Synthesis and properties of novel photochromic poly(methyl methacrylate-*co*-diarylethene)s

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Novel poly(methyl methacrylate)s substituted with photochromic diarylethenes as the main backbone or pendant functional groups were prepared by atom transfer radical polymerization (ATRP), using methyl methacrylate and 5,5′-dihydroxymethyl substituted dithienylethene as the monomers. The concentration of diarylethene in the poly(methyl methacrylate-*co*-diarylethene)s can be regulated by controlling the polymerization conditions. The resulting photochromic copolymers exhibit good photochromic properties, good fluorescence, easy film-forming performance, and outstanding thermal properties.

Introduction

In recent years, diarylethenes (DAE(s)) have attracted much attention in the research of photochromism due to their good thermal stability and impressive feature of resistance to fatigue.[1] Thus, DAE compounds have found wide applications in optical memory, data storage,[2] and molecular-switches,[3] *etc*. In practice, small molecular DAEs are always transformed into photochromic polymers which tend to form desired films, fibers and flakes.[4] When used as optical materials, these polymers must have the desired photochromic properties in the solid state. However, studies on the photochromism of DAEs are now mostly focused on the solution system,[5] and few are involved in the solid state system.[6]

Up until now, photochromic polymers have usually been prepared by mechanical dispersion of small molecular DAEs in a polymer matrix. Though this method is easy to operate, it always suffers from low content (up to 5 mass%) and uneven distribution of photochromic small molecules in polymers, easy phase separation of DAE and the polymer matrix, limitation of information capacity by diffusion, *etc*.[7] Therefore, to overcome the above disadvantages, some recent reports have focused on the preparation of photochromic polymers with a photochromic portion chemically bonded to the polymeric parts.[4b,7e] However, traditional methods for synthesizing both small and polymeric DAE compounds have some drawbacks: syntheses and modification of small DAE molecules usually require multiple steps and suffer from low yield, harsh conditions, tedious workup, *etc*.,[8] while traditional radical polymerization for polymers is always hard to control and causes low yield, and broad molecular weight distribution. Recent progress in controlled/living radical polymerization (CRP), and especially in atom transfer radical polymerization (ATRP), has provided a powerful tool for preparing nearly monodispersed polymers with controlled molecular weights.[9] Well-defined and multi-functional polymer brushes can also be prepared *via* ATRP.[10]

In the past few years, several reports have utilized ATRP to prepare photochromic polymers, but the work was mainly on spirobenzopyran and azoaromatic photochromic compounds.[11] Herein, we describe the synthesis and properties of novel poly(methyl methacrylate)s (PMMA(s)) by the copolymerization of 5,5′-dihydroxymethyl substituted dithienylethene and methyl methacrylate (MMA) monomers. We preferred to choose MMA monomers, because PMMAs are usually optically transparent and appropriate in optical devices.

Results and discussion

1 Synthesis and weight distribution of PMMA 3 and PMMA-*co*-PDAE 4

PMMA **3** is an approximately symmetrical polymer with a DAE center and two PMMA side chains. Firstly, DAE bromide initiator **1** was prepared easily from 5,5′-dihydroxymethyl substituted dithienylethene by esterification reactions in an almost quantitative yield. Then, the catalysts CuBr and 2,2′-bipyridine (BPY), the monomer MMA, together with DAE initiator **1**, undergo ATRP reactions to form PMMA **3** in a moderate to high yield (Scheme 1). The above bulk polymerization was performed at 70 °C under vacuum. PMMA-*co*-PDAE **4** is another polymer that has a DAE center and one or more PMMA side chains, and the side chains contain DAE units. To synthesize PMMA-*co*-PDAE **4**, dithienylethenyl mono-acrylate monomer **2** was preliminarily prepared from 5,5′-dihydroxymethyl substituted dithienylethene and acrylyl chloride (Scheme 2). The relatively low yield (45%) in the synthesis of compound **2** may be ascribed to the formation of a bis-esterification side product. Thereafter, synthesis of PMMA-*co*-PDAE **4** was accomplished from initiator **1**, MMA and monomer **2** under ATRP reaction conditions (Scheme 3).

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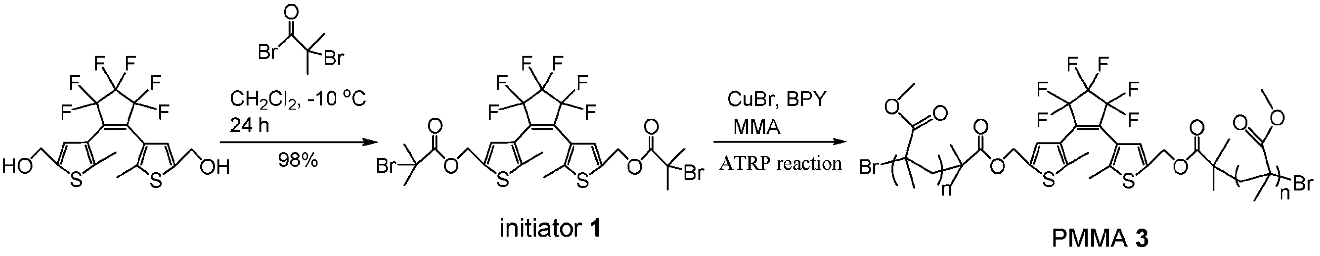
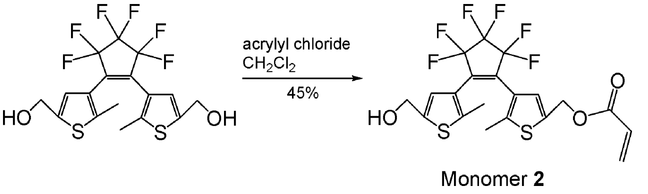
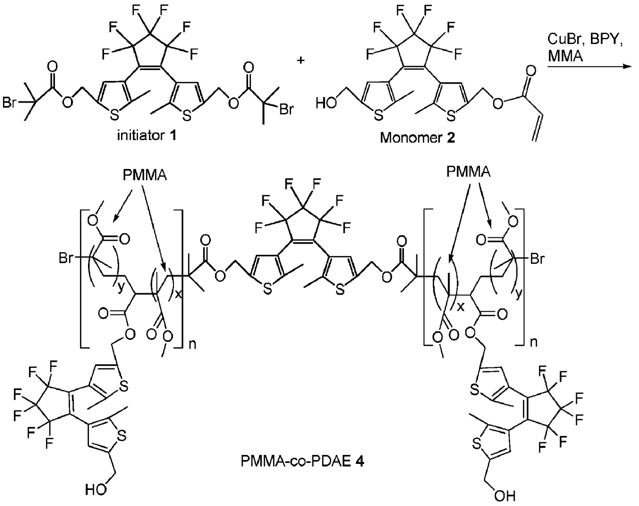


Scheme 1 Synthesis of PMMA **3** by ATRP method.



Scheme 2 Synthesis of monomer **2** by mono-esterification.



Scheme 3 Synthesis of PMMA-*co*-PDAE **4** by ATRP method.

The molar mass of PMMA **3** was studied by gel permeation chromatography (GPC). As shown in Table 1, the number average molecular weight (M_n) of the polymers can be regulated by changing the monomer : initiator feed ratio. The data in Table 1 measured by GPC show that, as the [monomer] : [initiator] molar feed ratio ranges from 400 : 1 to 1600 : 1, the M_n value of the resulting PMMA **3** homopolymer increases from 10 371 to 31 973 g mol^{-1}, while the polydispersity index (PDI) remains at around 1.3 (Entries 1–4, Table 1). For PMMA-*co*-PDAE **4**, when the feed ratio changes from 400 : 2 : 1 to 400 : 10 : 1, the corresponding M_n increases from 11 680 to 30 443 (Entries 5–7, Table 1). This phenomenon is consistent with the "controlled" characteristics of ATRP, *i.e.* greater ratio of monomers corresponds to higher molecular weight.

Weight percentages of the DAE and M_n of PMMA **3** were also calculated from ^{1}H NMR results (Fig. 1A and Table 1). Fig. 1A shows the ^{1}H NMR spectrum of PMMA **3**. The chemical shift at 7.0 ppm can be attributed to the two aryl protons on the two thiophene rings of the DAE center (a in Fig. 1A). The chemical shift at 3.5 ppm is associated with the methoxy group (–OCH$_3$) in the MMA unit (b in Fig. 1A). The MMA content in one PMMA **3** molecule can be determined as follows:

$$N_1 = S_2/(1.5S_1) \qquad (1)$$

in which N_1 is the number of MMA repeating units in PMMA **3**, S_1 is the area of the two aryl protons at 7.0 ppm, and S_2 is the area of the methoxy protons (–OCH$_3$) at 3.5 ppm in the MMA unit. Thus, approximately, M_n of PMMA **3** is the sum of the molecular weight of one initiator and N_1 MMA units. The weight percentage of the DAE can be easily calculated by the following equation:

$$W_1 = (428/M_{n3}) \times 100 \qquad (2)$$

in which W_1 is the weight percentage of the DAE in PMMA **3**, 428 is the molecular weight of the DAE center (5,5′-dihydroxymethyl substituted dithienylethene), and M_{n3} is M_n of PMMA **3**. The ^{1}H NMR-derived compositions and M_n of PMMA **3** are given in Table 1. The data in Table 1 indicate

Table 1 Characteristics of the PMMA **3** and PMMA-*co*-PDAE **4** copolymer

Entry	Sample	Monomer : initiator	$M_n{}^a$/g mol^{-1}	$M_w{}^a$/g mol^{-1}	PDI^a	$M_n{}^b$/g mol^{-1}	DAE^b (wt%)
1	PMMA **3-1**	400 : 1^c	10 371	14 889	1.33	8000	5.35
2	PMMA **3-2**	600 : 1^c	13 220	15 851	1.21	10 000	4.28
3	PMMA **3-3**	1000 : 1^c	28 094	37 476	1.34	27 100	1.58
4	PMMA **3-4**	1600 : 1^c	31 973	43 986	1.34	40 000	1.07
5	PMMA-*co*-PDAE **4-1**	400 : 2 : 1^d	11 680	14 364	1.23	16 100	10.63
6	PMMA-*co*-PDAE **4-2**	400 : 6 : 1^d	22 187	26 769	1.20	25 000	5.14
7	PMMA-*co*-PDAE **4-3**	400 : 10 : 1^d	30 443	36 553	1.20	33 500	3.26

[a] The characteristics of PMMA **3** and PMMA-*co*-PDAE **4** were measured by GPC in THF solvent. [b] The characteristics of PMMA **3** and PMMA-*co*-PDAE **4** were calculated from ^{1}H NMR spectra. [c] "Monomer : initiator" means "the molar ratio of MMA and initiator **1**". [d] "Monomer : initiator" means "the molar ratio of MMA, monomer **2** and initiator **1**".

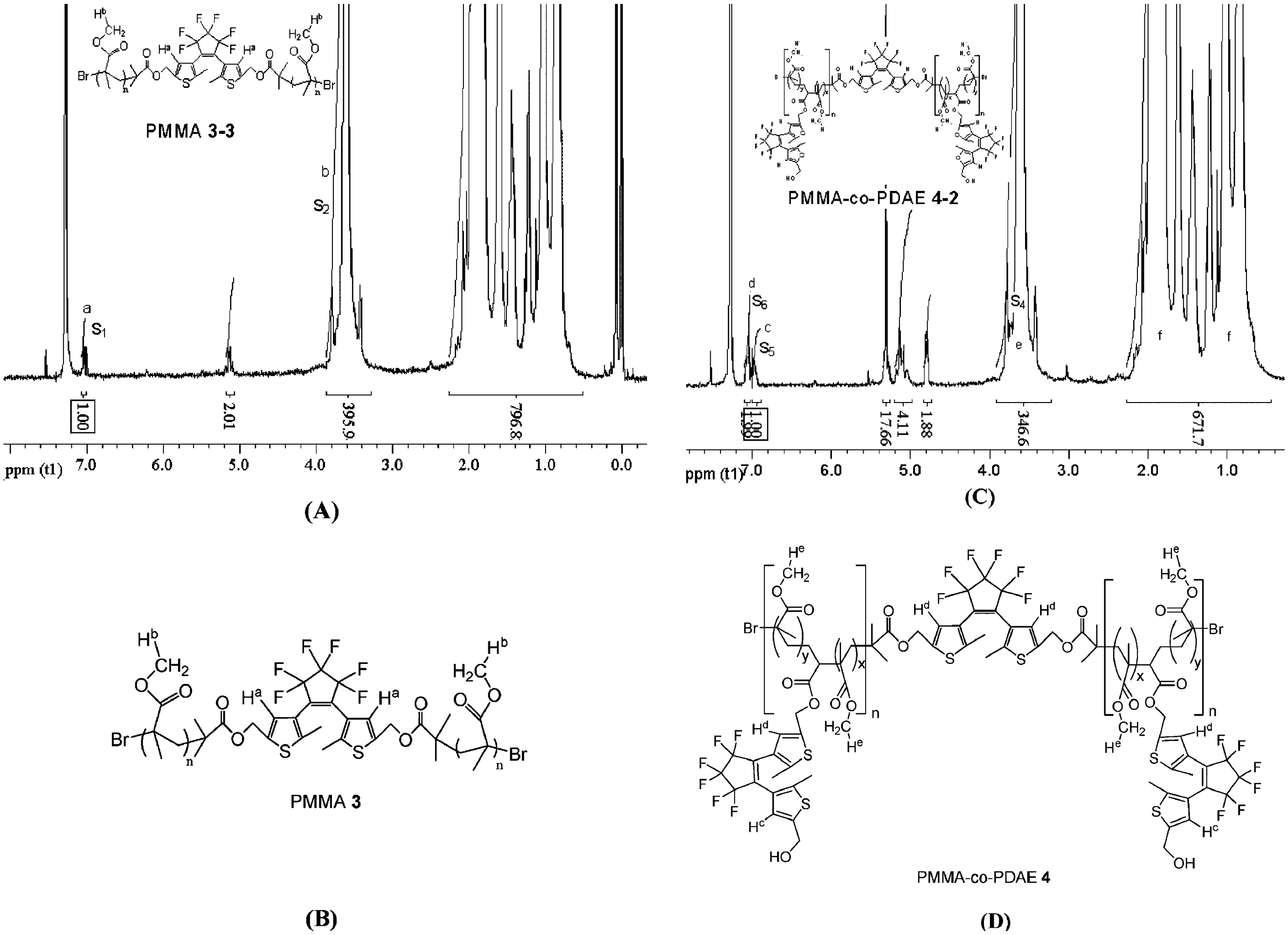


Fig. 1 (A) ^{1}H NMR spectrum of PMMA **3-3**; (B) proton labeling in the chemical structure of PMMA **3**; (C) ^{1}H NMR spectrum of PMMA-*co*-PDAE **4-2**; (D) proton labeling in the chemical structure of PMMA-*co*-PDAE **4**.

that M_n values of PMMA **3** increase with the increasing [monomer]/[initiator] molar feed ratio, while the weight percentage of the DAE (W_1) decreases regularly, which is consistent with molecular structure changes.

In PMMA-*co*-PDAE **4**, the chemical shift at 6.96 ppm is assigned to one proton of the thiophene ring in the side chain (c in Fig. 1C), while the signal at 7.04 ppm accounts for the rest of the aryl protons on the thiophene rings (d in Fig. 1C). The chemical shift at about 3.5 ppm is associated with the methoxy groups (–OCH$_3$) in the MMA units (e in Fig. 1C), and the signal in the region of 0.8–2.1 ppm is attributed to the protons (–CH(CH$_3$)–CH$_2$– in the MMA units and –CH$_3$ bonded to the thiophene ring) in MMA and DAE (f in Fig. 1C). The number of MMA units in one PMMA-*co*-PDAE **4** molecule can be obtained as follows:

$$N_2 = S_4/(1.5S_3) \tag{3}$$

$$S_3 = S_6 - S_5 \tag{4}$$

where N_2 is the number of MMA units in one PMMA-*co*-PDAE **4** molecule, S_3 is the area difference of protons at 7.04 and 6.96 ppm, S_4 is the area of protons in methoxy groups (–OCH$_3$) at about 3.5 ppm, S_5 is the area of protons at 6.96 ppm, and S_6 is the area of protons at 7.04 ppm. For example, in the ^{1}H NMR spectrum of a PMMA-*co*-PDAE **4-2** molecule (Fig. 1C), S_3 is 0.99, S_4 is 347, so N_2 is 234. Thereafter, M_n of PMMA-*co*-PDAE **4-2** can be easily calculated. Then, the weight percentage of the DAE is calculated as follows:

$$W_2 = [(2S_5/S_3 + 1) \times 428]/M_{n4} \times 100 \tag{5}$$

in which W_2 is the weight percentage of the DAE in one PMMA-*co*-PDAE molecule, S_3 is the area difference of protons at 7.04 and 6.96 ppm, S_5 is the area of protons at 6.96 ppm, 428 is the molecular weight of the DAE (5,5′-dihydroxymethyl substituted dithienylethene), and M_{n4} is the molecular weight of PMMA-*co*-PDAE **4**. Thus, ($2S_5/S_3$) represents the number of DAE units in the side chains, and [($2S_5/S_3 + 1) \times 428$] is the total molecular weights of all DAE units in one PMMA-*co*-PDAE **4** molecule. The calculated M_{n4} and weight percentages of DAE are also illustrated in Table 1. In PMMA-*co*-PDAE **4**, the value of M_{n4} increases with the increasing feed ratio of monomer **2**. Unfortunately, the weight percentage of the DAE decreases with increasing feed ratio of monomer **2**, and such an undesired result may be attributed to the larger M_{n4} value that concealed the increasing trend of the absolute value of the DAE.

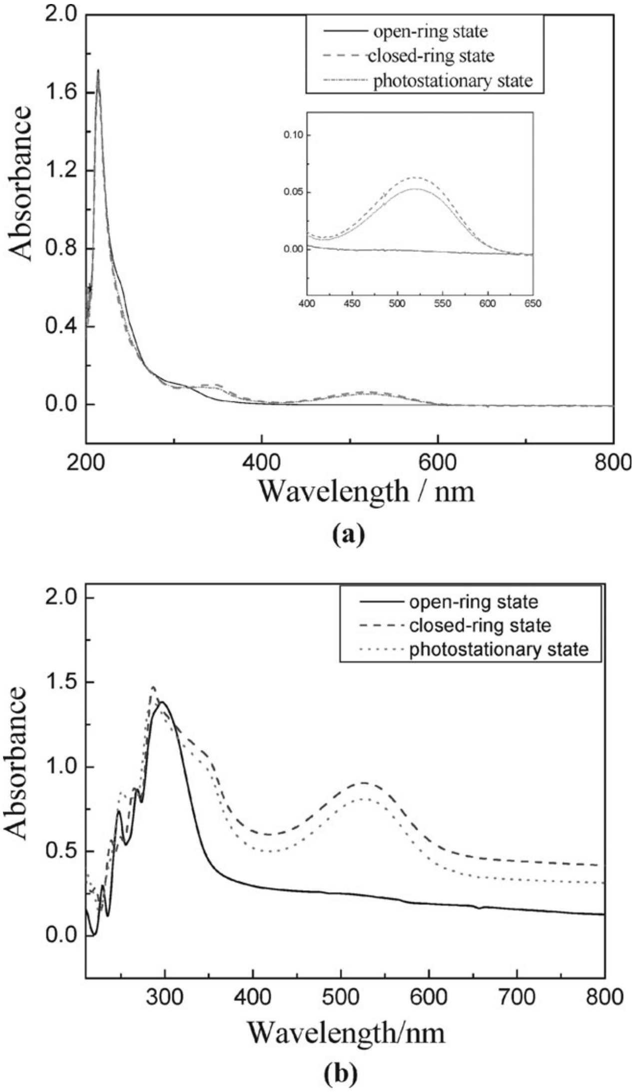


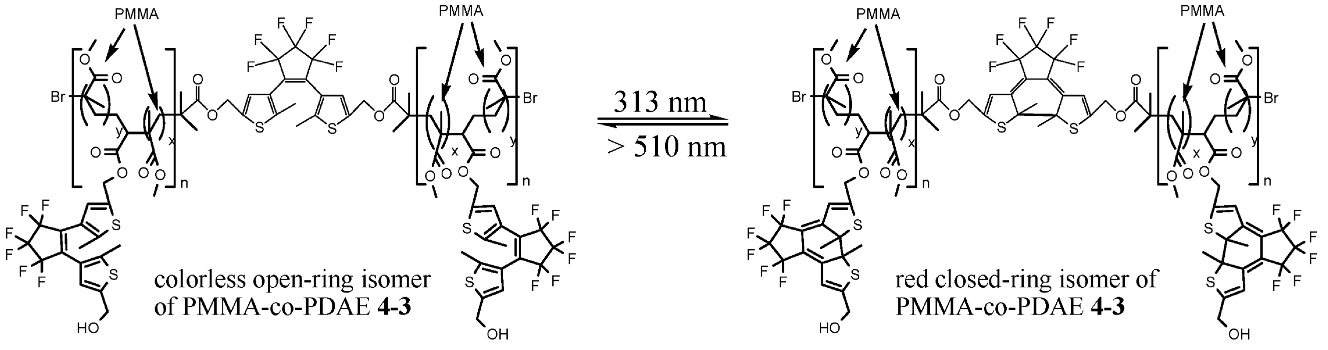
Fig. 2 Absorption spectra of PMMA-*co*-PDAE **4-3**: (a) in THF (1.0×10^{-4} mol L^{-1}); (b) PMMA-*co*-PDAE **4-3** amorphous film.

2 Photochromism of PMMA-*co*-PDAE 4-3 and other polymers

The photochromic properties of the copolymers were studied by UV absorption spectroscopy. Fig. 2 shows the absorption spectra of PMMA-*co*-PDAE **4-3**. The absorption maximum of PMMA-*co*-PDAE **4-3** was observed at 214 nm (Fig. 2a). Upon irradiation with 313 nm UV light, the color of the THF solution turned red, in which the absorption maximum was observed at 523 nm, indicating the formation of a closed-ring isomer. The red turned colorless upon irradiation with visible light ($\lambda > 510$ nm), which means that the closed-ring isomer reversed to its open-ring counterpart (Scheme 4). In PMMA amorphous film, PMMA-*co*-PDAE **4-3** had good photochromic property also, as shown in Fig. 2b. Upon irradiation with 313 nm light, the color of the PMMA-*co*-PDAE **4-3** film changed from colorless to red with the appearance of a new broad absorption band at $\lambda_{max} = 528$ nm, which was assigned to the formation of the closed isomer. The colored PMMA film can return to colorless on irradiation with appropriate visible light ($\lambda > 510$ nm). Compared with the maximal absorption in THF solution, the little red shift of the ring-closed form of the PMMA-*co*-PDAE **4-3** film can be ascribed to the stabilization of molecular arrangement in the solid state.[12] PMMA-*co*-PDAE **4-1** and PMMA-*co*-PDAE **4-2** revealed similar photochromic properties as PMMA-*co*-PDAE **4-3**. Nevertheless, in comparison with PMMA-*co*-PDAE **4-3**, PMMA **3** showed relatively weak photochromism, which may be attributed to the relatively low content of DAE in PMMA **3** polymers.

3 Fluorescence properties of PMMA-*co*-PDAE 4-3 and other copolymers

Here, we chose PMMA-*co*-PDAE **4-3** as the example, because it has the strongest fluorescence intensity among the three PMMA-*co*-PDAE **4**s. As shown in Fig. 3, the concentration effect on the fluorescence spectrum of PMMA-*co*-PDAE **4-3** was examined in THF solution at room temperature. When the concentration increased from 1.0×10^{-6} mol L^{-1} to 2.0×10^{-5} mol L^{-1}, the maximal emission almost arose at 350 nm, and the relative fluorescence intensity increased dramatically. However, when the concentration of PMMA-*co*-PDAE **4-3** in THF was increased from 2.0×10^{-5} mol L^{-1} to 1.0×10^{-3} mol L^{-1}, the relative fluorescence intensity decreased abruptly, especially from 2.0×10^{-4} mol L^{-1} to 1.0×10^{-3} mol L^{-1}. At a higher concentration of 10^{-3} mol L^{-1}, the fluorescence has quite a low intensity, which can be attributed to molecular aggregation and fluorescence quenching.[13] Other products PMMA **3-1**, PMMA **3-2**, PMMA **3-3**, PMMA **3-4**, PMMA-*co*-PDAE **4-1**, and PMMA-*co*-PDAE



Scheme 4 Photochromic reactions of PMMA-*co*-PDAE **4-3**.

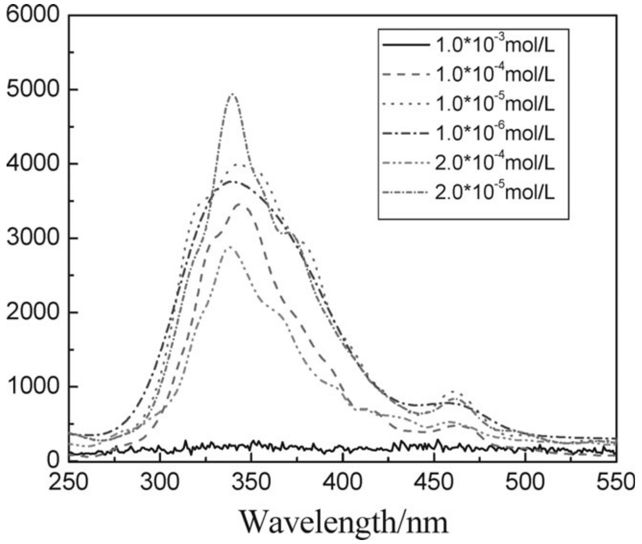


Fig. 3 Fluorescence spectra of PMMA-*co*-PDAE **4-3** at various concentrations in THF at room temperature, monitored at 315 nm.

Table 2 Fluorescence properties of PMMA **3** at room temperature in various concentrations, excited at 335 nm

Concentration/ mol L^{-1}	Maximal relative intensity of fluorescence			
	PMMA **3-1**	PMMA **3-2**	PMMA **3-3**	PMMA **3-4**
1.0×10^{-5}	1757	1500	1727	1301
1.0×10^{-4}	1379	1443	1447	1394
1.0×10^{-3}	1122	1349	942	1016

Table 3 Fluorescence properties of PMMA-*co*-PDAE **4** at room temperature in various concentrations, excited at 350 nm

Concentration/ mol L^{-1}	Maximal relative intensity of fluorescence		
	PMMA-*co*-PDAE **4-1**	PMMA-*co*-PDAE **4-2**	PMMA-*co*-PDAE **4-3**
1.0×10^{-5}	3325	3560	4258
1.0×10^{-4}	1994	3350	3510
2.0×10^{-4}	1077	2650	2934

4-2 showed a similar concentration effect. The results are summarized in Table 2 and Table 3, respectively. However, for PMMA **3**, the relative fluorescence intensity showed a relatively complex change at various concentrations.

4 Thermal properties of PMMA 3 and PMMA-*co*-PDAE 4

The thermal properties of PMMA **3** and PMMA-*co*-PDAE **4** were studied using differential scanning calorimetry (DSC) under a nitrogen atmosphere. The glass-transition temperature (T_g) of PMMA **3** increases from 119 °C to 125 °C as the M_n increases from 10 371 to 31 973. The glass-transition temperature (T_g) of PMMA-*co*-PDAE **4** copolymer increases from 125 °C to 130 °C as M_n increases from 9680 to 14 692. Such high glass-transition temperatures will make it possible for **3** and **4** to be optical switch materials.[14]

Conclusions

In conclusion, novel copolymers of PMMAs containing dithienylethenes were synthesized efficiently *via* ATRP methodology. The copolymers feature narrow molecular weight distribution, good photochromic and fluorescent properties, and high glass-transition temperatures. The polymers can be used as potential optical switch and other photo-materials.

Experimental

Materials

Commercial THF, BPY, and methanol were used without purification; CuBr (CuBr, 99%, Aldrich) was purified with HOAc to afford a white powder; MMA was washed in saturated aqueous NaOH, and then distilled under reduced pressure; DAE initiator **1** and DAE monomer **2** were synthesized by ourselves.

Compound characterization

The structures of the monomers and polymers were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy on a Bruker AV 400 MHz spectrometer, with tetramethylsilane (TMS) as the standard. $CDCl_3$ was used as the solvent. Gel permeation chromatography (GPC) was performed on an HP 1100 HPLC, equipped with a Waters 2414 refractive index detector and three Styragel HR 2, HR 4, HR 5 of 300 × 7.5 mm columns (packed with 5 μm particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 500–1 000 000. THF was used as the eluent at a flow rate of 1 mL min^{-1} at 40 °C. PMMA standards were used as the reference. Differential scanning calorimetry (DSC) was conducted on a DSC 822e (Mettler Toledo Co., Zurich, Switzerland) apparatus at a heating rate of 10 °C per minute under N_2 atmosphere. The FTIR spectra were recorded *via* the KBr pellet method by using a Bruker V70 FTIR spectrophotometer. The mass spectra were recorded on a high resolution ESI–FTICR mass spectrometer (Varian 7.0T FTICR-MS). UV–vis absorption spectra were measured using a Perkin Elmer Lambda-900 spectrophotometer. The photoluminescence were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

Preparation of the amorphous films

PMMA (100 mg) was added to dichloromethane (2 mL) solvent, and the mixture was stirred ultrasonically to form a homogeneous solution. The sample was prepared by ultrasonically dissolving PMMA-*co*-PDAE **4** (10 mg) in 1 mL of the above solution, respectively. Then the solution was spin-coated on a glass substrate with a spin rotation speed of 1500 rpm for 1 min, and the coated layer was dried at 60 °C for 2 h to obtain the desired amorphous film.

Synthesis of dithienylethene initiator 1

5,5′-Dihydroxylmethyl substituted dithienylethene (200 mg, 0.466 mmol) and triethylamine (103 mg, 1.02 mmol) were dissolved in dichloromethane. The resulting solution was cooled to −10 °C, and 2-bromoisobutyryl bromide (225 mg, 0.98 mmol) in dichloromethane was added portionwise. After the completion of the addition, the reaction mixture was stirred at room temperature for 24 h. The mixture was washed with water, and the CH_2Cl_2 layer was dried over magnesium sulfate. CH_2Cl_2 was removed at reduced pressure to give the oily product **1** (333 mg, 98%). IR: υ 2972, 2931, 1737, 1541, 1469, 1373, 1273, 1115, 1045 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 6H), 1.85 (s, 12H), 5.17 (s, 4H), 6.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 143.5, 135.6, 128.1, 124.5, 61.53, 55.3, 30.7, 14.3; MS *m*/*z*: 723.9273 (M^+), 746.9273 (+Na), theoretical value 746.9279 (+Na).

Synthesis of dithienylethene monomer 2

The preparation of dithienylethene monomer **2** was similar to that of dithienylethene initiator **1**. In this step, acrylyl chloride was used as the acylation reagent. After common workup, dithienylethene monomer **2** was obtained in 45% yield. IR: υ 3441, 2957, 2924, 1727, 1635, 1442, 1408, 1338, 1274, 1112 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.87 (s, 3H), 1.93 (s, 3H), 4.73 (s, 2H), 5.23 (s, 2H), 5.87 (d, 1H), 6.13 (dd, 1H), 6.43 (d, 2H), 6.93 (s, 1H), 7.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 143.3, 142.4, 142.1, 136.1, 131.6, 128.1, 127.9, 124.8, 124.5, 124.3, 60.3, 59.9, 14.3; MS *m*/*z*: 482. 0377 (M^+), 505.0337 (+Na), theoretical value 505.0344 (+Na).

Typical procedure for the synthesis of PMMA 3-4 by ATRP

A mixture of initiator **1** (10.9 mg, 0.015 mmol), CuBr (4.5 mg, 0.03 mmol), BPY (15 mg, 0.09 mmol) and MMA (2.403 g, 24 mmol) was introduced into a glass tube, degassed by three freeze–evacuate–thaw cycles and sealed under vacuum. The sealed tube was placed in an oil bath at 70 °C for 80 min, and then the polymerization mixture was diluted with THF and eluted through an alumina column to remove the copper bromide complex. The eluted THF solution was then poured into excess methanol to precipitate PMMA polymer **3-4** (81% yield) as a white powder. IR: υ 2951, 1726, 1437, 1242, 1192, 1148 cm^{-1}.

Typical procedure for the synthesis of PMMA-*co*-PDAE 4-3 by ATRP

A mixture of initiator **1** (16.0 mg, 0.022 mmol), CuBr (6.7 mg, 0.044 mmol), BPY (22.0 mg, 0.133 mmol), MMA (881 mg, 8.8 mmol) and dithienylethene monomer **2** (106.1 mg, 0.22 mmol) was introduced into a glass tube. In a similar manner, the polymer PMMA-*co*-PDAE **4-3** was prepared as a white powder in 73% yield. IR: υ 3396, 2952, 1726, 1444, 1243, 1149 cm^{-1}.

Acknowledgements

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