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# Synthesis of Poly(methyl methacrylate) Labeled with Fluorescein Moieties via Atom Transfer Radical Polymerization

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Fluorescein chromophore-labeled poly(methyl methacrylate) (PMMA) was prepared via atom transfer radical polymerization (ATRP) with two novel bromine-containing fluorescein derivatives, 3,6-bis(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Fla-Br) and 3-(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Flb-Br), as the functional initiators and CuBr/PMDETA as the catalyst, respectively. The above mentioned fluorescein containing bromine were synthesized in our lab. The ATRP of PMMA was proved in a controlled fashion. The resultant PMMA with narrow molecular weight distribution was endowed with the fluorescein chromophore incorporated into the polymer backbone. The presence of the fluorescein labeling of the polymers was confirmed by <sup>1</sup>H-NMR and GPC trace under UV detector. The UV spectroscopy and fluorescence measurements of the resultant polymer gave further evidence of the functionality of the fluorescein labeling.

**Keywords:** labeled polymer; ATRP; fluorescein

## 1 Introduction

Well-defined polymers containing precisely placed aromatic chromophores have attracted increasing interest due to their applications such as energy transfer studies, light emitting diodes and fluorescent labeling (1–13). A number of excellent works on the well-defined polymers and dendrimers containing aromatic chromophore labels, such as naphthalene (14, 15), anthracene (16–21), carbazole (22–25), fluorine (26), pyrene (27–35), perylene (36–38), naphthalimide (39) and fluorescein units (40), have been reported. These functional aromatic chromophores could be immobilized at the chain end, in the middle of the main chains, or on the polymeric chains with pendent groups.

Various methods have been developed to attach aromatic chromophore moieties to polymers. One is coupling reactions between polymer anions and electrophilic chromophores. However, this method usually results in partial chromophore incorporation. Conventional free radical polymerization is also used for its easy performing, but the structures of the polymers obtained in this way are poorly-defined. Anionic

polymerization could be utilized to solve this problem, and well-defined polymers with predetermined molecular weights and narrow molecular weight distributions were obtained. However, it is difficult to apply widely due to the stringent reaction conditions and the limit of the monomers. Recently, atom transfer radical polymerization (ATRP) has received much attention due to its versatility (41–44). The ATRP not only provides polymers with controlled molecular weights and narrow molecular weight distributions, but also can be performed using conventional radical polymerization procedures for a variety of monomers, avoiding the stringent reaction conditions needed for living ionic polymerization. Many polymers with narrow molecular weight distributions and specific functional groups have been obtained from ATRP (15, 19–21, 26, 43, 44).

Fluorescein and their derivatives were widely employed in technology, for instance, to label macromolecules for detection in capillary electrophoresis, (45) to label primers used in automated DNA sequencing, (46) due to its strong absorption in visible range, high fluorescence quantum yield and high photostability. Mahesh et al. (47) prepared segmented polyurethanes by chain extending from fluorescein to enhance thermal and mechanical properties. Nakanishi et al. (40) synthesized polymers doubly labeled with anthracene and fluorescein by the reactions of a random copolymer of styrene and chloromethylstyrene with potassium salt of 9-anthracenecarboxylic acid and fluorescein monosodium

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salt. Periyayya et al. (48) synthesized low molecular weight polyesters containing fluorescein units in the backbone. However, the attention on the approach of conjugating fluorescein to macromolecules is still insufficient. In this paper, we present the synthesis of fluorescein-labeled PMMA via ATRP, using 3,6-bis(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Fla-Br) and 3-(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Flb-Br) as the functional initiators.

## 2 Experimental

### 2.1 Materials

Methyl methacrylate (MMA) (Chemical pure, Shanghai Chemical Reagent Co., Ltd., China) was washed with an aqueous solution of sodium hydroxide (5 wt%) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the MMA was vacuum distilled over  $\text{CaH}_2$  and then stored under nitrogen at  $-20^\circ\text{C}$ .  $\text{CuBr}$  (98%, Aldrich) was purified by stirring in acetic acid, washing with acetone, and then drying under vacuum.

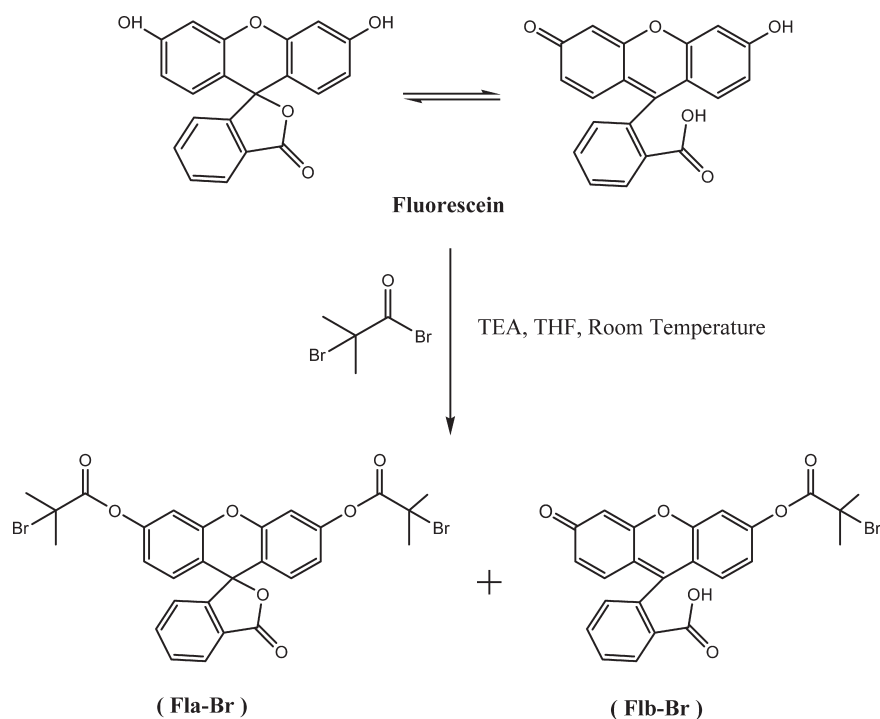
$N, N, N', N''$ -pentamethyldiethylenetriamine (PMDETA) (Chemical pure, Jiangsu Liyang Jiangdian Chemical Factory) and triethylamine (TEA) (Chemical pure, Shanghai Chemical Reagent Co., Ltd., China) were dried with 4Å molecular sieve and distilled under vacuum. Anisole and  $N, N$ -dimethylformamide (DMF) (Analytical reagent, Shanghai Chemical Reagent Co., Ltd., China) was purified by distilling

under vacuum. Tetrahydrofuran (THF) (Analytical reagent, Shanghai Chemical Reagent Co., Ltd., China) was purified by distilling in the presence of sodium metal. Fluorescein (Fluka) was used as received. All other solvents and reagents were purchased from commercial sources and were used as received.

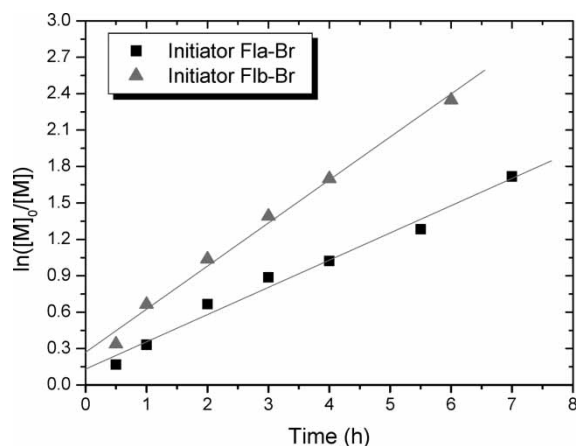
### 2.2 Synthesis of Initiators of Fla-Br and Flb-Br

Triethylamine (4.2 mL, 0.03 mol) was added to a solution of fluorescein (3.32 g, 0.01 mol) in dry tetrahydrofuran (THF) (100 mL). The solution was stirred in an ice bath under nitrogen, and 2-bromoisobutyryl bromide (3.7 mL, 0.03 mol) in dry THF (4 mL) was added dropwise over a period of 0.5 h. The reaction mixture was stirred at  $0^\circ\text{C}$  for 1 h and then at  $25^\circ\text{C}$  overnight. Triethylammonium bromide was removed by filtration. The solvent was then removed with a rotary vacuum distillatory to give a brown solid. The obtained crude product was purified by passing through a silica column (petrol ether and ethyl acetate, v/v = 3:1) with fraction collection. The first fraction was removed under vacuum and then recrystallized from ethanol to produce a white solid (Fla-Br). Another fraction was distilled off under reduced pressure to obtain a yellowish solid (Flb-Br).

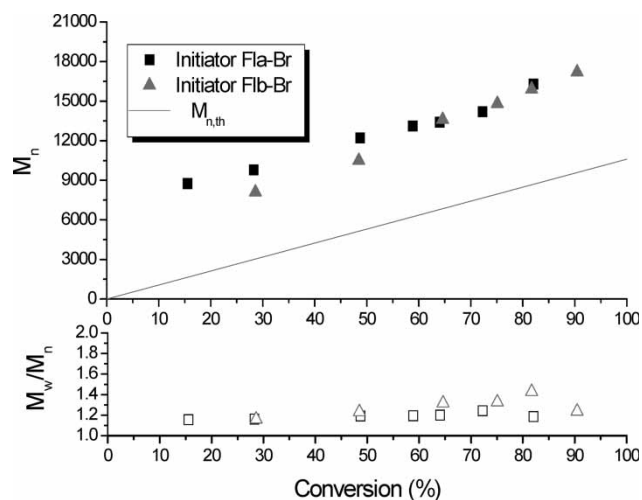
Fla-Br: Yield: 3.11 g, 49%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 2.07 (s, 12H), 6.87 (s, 4H), 7.14–7.19 (t, 3H), 7.63–7.71 (q, 2H), 8.04–8.06 (d, 1H). Element analysis:  $\text{C}_{28}\text{H}_{22}\text{O}_7\text{Br}_2$  (630.28) Found: C: 52.83 (Calcd: 53.36), H: 3.60 (Calcd:



**Sch. 1.** The synthetic route of difunctional initiator, 3,6-bis(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Fla-Br), and monoinitiator, 3-(2'-bromo-2'-methyl-propionic acid) fluorescein ester (Flb-Br).



**Fig. 1.** Kinetic plots for the polymerizations of MMA using Fla-Br or Flb-Br as the initiator in anisole at 80°C.  $[MMA]_0/[Initiator]_0/[CuBr]_0/[PMDETA]_0 = 100/1/1/2$ , monomer/anisole = 1/3 (v/v).



**Fig. 2.** Evolution of  $M_{n, GPC}$  and  $M_w/M_n$  with conversion for the polymerizations of MMA using Fla-Br or Flb-Br as the initiator in anisole at 80°C.  $[MMA]_0/[Initiator]_0/[CuBr]_0/[PMDETA]_0 = 100/1/1/2$ , monomer/anisole = 1/3 (v/v).  $M_{n, th} = (MMA \text{ weight}/[Initiator]_0) \times \text{conversion}$ .

3.52). Flb-Br: Yield: 1.5 g, 24%.  $^1H$ -NMR ( $CDCl_3$ , ppm): 2.07 (s, 6H), 6.54–6.56 (d, 1H), 6.62–6.64 (d, 1H), 6.73 (s, 1H), 6.83 (s, 2H), 7.12–7.16 (q, 2H), 7.62–7.71 (q, 2H), 8.03–8.05 (d, 1H). Element analysis:  $C_{24}H_{17}BrO_6$  (481.29) Found: C: 59.93 (Calcd.: 59.89), H: 3.92 (Calcd.: 3.56).

### 2.3 Polymerization Procedures

As a representative example, a dry glass tube was charged with CuBr, initiator (Fla-Br or Flb-Br), MMA, PMDETA and anisole. The reaction solution was put through three freeze-vacuum-thaw cycles to remove the dissolved oxygen. The tube was sealed under an argon atmosphere, immersed in an oil bath held by a thermostat at the desired temperature under rigorous stirring. At the desired polymerization time, the reaction was quenched in ice water and the tube was then opened. The contents were dissolved in THF and precipitated into about 250 mL of methanol. The polymers were filtered and dried at 50°C under vacuum to constant weight.

### 2.4 Characterizations

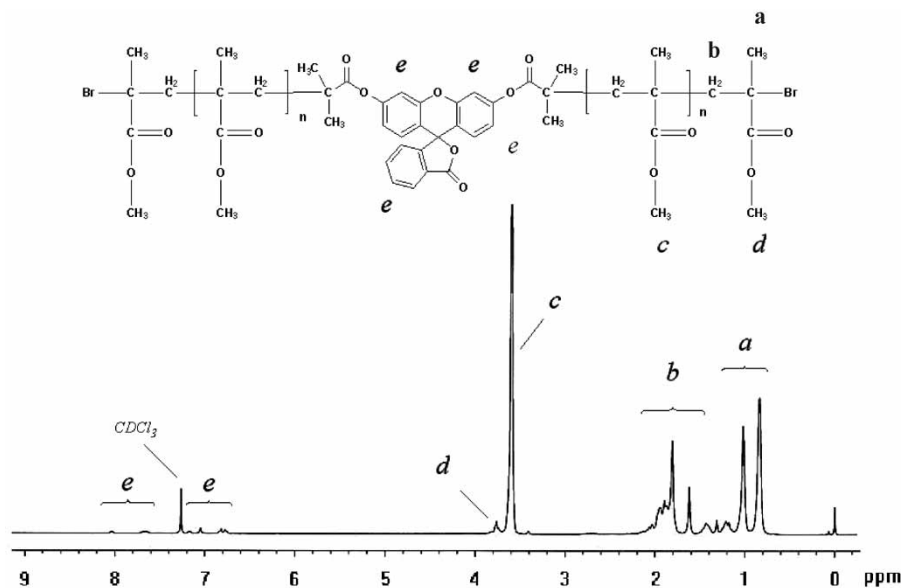
Conversion of monomer was determined gravimetrically. The samples were passed through neutral alumina before characterization. Molecular weights and molecular weight distributions were obtained using a Waters 1515 gel permeation chromatography (GPC) equipped with refractive-index and UV detector and HR1, HR3 and HR4 columns with a molecular weight range of 100–500,000 calibrated with narrow molecular weight distribution poly(methyl methacrylate) standard sample. THF was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> and at 30°C. The end groups of the polymers were analyzed by  $^1H$ -NMR spectroscopy using an Inova 400-MHz NMR instrument with tetramethylsilane (TMS) as the internal standard in  $CDCl_3$  at ambient temperature. The UV–Vis absorption spectra of the polymers and initiators in chloroform were recorded on a Shimadzu-RF540 spectrophotometer. The fluorescence spectra were obtained on a Perkin-Elmer LS-50B fluorescence spectrophotometer with  $CHCl_3$  as the solvent. Elemental analyses (EA) of C, H and N were measured by the EA1110 CHND-S.

**Table 1.** ATRP Results of MMA using Fla-Br as the initiator under different conditions at 80°C

Molar ratio <sup>a</sup>	Anisole/Monomer (v/v)	Time (h)	Conversion (%)	$M_{n, GPC}$	$M_{n, th}$	$I_{eff}^b$	$M_w/M_n$
250:1:1:2	3:1	2	30.4	13200	7600	0.58	1.10
		5	56.4	22800	14100	0.62	1.11
		7	71.2	23900	17800	0.74	1.16
		10	82.1	26600	20500	0.77	1.13
100:1:1:2	1:1 bulk	3	61.7	12000	6200	0.52	1.16
		1.5	68.1	12900	6800	0.53	1.47

<sup>a</sup>The molar ratio represents  $[MMA]_0/[Initiator]_0/[CuBr]_0/[PMDETA]_0$ .

<sup>b</sup>Initiation efficiency ( $M_{n, th}/M_{n, GPC}$ ).



**Fig. 3.**  $^1\text{H-NMR}$  spectrum of PMMA obtained via ATRP of MMA using Fla-Br/CuBr/PMDETA as the initiation system. Sample:  $M_{n,\text{GPC}} = 9800$ ,  $M_w/M_n = 1.16$ .

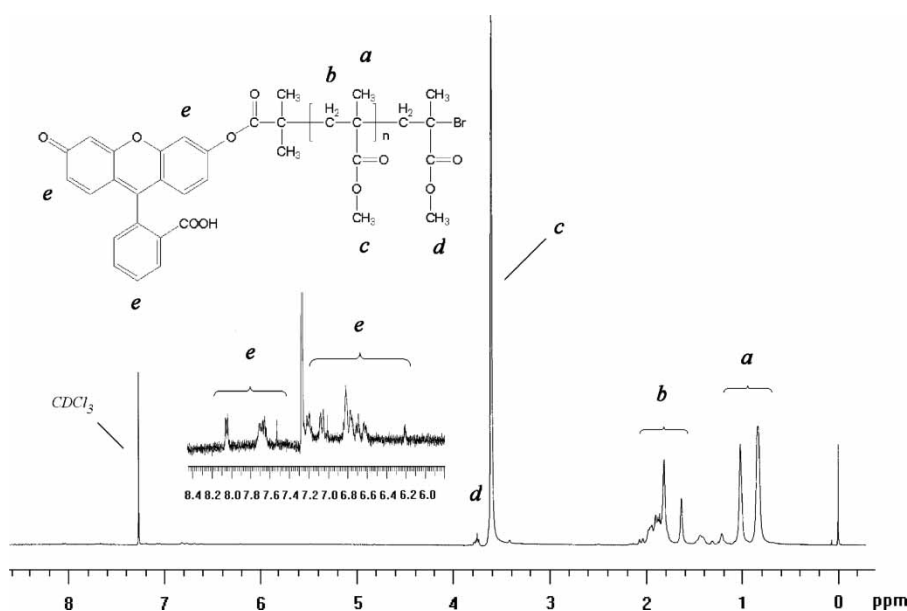
### 3 Results and Discussion

#### 3.1 ATRP of MMA

The difunctional initiator (Fla-Br) and monofunctional initiator (Flb-Br) were achieved by condensation of fluorescein and 2-bromoisobutyryl bromide. The structures of the initiators and the reaction route are shown in Scheme 1.

The ATRP of MMA was carried out using Fla-Br or Flb-Br as the functional initiators and CuBr/PMDETA as the

catalyst. Figure 1 shows the kinetic plots of  $\ln([M]_0/[M])$  against polymerization time (in which  $[M]_0$  and  $[M]$  represent the initial monomer concentration and the instantaneous monomer concentration), respectively. A linear relationship was observed, indicating that the radical concentration almost remained a constant throughout the course of the polymerizations. Figure 2 shows the number-average molecular weights ( $M_n$ ) and molecular weight distributions ( $M_w/M_n$ ) of the produced polymers as a function of monomer



**Fig. 4.**  $^1\text{H-NMR}$  spectrum of PMMA obtained via ATRP of MMA using Flb-Br/CuBr/PMDETA as the initiation system. Sample:  $M_{n,\text{GPC}} = 16000$ ,  $M_w/M_n = 1.34$ .

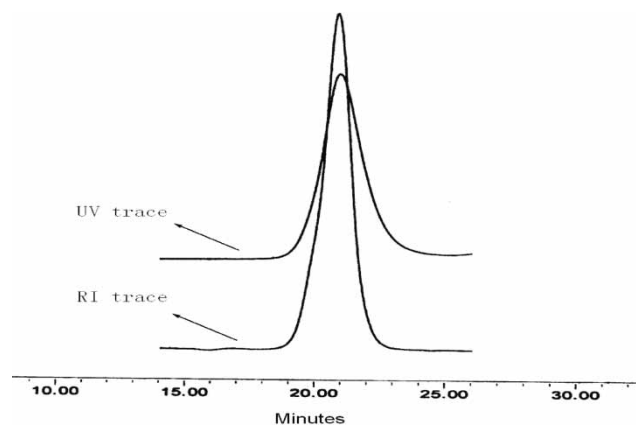
conversion. The  $M_n$ s of polymers increased linearly with the increase of monomer conversions, but higher than the theoretical values ( $M_{n,th}$ ), indicating a lower initiation efficiency (about 0.5). From Figure 2, one can also observe that the resultant PMMAs have relatively narrow polydispersity indices ( $M_w/M_n$ ) ( $M_w/M_n < 1.42$ ) up to a conversion of 90%, which reveals that the polymerizations were proceeded in a controlled fashion.

The polymerizations of MMA were also carried out under different molar ratios of monomer to initiator. The results are shown in Table 1. As expected, the conversions of monomer increased with the decrease of molar ratios of monomer to initiator under the same polymerization conditions. This was due to more initiator decomposed in the reaction system when smaller molar ratios of monomer to initiator were used. In addition, the molecular weights of the polymers increased with the increasing monomer conversion and narrow polydispersity indices ( $M_w/M_n$ ) were lower than 1.26.

To verify the effect of solvent (anisole) on the polymerization of MMA, several polymerizations were carried out in different monomer concentrations. The results are shown in Table 1. The polymerization rates decreased with the increase of the amount of solvent, as expected.

### 3.2 Characterization of PMMA Capped with Fluorescein

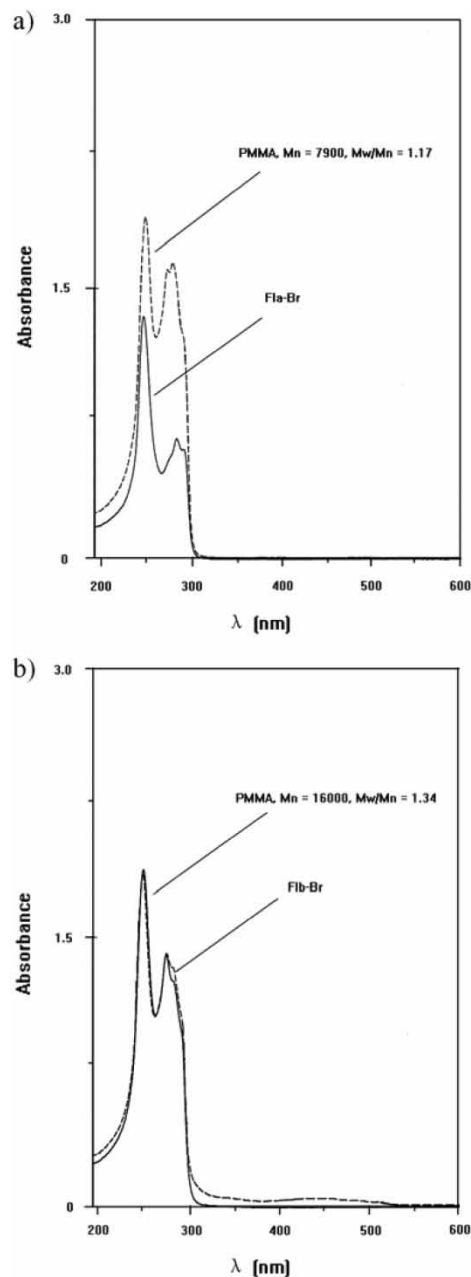
The chemical structures of the fluorescein-labeled polymers prepared by ATRP were determined by  $^1\text{H-NMR}$  spectroscopy. As shown in Figures 3 and 4, the chemical shift signals of aromatic protons derived from the initiators were observed in the 6.78–8.05 ppm range (Peak *e* in Figures 3 and 4). The chemical shift at 3.78 ppm (Peak *d* in Figures 3 and 4) was assigned to the protons of the methoxyl group ( $-\text{OCH}_3$ ) next to bromine atom at the end chain. The chemical shift at 3.60 ppm (Peak *c* in Figures 3 and 4) was assigned to the protons of the  $-\text{OCH}_3$  in PMMAs. The



**Fig. 5.** GPC traces of PMMA functionalized by fluorescein unit from ATRP of MMA using Fla-Br as the initiator. Sample:  $M_n = 8700$ ,  $M_w/M_n = 1.16$ ;  $\lambda = 254$  nm.

chemical shift at 1.15 ppm (*a* in Figures 3 and 4) was attributed to the protons of the methyl group in PMMAs. These characteristic chemical shifts indicate that the fluorescein chromophore from initiator Fla-Br or Flb-Br has been successfully incorporated into the PMMAs when using Fla-Br or Flb-Br as the ATRP initiator.

In order to further verify that the fluorescein unit was definitely attached in the middle of polymeric chains according to the mechanism of ATRP, the functional group analysis of the



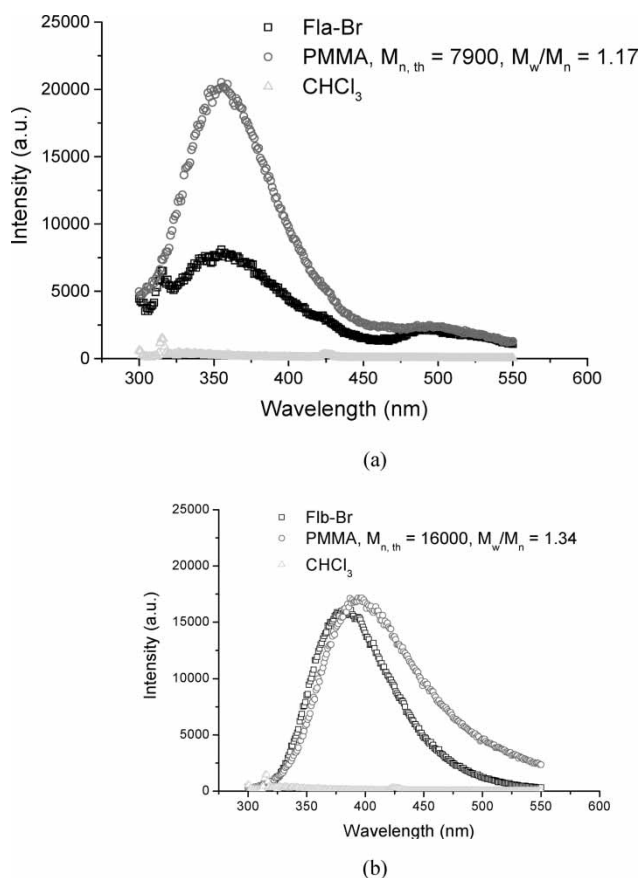
**Fig. 6.** UV spectra of initiators and polymers functionalized by fluorescein units in chloroform. The concentration of fluorescein moieties is  $2.0 \times 10^{-4}$  mol/L except for Fla-Br ( $1.0 \times 10^{-4}$  mol/L).



resultant PMMA using Fla-Br as the initiator was carried out by GPC equipped with RI and UV detector. The results are shown in Figure 5. The RI trace shows a symmetrical peak, corresponding to the  $M_n$  value of 8700 and the  $M_w/M_n$  of 1.16. The UV trace at 254 nm indicates that fluorescein unit has been incorporated into the polymer, because PMMA itself does not have UV absorption at 254 nm (49). These results indicate that the generation of chemical bond between fluorescein unit and PMMA.

### 3.3 Spectral Properties of the Polymers Functionalized by Fluorescein Unit

Figure 6 depicts the absorption spectra of the initiators, Fla-Br and Flb-Br, as well as fluorescein unit end-capped PMMA in chloroform. Two strong absorptions of the initiators appeared at 250 nm and 280 nm, respectively, which corresponded to the respective absorption of fluorescein moiety from Fla-Br and Flb-Br. The shape and range of absorption for the obtained PMMAs were quite similar to those of Fla-Br or Flb-Br due to the attachment of the fluorescein moiety in the polymer chains.



**Fig. 7.** Fluorescence spectra of initiators and PMMA in  $\text{CHCl}_3$  at room temperature. The concentration of fluorescein moieties is  $2.0 \times 10^{-4}$  mol/L except for Fla-Br ( $1.0 \times 10^{-4}$  mol/L),  $\lambda_{\text{ex}} = 374$  nm.

The fluorescence emission spectra of fluorescein-labeled PMMA and its respective initiator are shown in Figures 7a and b, respectively. Both spectra display the labeled PMMA possessing the same structure characteristic as the resultant fluorescein-based initiator. These suggest that the fluorescein chromophore has been incorporated to the polymer chain for Fla-Br as the ATRP initiator or attached at the end of the PMMA chain for Flb-Br as the ATRP initiator. As shown in Figure 7b, a red-shift ( $\sim 11$  nm) can be observed for the labeled PMMA compared to Flb-Br, which was produced from interaction between the labeled fluorescein moieties and neighboring MMA units (19).

The fluorescence emission spectra of Fla-Br, Flb-Br and PMMA were also investigated in DMF. However, the results showed that the fluorescence intensity of the derivatives were weak, compared to the strong fluorescence of fluorescein around 530 nm, which was the maximum emission wavelength of fluorescein in DMF. This may result from the fluorescein unit in initiators and PMMA had no alternative but to exist as a disassociated quinoid in a solution of DMF, since the two hydroxyls were blocked by esterification. A similar observation was also found in the previous literatures for derivatives of fluorescein (50, 51).

## 4 Conclusions

Two novel fluorescein derivatives containing bromine (Fla-Br and Flb-Br) have been synthesized in our lab. The ATRPs of MMA in anisole could be successfully carried out using Fla-Br or Flb-Br as an initiator and  $\text{CuBr}/\text{PMDETA}$  as a catalyst. The thorough characterization of all these fluorescein-labeled polymers was investigated from  $^1\text{H-NMR}$  measurement. The results indicated that the expected molecular structures have been obtained with a good correlation to structures of the initiator and MMA. GPC analysis showed that the PMMA polymers with the fluorescein group had narrow molecular weight distribution. The fluorescein chromophore incorporated into the polymer backbone showed strong UV absorption due to the fluorescein moiety in the middle or end of the polymer chains.

## 5 Acknowledgments

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