled in bulk and in solution at quite low temperature such as 75 or 60°C. The molecular weights of so-obtained PMMA were high and polydispersities were quite narrow ($M_w/M_n = 1.20\text{--}1.31$). End group analysis result using ¹H NMR spectroscopy shows that the polymer obtained is ω-functionalized by a chlorine atom. With the Cl atom at the chain end, PMMA obtained could be used as macroinitiator to proceed chain-extension reaction with MMA and block copolymerization reaction with styrene in the presence of CuCl/bipy catalyst via a conventional ATRP process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Living/controlled radical polymerization; Reverse atom transfer radical polymerization; Diethyl 2,3-dicyano-2,3-diphenylsuccinate/FeCl₃/PPh₃

1. Introduction

It is well known that radical polymerization plays a significant role in the industrial process. But due to its irreversible bimolecule termination, it is very difficult to proceed in a living/controlled manner [1]. The concept of living radical polymerization with iniferter was first introduced by Ostu in 1982 [2], since then many researchers around world have devoted their efforts into this field. In 1993, Georges et al. [3,4] reported on the living nitroxide-mediated stable free radical polymerization (SFRP) of styrene. Later Sawamoto et al. [5] and Matyjaszewski et al. [6] reported a novel polymerizable method that is based on the transition metal catalyzed atom transfer radical addition (ATRA, an efficient way for carbon–carbon bond formation in organic synthesis). Matyjaszewski named the process as atom transfer radical polymerization (ATRP).

In ATRP, alkyl halide species, RX, were used as initiators and transition metal compounds at lower oxidation state, such as Cu(I), Fe(II), Ru(II), or Ni(II), complexed with suitable ligands, M_tⁿ/LX, as catalysts. Various types of monomers such as styrene (St) [1,6–9], methyl methacrylate (MMA) [9,10], methyl acrylate (MA) [11], acrylonitrile [12], and *n*-butyl acrylate [13] etc. were successfully

polymerized by this method and it exhibits some characteristics of living polymerization. ATRP has also been successfully used to prepare functional polymers, such as block, graft copolymers etc. [6,14–16].

The living/controlled radical polymerization of MMA has been widely investigated using ATRP method, among them a large variety of transition metal compounds were used as catalyst: Cu(I) [10,17–20]; Ru(II) [5,21,22]; Ni(I) [23]; Rh(II) [24]; and Fe(II) [9,25]-based systems. It has been reported that the PMMA with well-controlled molecular weights and narrow molecular weight distributions could be obtained with iron-based catalyst systems that is RX/FeCl₂/PPh₃ [25], RX/FeBr₂/dNbipy (4,4'-bis(5-nonyl)-2,2'-bipyridine) or N(nBu)₃ [9].

Though the above-mentioned conventional ATRP method is an efficient way to maintain living/controlled radical polymerization of various vinyl monomers, it has two major problems: the toxicity of the halide species RX and the oxidation of the catalyst M_tⁿ/LX, by the oxygen in air [26]. To overcome the drawbacks, the “reverse” and “alternative” ATRP was recently promoted by Matyjaszewski et al. [27,28] and Teyssié et al. [26], respectively. Wang and Matyjaszewski [27] reported the living/controlled radical polymerization of styrene via a reverse ATRP under

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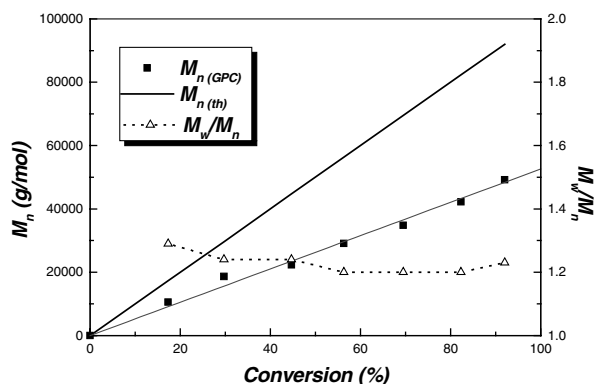


Fig. 1. Dependence of number-average molecular weight and molecular weight distribution of PMMA on conversion at 75°C in bulk polymerization of MMA. Conditions: $[MMA]_0 = 9.38 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 18.8 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 56.3 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 4.69 \times 10^{-3} \text{ mol l}^{-1}$.

heterogeneous conditions employing AIBN/CuCl₂/bipy as initiating system, but it is uncontrolled for both MMA and MA. Shortly thereafter, by using alkyl substituted bipyridine ligand such as dNbipy as a ligand instead of bipy, Xia and Matyjaszewski [28] described the reverse ATRP under homogeneous condition, in which *living/controlled* polymerization of St, MMA, and MA were all successfully carried out. More recently, Teyssié et al. [26] reported that the AIBN/FeCl₃/PPh₃ system could be used for the synthesis of well-defined PMMA in bulk and solution polymerization of MMA at 85°C. The PMMA so-obtained is α -functionalized by an isobutyronitrile group and ω -functionalized by a chlorine group.

As mentioned above this type of ATRP approach the same type of equilibrium starting from conventional radical initiators such as peroxides or diazo compounds. The efforts to exploit a new kind of initiator for the reverse ATRP system should be an interesting work, which can initiate the polymerization at lower temperature and the so-obtained polymer should have narrower polydispersities. To gain this

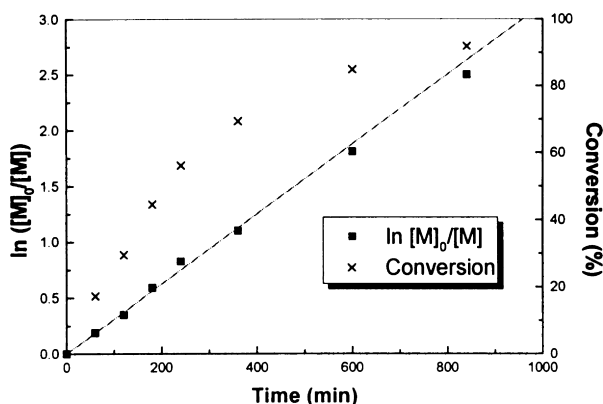


Fig. 2. Time dependence of $\ln([M]_0/[M])$ and conversion at 75°C in bulk polymerization of MMA. Conditions: $[MMA]_0 = 9.38 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 18.8 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 56.3 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 4.69 \times 10^{-3} \text{ mol l}^{-1}$.

goal, we employed a carbon–carbon bond thermal iniferter such as diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), into the reverse ATRP system,¹ i.e. DCDPS/FeCl₃/PPh₃, to produce a new initiating system and a well-defined PMMA with high molecular weight and a narrow polydispersity was obtained through this process. End group analysis showed that the PMMA obtained are ω -functionalized by a chlorine group, which is further confirmed by the extension and copolymerization of PMMA in the presence of CuCl/bipy with fresh MMA and St, respectively, via a conventional ATRP process.

2. Experimental

2.1. Materials

FeCl₃·6H₂O was dehydrated by the reactions with thionyl chloride [29]. CuCl was purified by stirring in acetic acid, filtered and washed with ethanol and dried. 2,2'-Bipyridine (bipy) was recrystallized from acetone. Methyl methacrylate was dried over CaH₂ and distilled under vacuum. Triphenylphosphine was recrystallized from ethanol to eliminate triphenylphosphine oxide [26]. DCDPS was prepared according to the reported procedure [30,31]. Solvent and other reagents were purified by standard methods.

2.2. Polymerization

The polymerization was carried out in a sealed tube equipped with a three-way stopcock under vacuum. After the reaction components were charged into a dry glass tube, the tube was sealed under vacuum performed with the three-pump-thaw cycles and immersed in an oil bath thermostated at desired temperature. At certain time intervals, the glass tubes were taken out and broken. The resultant polymers were dissolved in THF and precipitated in petroleum ether, and then dried. The conversion of polymerization was determined gravimetrically.

2.3. Measurements

The number-average molecular weight (M_n) and molecular weight distribution or polydispersity index (M_w/M_n) of the polymers were determined at 35°C with Gel Permeation Chromatography (Waters Associates Model HPLC/GPC 515 liquid chromatography, equipped with a refractive index detector, HT2 + HT3 + HT4 μ -Styragel columns and calibrated with standard polystyrene), using THF as eluent and a flow rate of 1.0 ml min⁻¹. ¹H NMR spectra were taken at 25°C with a Bruker ARX400 (400 MHz) spectrometer with DMSO-d₆ or CDCl₃ and tetramethylsilane (TMS) as solvent and internal reference, respectively.

¹ An interesting work in our lab about the living/controlled radical polymerization of styrene with DCDPS/FeCl₃/PPh₃ initiating system is to be published in *J Polym Sci Part A Polym Chem*.

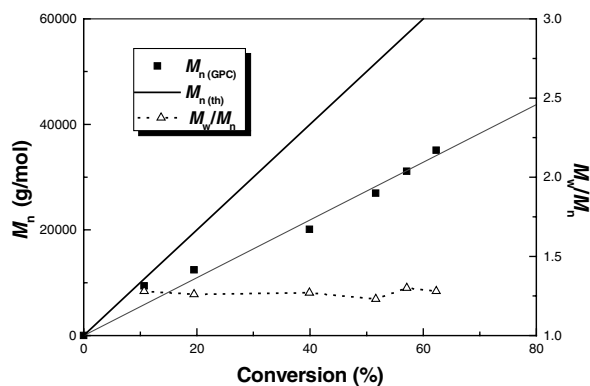


Fig. 3. Dependence of number-average molecular weight and molecular weight distribution of PMMA on conversion at 75°C in toluene solution polymerization of MMA. Conditions: $[MMA]_0 = 6.25 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 12.5 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 37.5 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 3.13 \times 10^{-3} \text{ mol l}^{-1}$.

The glass transition temperature (T_g) was determined with a TA DSC-2010 Differential Scanning Calorimeter at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Living/controlled polymerization of MMA

Bulk polymerization of MMA initiated with DCDPS/ $FeCl_3$ / PPh_3 system was carried out at 75°C ($[MMA]_0/[DCDPS]_0/[FeCl_3]_0/[PPh_3]_0 = 2000/1/4/12$), the results are shown in Figs. 1 and 2. From Fig. 1, we can see that the number-average molecular weight $M_{n(GPC)}$ of PMMA increases linearly with an increase of conversion from 10,600 to 49,300, though less than the calculated values assuming that one molecule of DCDPS generates two living polymer chains. The molecular weight distribution

remained quite narrow during the whole way of polymerization and decreased slightly in the range of 1.29–1.20. While in a comparison experiment MMA was polymerized with DCDPS alone in bulk polymerization (DCDPS/ $FeCl_3$ / PPh_3 /MMA = 1/0/0/2000, at 75°C), the conversion reached 16.9% after 1.5 h, the molecular weight ($M_{n(GPC)}$) increased up to 200,800 and the polydispersity is broader ($M_w/M_n = 1.72$). From these results, we can see that during the same conversion the $M_{n(GPC)}$ and MWD in the comparison experiment are greatly higher than those produced by the ATRP method. Thus, in this system, DCDPS acts as an initiator rather than an iniferter. The logarithmic conversion data $\ln([M]_0/[M])$ plotted against time t as shown in Fig. 2, gave a straight line passing through the origin, which shows the kinetics is first-order in monomer and concentrations of the growing species keep constant during the polymerization. All these convincingly prove that the living/controlled radical polymerization of MMA was well carried out in bulk at 75°C with the DCDPS/ $FeCl_3$ / PPh_3 initiating system.

The solution polymerization of MMA with the initiating system was carried out in toluene at 75°C. As shown in Fig. 3, the $M_{n(GPC)}$ of PMMA increases linearly with the increase of conversion and the polydispersity indices are narrow ($M_w/M_n < 1.31$). The plot of $\ln([M]_0/[M])$ versus time t (in Fig. 4) appears as a straight line not passing through the origin which indicates that the kinetics is first-order in monomer and the concentration of propagating radicals are constant during the solution polymerization, but there is an induction period. The reason might be that the lower concentration of DCDPS caused the slower decomposition of initiator and at the same time $FeCl_3$ was highly excess compared to the free radicals generated. So the polymerization was inhibited. Comparing the kinetic plot of PMMA in bulk with that of the solution polymerization, it shows that at the same experimental condition the bulk polymerization is much faster than the solution polymerization. From the slopes of the straight kinetic plots in Figs. 2 and 4, we calculated the apparent propagation rate constants (k_p^{app}), respectively. 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 [7,32], i.e. $[P^*] = k_p^{app}/k_p$. Kinetic data and estimated concentrations of growing radicals in the polymerization of MMA using the DCDPS/ $FeCl_3$ / PPh_3 initiating system are compiled in Table 1.

However, some deviation from the theoretical molecular weight was observed with this DCDPS/ $FeCl_3$ / PPh_3 initiating system. The similar deviation results of MMA polymerization were reported by Sawamoto et al. [5] and Teyssié et al. [33] with $CCl_4/RuCl_2(PPh_3)_2/MeAl(ODBP)_2$ and $CCl_4/Ni(CN^*)Br$ initiating systems, respectively.

PMMA can also be prepared at lower temperature such as 60°C and the first-order plot of the bulk polymerization of MMA at such low temperature is shown in Fig. 5. Then the same calculation was done and the concentration of growing

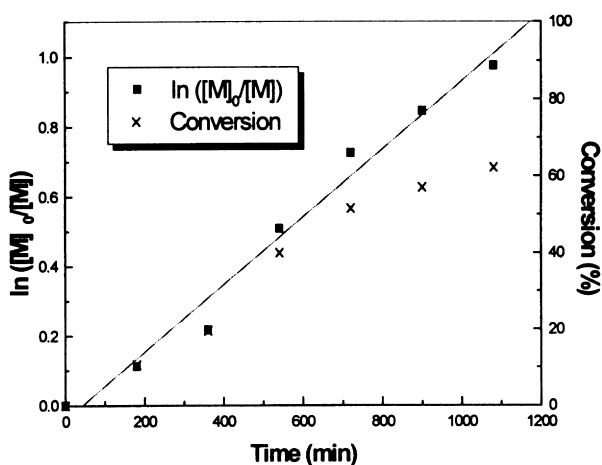


Fig. 4. Time dependence of $\ln([M]_0/[M])$ and conversion at 75°C in toluene solution polymerization of MMA. Conditions: $[MMA]_0 = 6.25 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 12.5 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 37.5 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 3.13 \times 10^{-3} \text{ mol l}^{-1}$.

Table 1

Kinetic data and estimated concentrations of growing radicals for bulk (conditions: $[MMA]_0 = 9.38 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 18.8 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 56.3 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 4.69 \times 10^{-3} \text{ mol l}^{-1}$) and solution (conditions in toluene: $[MMA]_0 = 6.25 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 12.5 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 37.5 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 3.13 \times 10^{-3} \text{ mol l}^{-1}$) polymerization of MMA with DCDPS/ $FeCl_3$ / PPh_3 initiating system

	Bulk	Solution
Temperature ($^{\circ}C$)	75	75
$[M]_0$ (mol l^{-1})	9.38	6.25
k_p^{app} (10^5 s^{-1})	5.18	1.62
k_p^a ($10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$)	1.08	1.08
$[P]$ (10^8 mol l^{-1})	4.78	1.49

^a Values extrapolated from 60 to $90^{\circ}C$; see Ref. [32].

species in this system was found to be $1.09 \times 10^{-8} \text{ mol l}^{-1}$. At $15^{\circ}C$ lower compared to $75^{\circ}C$, the concentration of growing radicals decreased by about four times.

In order to gain better understanding of the reverse ATRP mechanism, we have studied the effect of various concentrations of initiator on the level of the control of polymerization. As seen from Fig. 6, the molecular weight decreases with the increase in DCDPS concentrations at the same experimental conditions, while the polydispersity indices are essentially the same. Thus, in this system there appears to be no significant effect of $[DCDPS]_0$ on polydispersity indices. Indeed, even at a very low concentration of the initiator ($[MMA]_0/[DCDPS]_0 = 4000/1$), the polymerization of MMA occurs well and over a wide range concentration of DCDPS, $[MMA]_0/[DCDPS]_0$ changing from 1000 to 4000, the polydispersity remained quite low ($M_w/M_n \approx 1.20$).

3.2. Polymerization mechanism

The polymerization mechanism is proposed as depicted in Scheme 1. In the initiation step, it consists of the homolytic decomposition of DCDPS initiator to form the primary radicals (R^{\cdot}) and the addition of R^{\cdot} radicals with monomer,

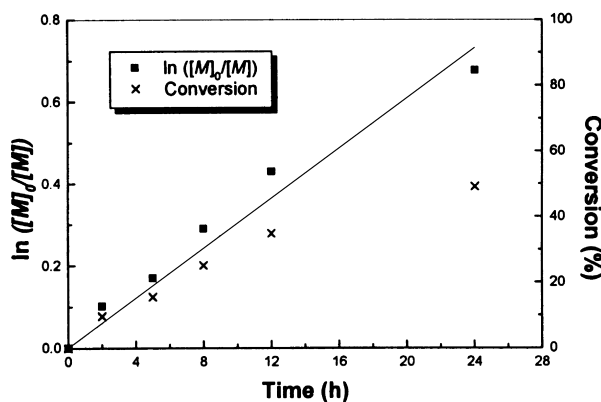


Fig. 5. Time dependence of $\ln([M]_0/[M])$ and conversion at $60^{\circ}C$ in bulk polymerization of MMA. Conditions: $[MMA]_0 = 9.38 \text{ mol l}^{-1}$; $[FeCl_3]_0 = 18.8 \times 10^{-3} \text{ mol l}^{-1}$; $[PPh_3]_0 = 56.3 \times 10^{-3} \text{ mol l}^{-1}$; $[DCDPS]_0 = 4.69 \times 10^{-3} \text{ mol l}^{-1}$.

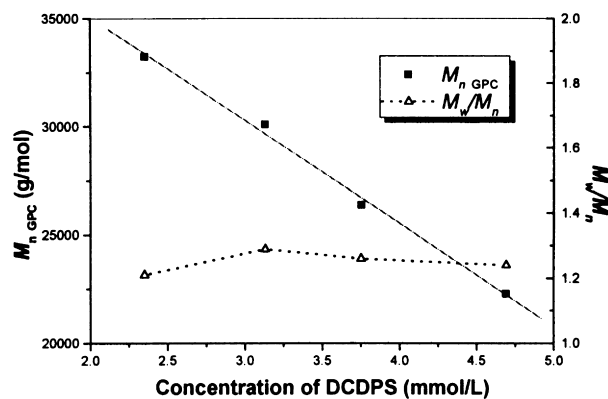


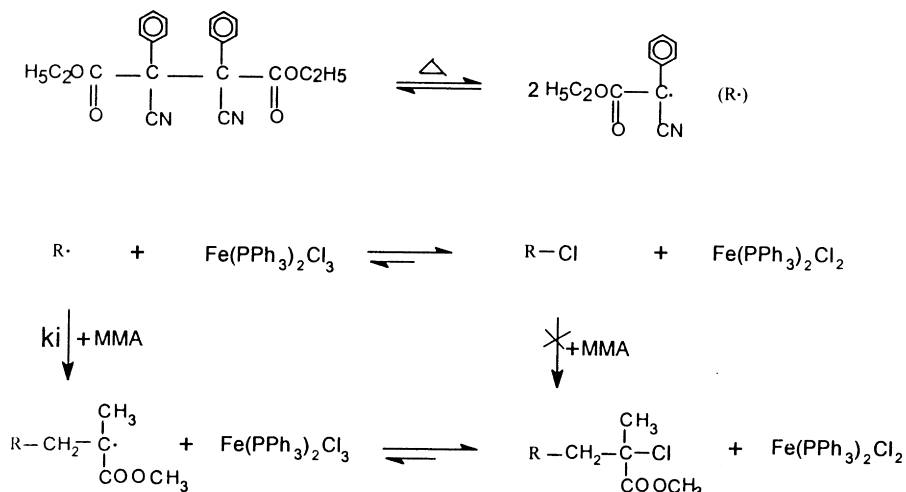
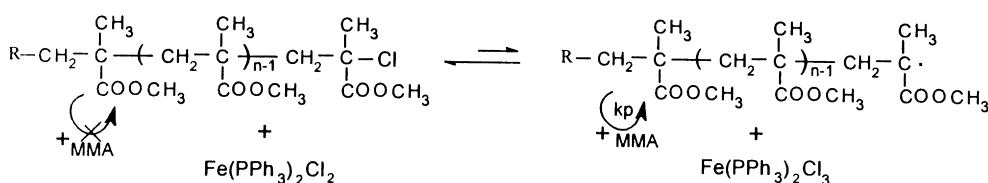
Fig. 6. Dependence of molecular weights and molecular weight distributions of PMMA (in bulk) on various concentrations of DCDPS, $[MMA]_0/[DCDPS]_0 = 4000/1$; $3000/1$; $2000/1$; and $1000/1$, respectively; $DCDPS/FeCl_3/PPh_3 = 1/4/12$.

then the activated monomer radicals react with $Fe(PPh_3)_2Cl_2$ by abstracting the chlorine atom to generate an organic chloride and a lower oxidation state metal complex $Fe(PPh_3)_2Cl_2$. The so-formed organic chloride can reversibly react with $Fe(PPh_3)_2Cl_2$ to regenerate radicals which can then react with the monomer to create propagating chains or directly to react with the catalyst to form the reduced species Fe^{2+} and the dormant species. Later, the polymer propagates via a conventional ATRP process (Scheme 1).

3.3. End group analysis and block copolymerization

End group analysis of the resultant PMMA was carried out by 1H NMR spectroscopy, as shown in Fig. 7. The methyl protons (d) of the terminal methyl ester unit were seen at 3.71 ppm, which departed from other methyl protons (c) of the repeated methyl esters (3.56 ppm), because it was affected by an ω -chlorine atom in the PMMA chain end. The protons (g) of the phenyl group that derived from DCDPS were seen at 7.78 ppm. Both of these results indicate that the end functionalized PMMA with an α -(carboxy-cyanophenyl)-methyl group from DCDPS fragments and an ω -chlorine group from catalyst was obtained by this initiating system. The molecular weight determined from the NMR spectrum ($M_{n(NMR)} \approx 2600$) is calculated from the peak intensity ratios between the methyl groups in main-chain repeated units (a) and the functional end groups (g). However, it is not close to that obtained from GPC ($M_{n(GPC)} \approx 4000$). This might be because the $M_{n(GPC)}$ of PMMA was obtained from polystyrene standard and they do not match well with the $M_{n(NMR)}$.

To investigate the *living* nature of the polymerization, the chain extension polymerization of MMA was carried out in toluene at $100^{\circ}C$ with a PMMA with $M_n = 10,800$ and $M_w/M_n = 1.31$ in the presence of $CuCl/bipy$ as catalyst via the conventional ATRP. The M_n of the resulting PMMA increases up to 130,600 and polydispersity index slightly decreases to 1.09, which can be essentially demonstrated by

Initiation:**Propagation:**

Scheme 1.

the GPC curves shown in Fig. 8. This result confirms the presence of a chlorine atom at the ω -chain end of the original PMMA that can serve as a macroinitiator.

By using the chlorine-terminated PMMA as the macroinitiator for the atom transfer radical copolymerization of styrene, PMMA-*b*-PSt block copolymer could be obtained. Fig. 9 displays the GPC trace of the copolymer and shows no additional peak, confirming that block copolymer has been formed. The T_g values of the copolymer were obtained with

DSC instrument: 114°C for PSt segments and 129°C for PMMA segments, respectively. T_g in the copolymer obtained through the ATRP method are little higher than those prepared by the traditional free-radical polymerization; recently, this interesting phenomenon was also observed by Teyssié et al. [23]. Moreover, the block copolymer composition can be calculated from the peak area of ^1H NMR spectrum, as shown in Fig. 10. The molar ratio of MMA and St units in the copolymer is 1:6. These results

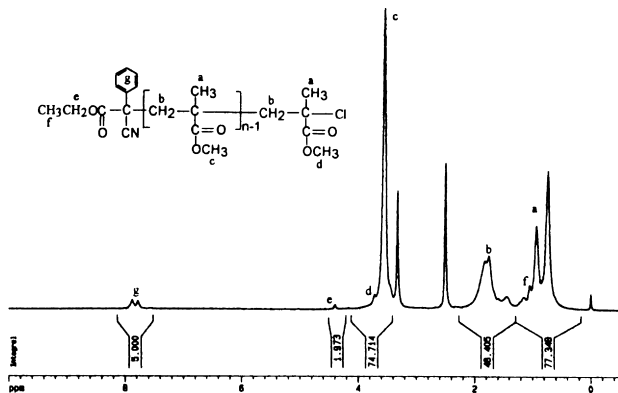


Fig. 7. ^1H NMR spectrum of resultant PMMA initiated with DCDPS/ FeCl_3 / PPh_3 (1/4/12) in bulk at 75°C, $M_n = 4,030$; $M_w/M_n = 1.37$ (in $\text{DMSO}-d_6$, 400 MHz).

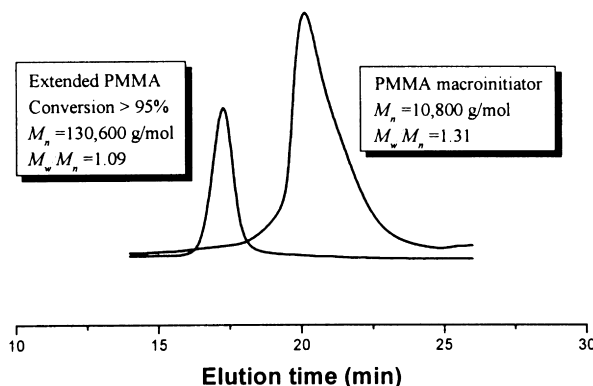


Fig. 8. GPC curves of PMMA before and after chain extension reaction in the presence of CuCl/bipy system at 100°C. Conditions: $t = 22$ h; $[\text{MMA}]_0 = 6.25 \text{ mol l}^{-1}$; $[\text{PMMA}]_0 = 6.18 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{CuCl}] = 6.25 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{bipy}]_0 = 19.8 \times 10^{-3} \text{ mol l}^{-1}$.

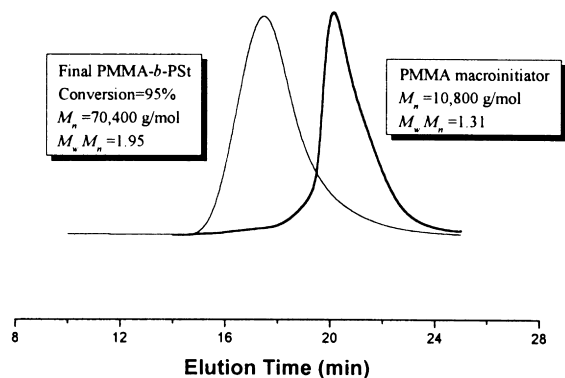


Fig. 9. GPC curves of PMMA before and after copolymerization with St in the presence of CuCl/bipy system at 100°C. Conditions: $t = 48$ h, $[St]_0 = 5.8 \text{ mol l}^{-1}$, $[PMMA]_0 = 5.76 \times 10^{-3} \text{ mol l}^{-1}$; $[CuCl] = 5.83 \times 10^{-3} \text{ mol l}^{-1}$; $[bipy]_0 = 17.4 \times 10^{-3} \text{ mol l}^{-1}$.

indicate that the DCDPS/FeCl₃/PPh₃ initiating system induces *living* polymerization via the reverse ATRP.

4. Conclusion

A reverse ATRP was performed with a new initiating system, i.e. DCDPS/FeCl₃/PPh₃ system, for the *living*/controlled radical polymerization of methyl methacrylate in bulk or in toluene at 75°C. A well-defined PMMA with a high molecular weight (up to 49,300) and quite a narrow polydispersity index ($M_w/M_n \approx 1.20$) was obtained using this system. The number-average molecular weights of polymers increased with the increase of monomer conversion and the first-order plots were made from which the concentrations of growing radicals were estimated. The ¹H NMR spectrum revealed the presence of an α -(carboxy-cyano-phenyl)-methyl group from DCDPS fragments and an ω -chlorine group from catalyst. Furthermore, the chain extension and block copolymerization reactions confirmed that the PMMA thus obtained could act as a macroinitiator with that of ω -chlorine group.

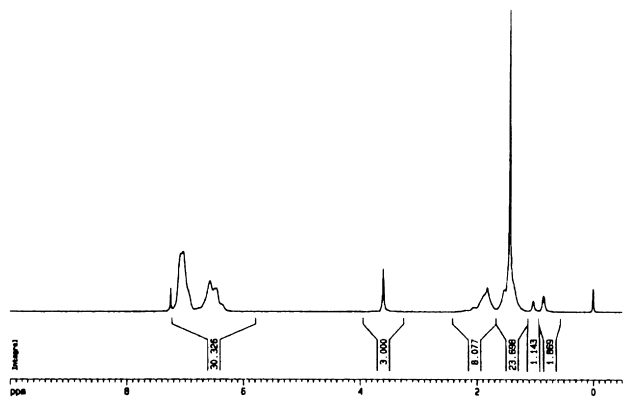


Fig. 10. ¹H NMR spectrum of PMMA-*b*-PSt initiated with PMMA/CuCl/bipy in toluene at 100°C, $M_n = 70,400$; $M_w/M_n = 1.95$ (in CDCl₃, 400 MHz).

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