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ORIGINAL PAPER

Synthesis of fluorescent poly(methyl methacrylate) via AGET ATRP

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Abstract Polymerization of methyl methacrylate (MMA) was successfully carried out via activator generated by electron transfer for atom transfer radical polymerization technique with naphthalene-1,5-diyl-bis (2-bromo-2-methylpropanoate) as an initiator, $CuCl_2$/bpy complex as a catalyst and tin(II) 2-ethylhexanoate ($Sn(EH)_2$) as a reducing agent in anisole. The polymerization showed typical features of “living”/controlled radical polymerization such as a linear increase of the molecular weights of the polymers with monomer conversion and relatively narrow polydispersities throughout the polymerization process. The resultant fluorescent poly(methyl methacrylate) was characterized by nuclear magnetic resonance spectroscopy, infrared absorption spectroscopy, ultraviolet absorption spectrophotometry and fluorescence spectrophotometry.

Keywords AGET ATRP · Fluorescent polymers · PMMA · Living radical polymerization

Introduction

Atom transfer radical polymerization (ATRP) has rapidly developed since it was first proposed in 1995 [1–7]. ATRP provides a very simple way to syntheses of well-defined polymers with control over all aspects of polymer molecular weight, polydispersity, composition, topology and terminal functionality [3–5]. However, there are a few limitations in ATRP, such as sensitive to air, transition metal complexes have to be removed from the reaction mixture and preferably recycled [7].

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In order to improve ATRP technique, a new method, activator generated by electron transfer for atom transfer radical polymerization (AGET ATRP), has been proposed by Matyjaszewski's group [8–10]. AGET ATRP uses a reducing agent to reduce the higher oxidation state transition metal into an active lower oxidation transition metal in situ. Since its proposition in 2005, AGET ATRP has successfully applied to polymer synthesis, including application in the presence of air [11–13], nano techniques [14, 15], and in the polymerization of various monomers in bulk and mini emulsion [16–23].

Fluorescent polymers are a kind of very important polymers with wide application, which can be successfully synthesized using various fluorescent initiators via ATRP technique, such as α-halooxazoles, 2-(4-chloromethyl-phenyl)-benzoxazole (CMPB) [24], porphyrin [25], and polyfluorene macroinitiator [26, 27]. However, to the best of our knowledge, there have been fewer reports about the synthesis of fluorescent polymers via AGET ATRP. Inspired by the advantages of AGET ATRP such as using oxidative stable state Cu(II) or Fe(III) complexes [12, 28–31] as the catalysts, in this work, we report the synthesis of fluorescent poly(methyl methacrylate) (PMMA) via AGET ATRP using naphthalene-1,5-diyl-bis(2-bromo-2-methylpropanoate) (NBM) as an initiator, $CuCl_2$/bpy complex as a catalyst, and tin(II) 2-ethylhexanoate ($Sn(EH)_2$) as a reducing agent. The fluorescent properties of the obtained PMMA were studied by fluorescence spectrophotometry.

Experimental section

Materials

The monomer, methyl methacrylate (MMA) (>99%), purchased from Shanghai Chemical Reagents Co. (Shanghai, China), was washed with an aqueous solution of sodium hydroxide (5 wt%) three times, followed by deionized water until neutralization, then dried over anhydrous magnesium sulfate, distilled under reduced pressure and stored at −18 °C. Tin (II) 2-ethyl hexanoate (∼90%), purchased from Stream Chemicals (MA, USA), 1,5-dihydroxynaphthalin (97%) purchased from Sigma-Aldrich Chemie (Steinheim, Germany), copper(II) chloride (>99%) and 2,2′-bipydidyl (bpy) purchased from Shanghai Chemical Reagents Co. (Shanghai, China). 2-Bromo-2-methylpropionyl bromide (98%), purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

Synthesis of bifunctional initiator naphthalene-1,5-diyl-bis(2-bromo-2-methylpropanoate)

A solution of 2-bromo-2-methyl-propionyl bromide (4.6 g, 0.02 mol) in 10 mL of chloroform was dropped into a solution of 1,5-dihydroxynaphthalin (1.6 g, 0.01 mol) in 100 mL of $CHCl_3$ in a threeneck flask at 0 °C. The resulting solution was stirred overnight. After filtration, the solvent was evacuated off, and the crude product was purified by re-crystallization from ethanol twice. A beige crystal (NBM) was obtained (1.90 g, 43% of yield). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.34–7.99 (6H, naphthalene-H), 2.19[12H, $C(CH_3)_2$]. ELEM. ANAL. Calcd.: C, 47.19; H, 3.96%. Found: C, 47.03%; H, 3.98%.

Polymerization

A typical AGET ATRP procedure was carried out as follows: a dry glass tube was quantitatively filled with $CuCl_2$, bpy, NBM and MMA in sequence and 1 mL of $Sn(EH)_2$ anisole solution (0.047 mol/L) was added. The mixture was bubbled with argon for 20 min, and the tube was sealed under argon, immersed into an oil bath held by a thermostat at the desired temperature (80 °C) to polymerize under stirring. The polymerization was stopped at a desired time by cooling the tubes with cold water. Afterwards, the tube was opened and the contents were diluted with THF ($\sim$2 mL). Then the solution was poured into a large amount of methanol/HCl (100/5, volume ratio) mixture ($\sim$200 mL). The polymers were filtered and dried under vacuum.

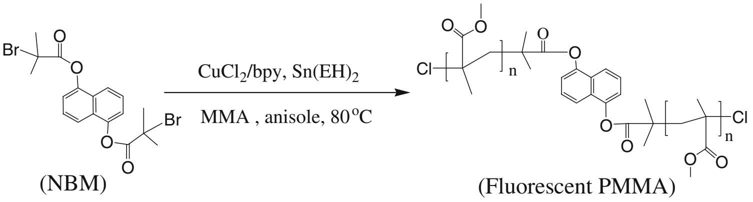
Characterizations

Conversion of monomer was determined by gravimetry. The molecular weights and molecular weight distributions of the polymers were determined on a Waters 1515 gel permeation chromatograph (GPC) equipped with refractive index detector (Waters2414), using HR 1, HR 2, and HR 4 (7.8 × 300 mm, 5 μm beads' size) columns with molecular weight range 100–500,000 g/mol. THF was used as an eluent at a flow rate of 1.0 mL min^{-1} and operated at 30 °C. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with PMMA standards from Waters. ^{1}H NMR spectra were recorded on a nuclear magnetic resonance (NMR) instrument (INOVA 400 MHz Spectrometer) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Elemental analysis of C and H were measured with an EA1110 CHNO-S instrument. The fluorescence spectra of the polymers and the initiator were recorded by HITACHI F-2500 Fluorescence Spectrophotometer with THF as solvent. The UV–vis absorption spectra of the polymers and the initiator in THF solution were determined on a Shimadzu RF540 spectrophotometer. FT-IR spectra were recorded on a NICOLET 380 FT-IR spectrometer.

Results and discussion

AGET ATRP of MMA using NBM as the initiators

The new naphthalene-containing bifunctional initiator, NBM (Scheme 1), was used in the AGET ATRP of MMA. $Sn(EH)_2$ was used as the reducing agent to generate Cu(I) from $CuCl_2$/bpy complexes in situ. According to the mechanism of ATRP, the resultant polymers (PMMA) should contain a fluorescent chromophore (naphthalene group)in the center of the polymer chains.



Scheme 1 Schematic diagram illustrating the process for the fluorescent PMMA via AGET ATRP technique

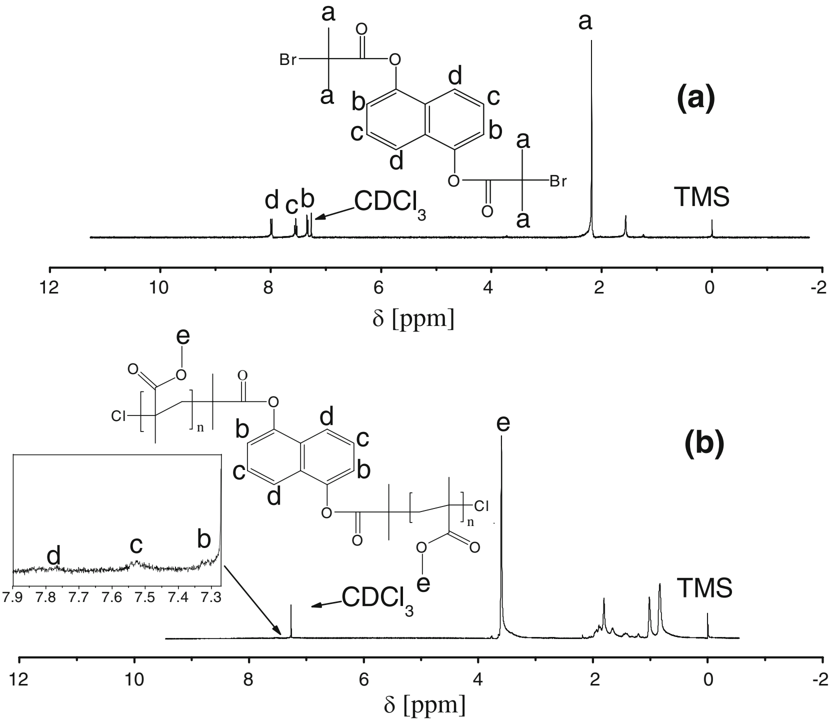


Fig. 1 ^{1}H NMR spectra of NBM (**a**) and PMMA (**b**) in $CDCl_3$. PMMA sample: $M_{n,GPC} = 18{,}600$ g/mol, $M_w/M_n = 1.46$

Figure 1 shows the ^{1}H NMR spectra of NBM (Fig. 1a) and resultant polymer (Fig. 1b) in $CDCl_3$. The signals at 2.2–2.3 ppm were attributed to protons of methyl next to halogen atoms, and the typical proton signals at 7.3–8.0 ppm were assigned to protons of naphthalene in Fig. 1a. These protons signals of naphthalene can also be seen in the resultant polymers (Fig. 1b), which indicated that the moieties in NBM were successfully attached to the polymer. The attachment also confirmed by IR spectra of NBM and obtained polymer PMMA, as shown in Fig. 2. The characteristic absorption bands of C–H of aryl stretching vibration of NBM and PMMA appeared at 3,020 and 3,004 cm^{-1}, respectively. Meanwhile, the absorption

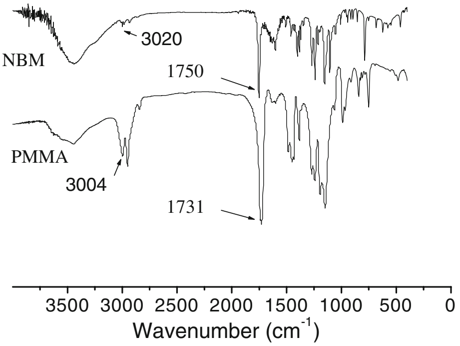


Fig. 2 FT-IR spectra of NBM and PMMA obtained via AGET ATRP of MMA using NBM as the initiator. PMMA sample: $M_{n,GPC} = 18{,}600$ g/mol, $M_w/M_n = 1.46$

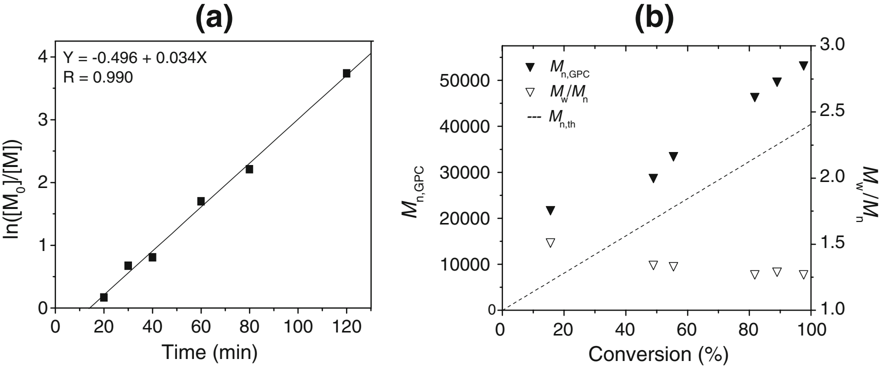


Fig. 3 Kinetic plot (**a**), dependence of M_n and M_w/M_n on conversion (**b**) for the AGET ATRP of MMA at 80 °C polymerization conditions: $[MMA]_0/[NBM]_0/[CuCl_2]_0/[bpy]_0/[Sn(EH)_2]_0 = 200{:}0.5{:}0.5{:}1.5{:}0.5$; $[MMA]_0 = 6.26$ M; solvent = anisole

bands of C=O stretching vibration of NBM and PMMA appeared at 1,750 and 1,731 cm^{-1}, respectively.

Figure 3a shows the kinetic plot of AGET ATRP of MMA with a molar ratio of $[MMA]_0/[NBM]_0/[CuCl_2]_0/[bpy]_0/[Sn(EH)_2]_0 = 200{:}0.5{:}0.5{:}1.5{:}0.5$ at 80 °C. The first-order kinetics indicated a constant radical concentration throughout the polymerization. However, an induction period ($\sim$15 min) was observed. This may be explained by slow establishment of the equilibrium between active and dormant species and the impurities in the reaction systems. Evolution of M_n with conversion was found to be linear as shown in Fig. 3b. Experimental M_n values were higher than the corresponding theoretical ones. This phenomenon may indicate inefficient initiation of NBM. However, the molecular weight distributions of the obtained PMMA decreased with the monomer conversion up to 98% ($M_w/M_n = 1.28$), demonstrating the nature of "living"/controlled radical polymerization.

Chain extension

According to the mechanism of AGET ATRP, if the end of the polymer chain has a halogen atom, it can be used as a macroinitiator to initiate the polymerization of a

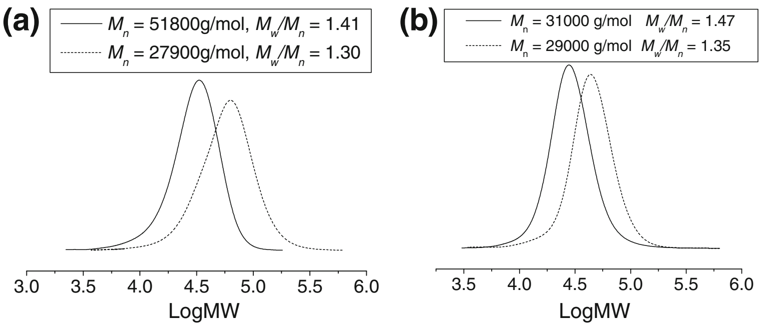


Fig. 4 GPC traces of the original PMMA and the corresponding chain-extended PMMA (**a**) (polymerization conditions: $[\mathrm{MMA}]_0/[\mathrm{NBM}]_0/[\mathrm{CuCl_2}]_0/[\mathrm{bpy}]_0/[\mathrm{Sn(EH)_2}]_0$ = 800:0.5:0.5:1.5:0.5; $[\mathrm{MMA}]_0$ = 6.26 M; solvent = anisole, temperature = 80 °C, time = 1.5 h, conversion = 26%.) as well as the triblock copolymer PS-*b*-PMMA-*b*-PS (**b**) (polymerization conditions: $[\mathrm{St}]_0/[\mathrm{NBM}]_0/[\mathrm{CuCl_2}]_0/[\mathrm{bpy}]_0/[\mathrm{Sn(EH)_2}]_0$ = 800:0.5:0.5:1.5:0.5; $[\mathrm{St}]_0$ = 5.82 M; solvent = anisole, temperature = 80 °C, time = 4 h, conversion = 22%.) using the original PMMA as the macroinitiator

fresh feed of monomer in the presence of AGET ATRP catalyst. Figure 4a shows the GPC curves of the polymers before and after the chain extension. The M_n of the PMMA increased from 27,900 to 51,800 g/mol after chain extension reaction. However, molecular weight distribution (M_w/M_n = 1.41) of the final polymer was broader than that (M_w/M_n = 1.30) of the PMMA macroinitiator, which may be assignable to both the side reaction in the period of chain propagation and some dead polymer chains existed in the macroinitiator. Furthermore, the PMMA macroinitiator was also used to initiate the polymerization of styrene in the same condition. The GPC curves of the PMMA macroinitiator and the final block polymer obtained after chain extension reaction are shown in Fig. 4b. A triblock copolymer, PS-*b*-PMMA-*b*-PS with M_n = 31,000 g/mol and M_w/M_n = 1.47, was obtained via AGET ATRP of styrene and the structure of triblock copolymer was confirmed by ^{1}H NMR, as shown in Fig. 5. The proton signal at 3.6 ppm (**a**) can be assigned to protons of methoxyl group in macroinitiator PMMA block, while proton signals from 6.2 to 7.2 ppm (**b**) corresponded to aromatic protons in PS blocks. Table 1 shows more chain extension results of styrene at the same condition as above. These results demonstrated the presence of a halogen atom at the both ends of the PMMA chains. All of these results further confirmed that the AGET ATRP of MMA initiated by NBM was a "living"/controlled radical polymerization.

UV–vis absorption and fluorescent property of the polymers

UV spectra of NBM and obtained polymers are showed in Fig. 6. The UV spectrum of the PMMA containing naphthalene moieties was similar to that of NBM in shape. Both NBM and the resultant polymers appeared intense absorption at 210–250 nm and weak absorption at 250–330 nm, corresponding to absorption of naphthalene moieties. Furthermore, as shown in Fig. 6, the molecular weight of the polymers had no obvious effect on the UV absorption intensity. These results confirmed that naphthalene moieties were covalently attached in the polymers.

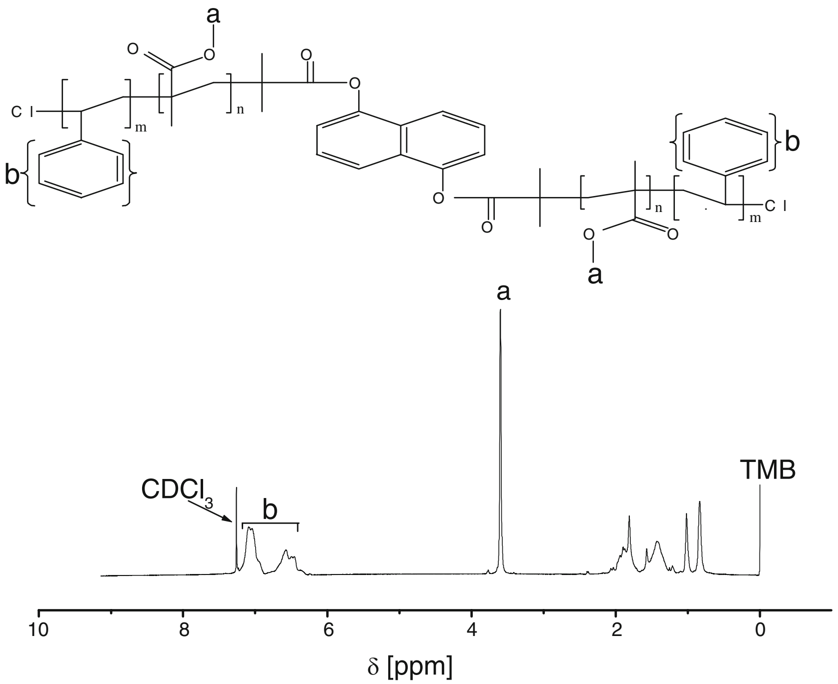


Fig. 5 ^{1}H NMR spectrum of the triblock copolymer: PS-*b*-PMMA-*b*-PS ($M_n = 31{,}000$ g/mol, $M_w/M_n = 1.47$)

Table 1 Chain extension results of styrene

M_n (g/mol) (before chain extension)	M_n (g/mol) (after chain extension)	M_w/M_n
29,000	31,000	1.47
29,000	33,000	1.50
18,100	21,200	1.42

Figure 7 shows the fluorescence emission spectra of NBM and PMMAs dissolved in THF at room temperature with excitation wavelength $\lambda_{ex} = 258$ nm. The results showed that the resultant polymers exhibited strong fluorescence emission in a short wavelength region, and the fluorescence maximum wavelength was 295 nm. From Fig. 7, it can also be seen that the fluorescence intensity of the polymers increased with the molecular weight of the polymers, as reported by documents [32–35]. The increase in the fluorescence intensity with molecular weight of PMMA may be assigned to the chromophore–chromophore interactions in the intramolecular system due to the increase of chain length [36–38].

As discussed above, the fluorescence intensity of PMMA increases with the PMMA molecular weight and it is proportional to number-average molecular weight (M_n), which opens the possibility to determine the molecular weight by end-

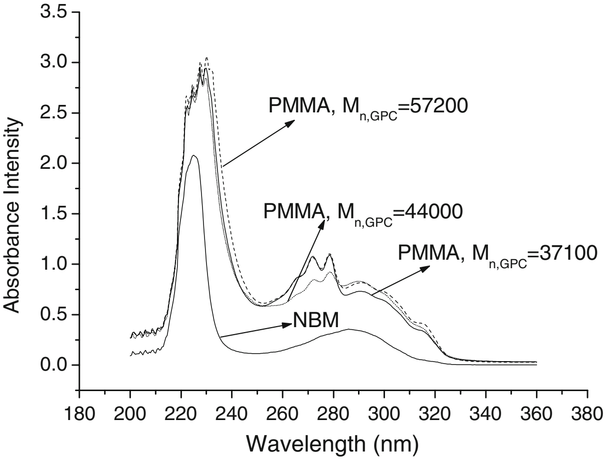


Fig. 6 UV spectra of NBM and PMMA containing naphthalene moieties in THF. The solution concentration of NBM moieties was 5×10^{-5} mol L^{-1}

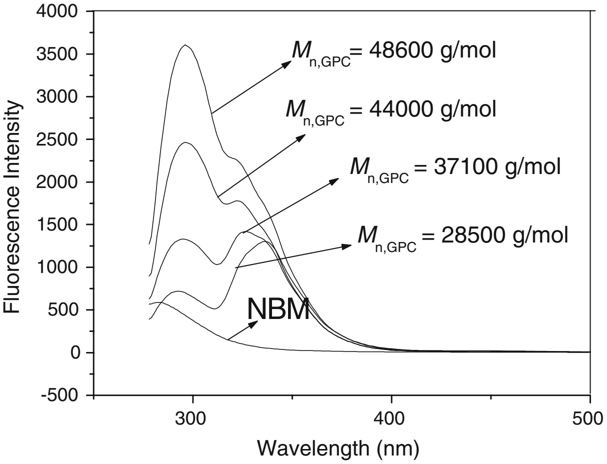


Fig. 7 Fluorescence spectra of NBM and PMMA in THF at room temperature. The concentration of NBM moieties was 5×10^{-5} mol L^{-1}, and the excitation wavelength was 258 nm

Table 2 M_n of the obtained PMMA determined from GPC and FS

Entry	M_n (determined by GPC)	M_n' (determined by FS)
1	29,100	30,000
2	33,700	32,400
3	39,400	37,036

group analysis using fluorescence spectroscopy. Table 2 shows M_ns of some PMMA samples determined from both GPC and fluorescent spectroscopy (FS). As shown in Table 2, All the M_ns from GPC are close to those from FS.

Conclusions

A bifunctional naphthalene-1,5-diyl-bis(2-bromo-2-methylpropanoate) (NBM) was successfully used as the initiator for the AGET ATRP of MMA and well-defined fluorescent polymers containing naphthalene moieties in the middle of the polymer chains were obtained. The polymerizations were well controlled with a linear increase of molecular weights of the polymers with monomer conversions and relatively narrow polydispersities. The fluorescence intensity of the resultant PMMA at 295 nm increased with the molecular weight of the polymers.

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