Atom Transfer Radical Polymerization of MMA Initiated by 2-(4-chloromethyl-phenyl)-benzoxazole and Fluorescent Property of PMMA

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Atom transfer radical polymerization (ATRP) of MMA was conducted using 2-(4-chloromethyl-phenyl)-benzoxazole as initiator, CuCl as catalyst, and PMDETA as ligand. The results show that the polymerization is a first order reaction with respect to monomer concentration. The polymerization displayed living character as evidenced by a liner increase of monomer weight with conversation and a relatively narrow distribution (Mn/Mw range from 1.30 to 1.45). The structure of PMMA was analyzed by ^{1}H-NMR and proved the polymerization could be controlled to some degree. The optical property of the initiator was well preserved in the resulting PMMA, and the end-functionalized PMMA exhibited fluorescent emission at 360 nm whether in DMF solution or in film state.

Keywords: 2-(4-chloromethyl-phenyl)-benzoxazole; fluorescent property; ATRP

1 Introduction

Synthesis of polymers with well-controlled architecture and predictable molecular weight is currently of great academic and industrial interests (1–4). Atom transfer radical polymerization (ATRP) is one of the relatively new and versatile methods for controlled polymerizations (5, 6), which allows polymers with controlled molecular weights and narrow molecular weight distributions to be prepared, and it is tolerant of a certain number of functional initiators. Various functionalized polymers with large conjugated function at α-end can be obtained using different initiators. For example, pyrene, anthracene end functionalized macromonomers were obtained using initiators containing pyrene, anthracene groups (7, 8), which can be used as photoresist materials, and fluorescent probes. Fullerene (C_{60}) terminal can be introduced to the α-end of polymer (9, 10), and C_{60}-containing polymers have special electronic and optical properties. Hydroxyl spirooxazine end fuctionalized PSt can be used as photochromic material (11). Moreover, the synthetic process that ATRP uses does not demand strict reaction conditions, and the

monomers of methacrylate can be polymerized in many ATRP systems even at ambient temperature (5, 6, 12–15).

On the other hand, much attention has been paid to benzoxazole derivatives (16–20) because of their optical applications such as photoluminescents (21, 22), whitening agents (23), and dye laser (24). Herein, we first introduce 2-(4-chloromethyl-phenyl)-benzoxazole (CMPB) as initiator to prepare α-end-functionalized PMMA. Due to the good fluorescent property of CMPB and the fine film forming property of PMMA, inducing CMPB to PMMA's terminal would be a very inspiring application, aiming at preparing optical materials.

In this paper, the ATRP of MMA using CMPB as initiator, and CuCl/PMDETA (PMDETA = N,N,N′,N″,N″-pentamethyldiethylenetriamine) as catalyst system is reported. The results show that the polymerization is well controlled. In particular, CMPB has high activity and can induce MMA even at ambient temperature. Furthermore, the functionalized PMMA shows good fluorescent property both in DMF solution and in film state.

2 Experimental

2.1 Materials

2-(4-chloromethyl-phenyl)-benzoxazole (98%, Lianyungang Based Chemical Co. Ltd.) was recrystallized with ethanol. MMA (CP, Shanghai Chemical Reagent Co., Ltd.) was

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purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and drying with magnesium sulfate anhydrous overnight, and finally distillated in vacuum. Copper(I) chloride (CuCl) (AR, Shanghai Zhenxing Chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried in vacuum. PMDETA (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distillated in vacuum. Cyclohexanone (AR) was dried with magnesium sulfate overnight and distillated in vacuum. Other agents were analytically pure and used without further purification.

2.2 Polymerization

All ATRP reactions were carried out following the same experimental procedure. CuCl, PMDETA, cyclohexanone, initiator, and MMA were mixed in a round-bottomed flask. The flask was sealed and cycled between vacuum and N_2 for four times. Then the flask was sealed under N_2 and placed in a preheated oil bath at a pre-determined temperature. Samples were taken at regular intervals for conversion and molecular weight analysis. The samples were dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.5,V/V). The precipitation was filtrated and dried under vacuum.

2.3 Instruments

^{1}H-NMR was measured by an INOVA 400 MHz NMR instrument, $CDCl_3$ as solvent. Element analysis was obtained by an Carlo Erba-MOD1106 instrument. Purity of the initiator was analyzed by a Waters515 HPLC. Conversion for monomer was determined by gravimetry. Molecular weights and the polydispersity relative to polyMMA were measured using a Waters1515 GPC with THF as a mobile phase and with column temperature of 30°C. UV-Vis spectrum was measured by a Perkin-Elmer λ-17 UV-Vis instrument. Room temperature emission and excitation spectra were carried out using a Edinburgh-920 fluorescence spectraphotometer.

3 Results and Discussion

3.1 Polymerization and Characterization of Polymers

The polymerization of MMA was processed by the use of CMPB as an initiator, and CuCl/PMDETA as the catalyst system. The mechanism of ATRP can be characterized by ^{1}H-NMR spectrum, kinetic plot and polydispersity, etc.

In the initiation process, the hemolytic cleavage of the alkyl halogen bond (CMPB) by the transition metal complex (CuCl) in the lower oxidation state generates an alkyl radical and a transition metal complex ($CuCl_2$) in the higher

oxidation state. The formed radicals can initiate the polymerization, by adding across the double bond of a vinyl monomer (MMA). Since the ATRP equilibrium is strongly shifted toward the dormant species, proportion of the productions formed by radical coupling or disproportionation is so small that it can be neglected. As a result of persistent radical effect, polymers with predictable molecular weights, narrow polydistribution, and high functionalities have been synthesized.

According to the proposed mechanism, the initiator group should be incorporated at the α-end of the polymer chain, while ω-end remains a terminal halide. It can be verified by ^{1}H-NMR (Figure 1). Signals at 8.18 ppm, 7.80 ppm, 7.59 ppm, and 7.37 ppm are attributed to the protons of CMPB, respectively.

The kinetic plot of $\ln([M]_0/[M])$ and conversion vs. time for the ATRP of MMA catalyzed by CuBr/PMDETA initiated by CMPB at 60°C is shown in Figure 2. Plus, $\ln([M]_0/[M])$ increases linearly with the polymerization time, where $[M]_0$ and $[M]$ denote the monomer concentrations at time 0 and t. It indicates the polymerization is first order kinetics and the concentration of growing radical is a constant. The polydispersity is relatively narrow ($M_w/M_n = 1.30-1.45$) (Figure 3). All of these results suggest a "living" polymerization process.

3.2 Influence of Temperature, Initiator, Catalyst and Solvent on Polymerization

The effect of the polymerization temperature on the rate of polymerization was investigated. Table 1 shows a good linear relationship between the rate of polymerization and temperature. With increasing polymerization temperature, the conversion of monomer grew, and number average molecular weights calculated increased as conversion. The rate of polymerization apparently increases with an increasing polymerization because of the increases in the rate constant for radical propagation. On the other hand, the reaction of radical coupling or disproportionation grows with increasing concentration of radical at high temperature, so the polydispersity index become a little wider when the temperature increases.

Polymerization can proceed even at ambient temperature. We considered whether the initiator in ATRP system can form an initiating radical species via homolytic cleavage of labile carbone-halogen bond by the metal catalysts. So we proved that CMPB could initiate MMA polymerization at 30°C by ^{1}H-NMR spectrum. The result is the same as in Figure 1, and PMMA was certain to be functionalized by the title initiator. It can be concluded that CMPB was a high active initiator, and its carbon-halogen bond can easily generate a radical species through electronic and steric effects of their substituents (25). The polydispersity became a bit lower than those in higher temperatures, which might be caused by low radical concentration at lower temperature.
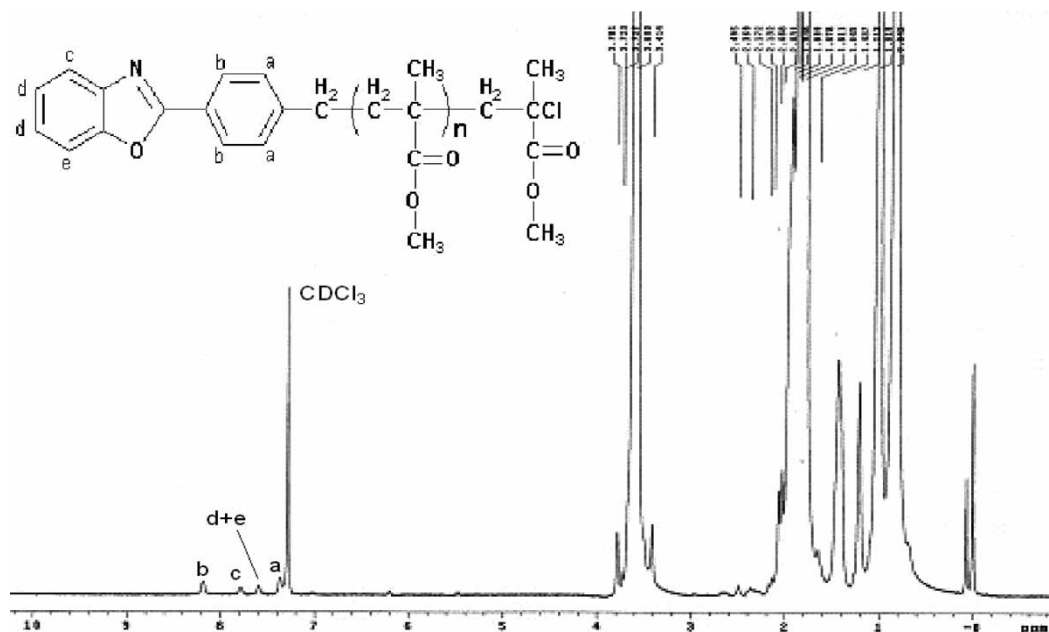
Fig. 1. ¹H-NMR spectrum of PMMA with CDCl₃ as solvent.

In order to select the advisable ligand for ATRP, CuCl/bpy (2,2′-bipyridine) was first employed as the catalyst system for the ATRP of MMA. As shown in Table 2, at the same polymerization, with increasing the concentration of bpy in polymerization system, conversion, number average molecular weights and polydistribution index have no obvious change, because a CuCl to bpy ratio of 1:1 is sufficient to achieve maximum rates and control of polymerization, and the concentration of bpy has little effect on polymerization; with decreasing the concentration of CuCl in polymerization and keeping the ratio of CuCl/bpy = 1:3 constant, number average molecular weights decrease and the polydistribution index becomes a little broad, because the concentration of radical in polymerization system decreases as that of catalyst, and the

polymerization rate reduces. If the concentration of catalyst is lower in polymerization, polydistribution index will become broader, and polymerization in bad control (9).

With bpy as ligand in ATRP, the polymerization is in control, but the polydistribution index is a little broad (M_w/M_n is about 1.52). Subsequently, CuCl/PMDETA was used as the catalyst system. As shown in Table 3, when the tridentate amine ligand (PMDETA) was employed in ATRP, the effects of the concentration of PMDETA and CuCl are the same as the corresponding bpy system, but the products have a lower polydistribution index and the rate of polymerization showed a significant increase. The higher polymerization rate of PMDETA as the ligand is partly attributed to the lower redox potential of CuCl/PMDETA complex than the CuCl/bpy complex, which shifts the equilibrium from

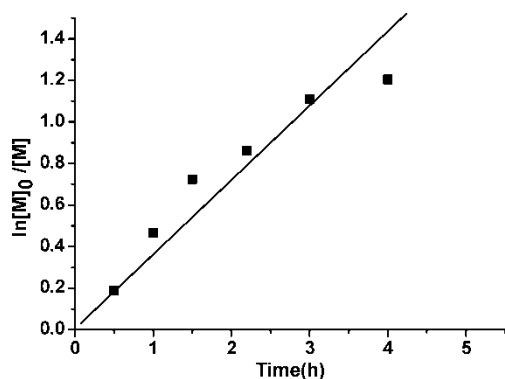**Fig. 2.** Kinetic plot for the polymerization of MMA in cyclohexanone solution (67%v/v) at 60°C ([MMA]/[initiator]/[CuCl]/[PMDETA] = 100:1:0.25:0.5).

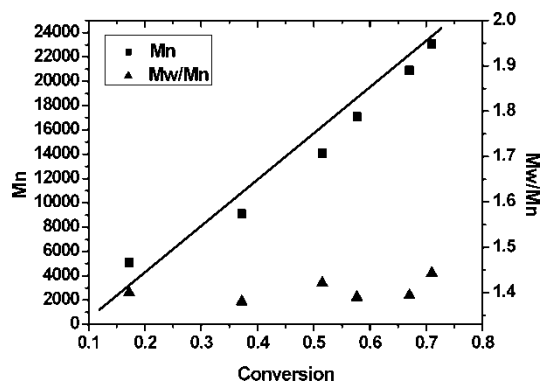**Fig. 3.** Evolution of M_n and M_w/M_n with conversion for the polymerization of MMA in cyclohexanone solution (67%v/v) at 60°C ([MMA]/[initiator]/[CuCl]/[PMDETA] = 100:1:0.25:0.5).

Table 1. Influence of temperature on polymerization of MMA in cyclohexanone solution (67%v/v) ([MMA]/[CMPB]/[CuCl]/[PMDETA] = 200:1:1:1)

Temperature (°C)	Time (h)	Conversion (%)	$M_{n \cdot GPC}$	$M_{n \cdot th}$	M_w/M_n
30	3	43.5	12500	8700	1.35
40	3	65.0	17481	13000	1.40
50	3	73.0	18590	14600	1.36
60	3	76.0	21030	15200	1.39
70	3	81.0	22103	16200	1.41
80	3	83.0	23501	16600	1.42

$M_{n \cdot th} = ([MMA]_0/[initiator]_0)*MW_{MMA}*conversion.$

Table 2. Influence of concentration of catalyst and ligand (2,2′-bipyridine) on polymerization of MMA at 60°C in cyclohexanone solution (67%v/v)

n(CuCl): n(bpy)	Time (h)	Conversion (%)	$M_{n \cdot GPC}$	$M_{n \cdot th}$	M_w/M_n
1:3	3	62.0	35198	12400	1.51
1:2	3	64.0	35695	12800	1.54
1:1	3	64.0	33782	12800	1.55
0.5:1.5	3	58.0	28976	11600	1.49
0.2:0.6	3	53.0	27525	10600	1.50
0.1:0.3	3	51.0	23100	10200	1.54

the dormant species toward the active species resulting in the generation of more radicals in the system. Thus, compared to bpy as ligand, utilizing PMDETA as ligand, a well-controlled radical process with faster polymerization rate can be achieved (26).

Table 4 shows the effects of monomer to CMPB mole ratio on conversion, molecular weight and the polydispersity of PMMA. With increasing mole ratio of monomer to initiator and keeping the concentration of Cu/PMDETA constant, number average molecular weights increased. Well-defined polymers with molecular weights determined by the ratio of

Table 3. Influence of concentration of catalyst and ligand(PMDETA) on polymerization of MMA at 60°C in cyclohexanone solution (67%v/v)

n(CuCl): n(PMDETA)	Time (h)	Conversion (%)	$M_{n \cdot GPC}$	$M_{n \cdot th}$	M_w/M_n
1:3	3	75.0	20638	15000	1.38
1:2	3	73.0	19542	14600	1.35
1:1	3	76.0	21030	15200	1.39
0.5:1	3	70.0	23079	14000	1.41
0.2:0.4	3	60.0	37872	12000	1.43
0.1:0.2	3	59.0	37828	11800	1.46

Table 4. Influence of concentration of CMPB on polymerization of MMA at 60°C in cyclohexanone solution (67%v/v)

n(MMA): n(CMPB)	Time (h)	Conversion (%)	$M_{n \cdot GPC}$	$M_{n \cdot th}$	M_w/M_n
50:1	3	80.0	15501	4000	1.41
100:1	3	78.0	19445	7800	1.35
200:1	3	76.0	21030	15200	1.39
300:1	3	64.0	24805	19200	1.38
400:1	3	60.0	27843	24000	1.39

consumed monomer to introduced initiator were obtained and the polydistribution index was generally lower.

ATRP of MMA with CMPB as initiator was also conducted in different solvents. At first, whether in mass homogeneous polymerization using anisole solvent or in heterogeneous polymerization using xylene as solvent, no product could be obtained. Then, we chose ketone solvents (Table 5), such as acetone, hypnone and cyclohexanone. The polymerizations were both in control with all types of ketone solvents and the optimal solvent is cyclohexanone with fast polymerization rate. It can be explained that CuCl/PMDETA has good solubility in DMF and that the concentration of the catalyst is larger than in others.

As shown in Table 5, in the same polymerization time, when $V_{Solvent}/V_{MMA + Solvent} = 67\%$, the concentration of MMA is optimal, and the polymerization exhibits better control than in other systems.

3.3. Fluorescent Property

The UV-Vis absorption wavelength of functionalized PMMA and CMPB are shownin Table 6. Their UV-Vis absorptions were almost at the same wavelength, because both of them have a 2-benzyl benzoxazole group which occurred at π-π^* transition.

As shown in Figure 4, PMMA initiated by CMPB could emit strong fluorescence at about $\lambda_{em} = 360$ nm with $\lambda_{ex} = 278$ nm, while the PMMA with the same molecular weight and

Table 5. Influence of solvents on polymerization of MMA at 60°C ([MMA]/[CMPB]/[CuCl]/[PMDETA] = 200:1:1:1)

Solvent	Time (h)	Conversion (%)	$M_{n \cdot GPC}$	$M_{n \cdot th}$	M_w/M_n
Acetone	3	58.0	16206	11600	1.50
Hypnone	3	64.0	18849	12800	1.51
Cyclohexanone (50%v/v)	3	70.0	28976	14000	1.44
Cyclohexanone (67%v/v)	3	76.0	21030	15200	1.39
Cyclohexanone (75%v/v)	3	75.0	23100	15000	1.40

Table 6. UV−Vis absorption and fluorescence emission data of polymer and CMPB in DMF solution at room temperature 25°C

	UV−Vis λ_{max}^a (nm)	Fluorescence λ_{em}^a (nm) emission
Functionalized PMMA	299	360
CMPB	299	390

$^a 10^{-4}$ M in DMF.
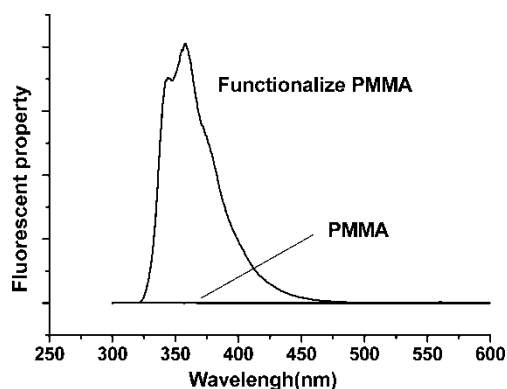
Fig. 4. The fluorescent intensity of functionalized PMMA and PMMA with $\lambda_{ex} = 280$ nm.

concentration in DMF solution (10^{-4} M) initiated by ethyl 2-bromoisobutyrate emitted relatively weak fluorescence. Obviously, introduction of a 2-benzyl benzoxazole group through CMPB successfully increases the fluorescent intensity of PMMA. We also studied the emission of its film, which is very similar with the pattern of it in DMF solution. This indicates that the fluorescent emission of the functional end group is well-preserved in solid state and also provides a new method to obtain practicable optical polymer film.

4 Conclusions

The polymerization of MMA using CMPB as initiator, CuCl as catalyst, PMDETA as ligand and cyclohexanone as solvent matched well to atom transfer radical polymerization. The factors influencing the ATRP system are discussed. As one of the most important factors, initiator CMPB is focused on because of its high activity and possible functionality. The result also shows that polymerization of MMA can be conducted successfully even at ambient temperature. Moreover, PMMA initiated by CMPB can emit strong fluorescence at $\lambda_{em} = 360$ nm with $\lambda_{ex} = 278$ nm both in DMF solution and in thin film. Further work about polymer's fluorescent property is under way.

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