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Reversible addition–fragmentation chain transfer polymerization of 7-(4-(acryloyloxy)butoxy)coumarin

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Abstract

The light sensitive vinyl monomer with coumarin unit, 7-(4-(acryloyloxy)butoxy)coumarin (7AC), was synthesized. The reversible addition–fragmentation chain transfer (RAFT) polymerization of 7AC, initiated by 2,2′-azobisisobutyronitrile (AIBN), was carried out using 2-cyanoprop-2-yl dithiobenzoate (CPDB) as a RAFT agent in *N*,*N*-dimethylformamide (DMF) solution. The kinetics exhibited first-order relationship with respect to the monomer concentration. The molecular weight of the polymer increased linearly with the monomer conversion. The chain extension of poly(7-(4-(acryloyloxy)butoxy)coumarin) (P7AC) using styrene (St) as the second monomer demonstrated that the obtained polymers were almost ‘‘living’’. The fluorescence intensity of P7AC increased with the molecular weight of P7AC and was stronger than that of the monomer. The obtained polymer had strong ultraviolet (UV) absorption at 322 nm. The molecular weights of the polymer had no effect on its ultraviolet absorption intensity. The coumarin structure existing in P7AC underwent $[2+2]$ cycloaddition reaction (photodimerization) under UV irradiation in tetrahydrofuran (THF) solution, which can be further used to prepare small particles from the single polymer.

Keywords: 7-(4-(Acryloyloxy)butoxy)coumarin; Light sensitive polymer; RAFT

1. Introduction

Recently, coumarin(benzo-2-pyrons) and its derivatives have attracted significant interest. These chemicals show characteristic properties, such as excellent fluorescent properties with high photoluminescence (PL) quantum efficiency, excellent photostability and extended spectrum range [1,2]. They are widely used in the fields of laser dyes, biology, medicine, and polymer science [3]. 7-Hydroxycoumarin (Scheme 1(a)) is a widely used structure in introducing the coumarin unit into polymer [3,4]. Due to its characteristic photocrosslinkable (photodimerization reaction) and liquid–crystalline properties, many researchers have paid much attention on the polymers containing coumarin units [4–9]. However, most of the side chain coumarin-containing polymers reported were synthesized by conventional free radical polymerization method [4–8]. The inherent limitations of conventional free radical polymerization methods are not conducive for the synthesis of well-defined polymers.

During the past two decades, ‘‘living’’/controlled free radical polymerizations (LFRPs) have been developed and considered as one of the most effective synthetic routes to obtain the polymers with well-defined structures, molecular weights and low polydispersities [10]. There are three main methods developed, e.g. nitroxide mediated living radical polymerization (NMP) [11], atom transfer radical polymerization (ATRP) [12–14], reversible addition–fragmentation chain transfer polymerization (RAFT) [15–18]. There are few reports on the synthesis of well-defined side chain coumarin-containing polymers by LFRP methods. Tian et al. synthesized copolymers of polystyrene (PS) and side chain coumarin-containing polymer via ATRP using bromine terminated PS as the macroinitiator [9]. Scaiano et al. used a coumarin–TEMPO agent to monitor the kinetics of activation/deactivation in the living free radical polymerization of styrene (St) [19]. RAFT polymerization is one of the most

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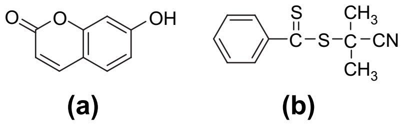


Scheme 1. Structure of (a) 7-hydroxycoumarin and (b) 2-cyanoprop-2-yl dithiobenzoate (CPDB).

versatile LFRP methods [20] and has been applied to a wide variety of vinyl monomers, such as St [21], methyl methacrylate (MMA) [22], methyl acrylate (MA) [23], acrylamide [24,25], octadecyl acrylate [26], etc. Ghiggino et al. using ruthenium-containing RAFT agents synthesized light harvesting styrene functionalized coumarin polymers (St-coumarin) [27]. The same group also reported the usage of St-coumarin to synthesize amphiphilic star-shaped polymer [28,29].

In the present work, we report on the preparation of coumarin-containing acrylate polymer, poly((7-(4-(acryloyloxy)-butoxy)coumarin) (P7AC)), under the controlled manner by RAFT polymerization. The characteristic polymerization behavior of the monomer, (7-(4-(acryloyloxy)butoxy)coumarin (7AC), was investigated. The polymers were characterized by UV–vis and fluorescence spectra. The post-crosslinking of P7AC via photodimerization reaction between the coumarin units under irradiation of UV light source was investigated. Using this technique, the fluorescence small particle can be prepared from the single polymer with pre-determined molecular weight and structure in future.

2. Experiments

2.1. Materials

7-Hydroxycoumarin was purchased from Sigma–Aldrich and used as received. Styrene (St, Shanghai Chemical Reagent Co. Ltd, 98%) was washed with 5% sodium hydroxide (NaOH) solution and deionized water until neutralization, dried overnight with anhydrous magnesium sulfate ($MgSO_4$), then distilled twice under reduced pressure, and stored in the refrigerator at −15 °C. 2,2′-Azoisobutyronitrile (AIBN, Shanghai Chemical Reagent Co. Ltd, 98%) was recrystallized from ethanol and kept in a refrigerator under 4 °C. 2-Cyanoprop-2-yl dithiobenzoate (CPDB, Scheme 1(b)) was synthesized according to the literature [30]. Other materials were obtained from Shanghai Chemical Reagent Co. Ltd. and used as received. The solvents used in UV and fluorescence measurements were distilled before use.

2.2. Synthesis of 7-(4-bromobutoxy)-coumarin (7BC) [31]

The synthetic route is shown in Scheme 2. Anhydrous K_2CO_3 (17.4 g, 124 mmol) was added into the mixture of 7-hydroxycoumarin (10.0 g, 62 mmol) and excess 1,4-dibromobutane (40 g, 186 mmol) in acetone (200 mL). The resulted suspension was heated to reflux for 24 h. The precipitate was filtered off and washed with acetone (3 × 100 mL). After the solvent was removed in reduced pressure, water was added, and the residue was extracted with CH_2Cl_2 (3 × 200 mL). The extract was dried with anhydrous $MgSO_4$, filtered, and evaporated in reduced pressure. The residue was then purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate (9:1, v/v) as an eluent, and resulted in a white solid (8.8 g, 82.6%).

EA Calcd.: C, 52.82%; H, 4.52%. Found: C, 52.55%; H, 4.41%.

^1H NMR ($CDCl_3$): 7.59 (d, 1H), 7.21 (m, 1H), 6.80 (m, 2H), 6.21 (d, 1H), 3.98 (t, 2H), 3.41 (t, 2H), 2.01–1.45 (m, 4H).

2.3. Synthesis of 7-(4-(acryloyloxy)butoxy)coumarin (7AC)

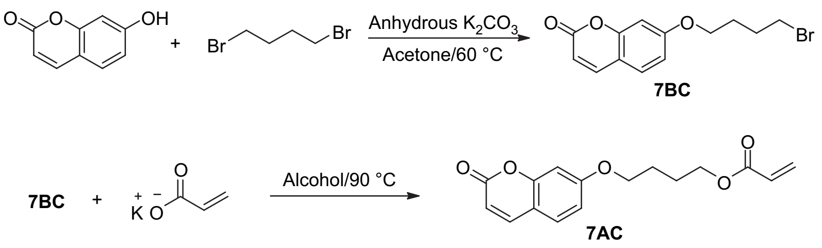
7BC (5.0 g, 18 mmol) and excess potassium acrylate (30 g, 27 mmol) were dissolved in ethanol (150 mL). Hydroquinone (0.02 g, 1.8 μmol) was added. The solution was heated to reflux for 24 h. The precipitate was filtered off and washed with ethanol (3 × 50 mL). After the solvent was removed in reduced pressure, water was added, and the residue was extracted with CH_2Cl_2 (3 × 100 mL). The residue was then purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate (3:1, v/v) as an eluent and resulted in a white solid (3.1 g, 60.8%).

EA Calcd.: C, 66.42%; H, 5.82%. Found: C, 66.66%; H, 5.59%.

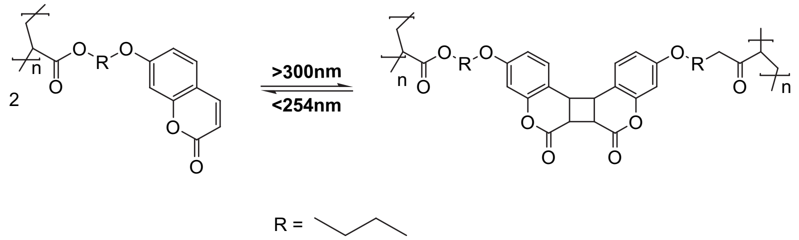
^1H NMR ($CDCl_3$): 7.59 (d, 1H), 7.21 (d, 1H), 6.80 (m, 2H), 6.48 (d, 1H), 6.25 (m, 1H), 6.15 (m, 1H), 5.81 (m, 1H), 4.21 (s, 2H), 4.01 (s, 2H), 1.82 (s, 2H), 1.52 (s, 2H).

2.4. General procedures of RAFT polymerization of 7AC

The following procedure was typical: a dry ampoule was filled with 7AC (0.5 g, 1.74 mmol), AIBN (2.85 mg,



Scheme 2. The synthetic route of the monomer, 7-(4-(acryloyloxy)butoxy)coumarin (7AC).



Scheme 3. Reversible photodimerization reaction of the poly(7-(4-(acryloyloxy)butoxy)coumarin) (P7AC).

0.0174 mmol), CPDB (11.5 mg, 0.0520 mmol), and *N*,*N*-dimethylformamide (DMF) (1.5 mL). The contents were purged with argon for approximately 10 min to eliminate the dissolved oxygen. Then, the ampoule was flame-sealed and placed in an oil bath held by a thermostat at the desired temperature to polymerize. At timed intervals, the ampoule was immersed into ice water and then opened. The contents were dissolved in 2 mL of tetrahydrofuran (THF) and precipitated into a 200 mL of methanol. The polymer was obtained by filtration and dried under reduced pressure for 24 h at room temperature. The conversion of the monomer was determined by gravimetry.

2.5. Chain-extension experiment

The RAFT polymerization of St was carried out using the same procedures as mentioned above except CPDB was substituted by P7AC obtained from RAFT polymerization of 7AC to prepare the block copolymer of P7AC-*b*-PS.

2.6. Photodimerization reaction

UV spot light source (L8333) (Hamamatsu Co. Ltd., Japan) (with a filter lens (ZWB2, education optical lens factory of Haian in Jiangsu Province)) was used as UV irradiation source. The ultraviolet intensity is 3500 mW/cm^2 (at 365 nm) and the distance between irradiation source and reaction solution is 2 cm. The photodimerization reaction, shown in Scheme 3, was carried out in THF solution and was monitored by Shimadzu UV-3150 UV–vis–NIR spectrophotometer.

2.7. Characterization

The number-average molecular weights (M_ns) and polydispersity indices (PDIs) of polymer were measured on a Waters 1515 gel permeation chromatograph (GPC) using THF as the eluent at a flow rate of 1.0 mL min^{-1}. Molecular weights were determined from standard polystyrene calibration. ^{1}H NMR spectra of the polymers were recorded on an Inova 400-MHz nuclear magnetic resonance (NMR) instrument with CDCl$_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. The fluorescence emission spectra of the polymers were obtained on a Perkin–Elmer LS-50B fluorescence spectrophotometer with DMF as solvents. The elemental analyses for C, H, and N were performed on a Leco CHNS microanalyzer. The UV–vis absorption spectra of the samples in DMF solutions were determined on a Shimadzu UV-3150 UV–vis–NIR spectrophotometer.

3. Results and discussion

3.1. RAFT polymerization of 7AC

In order to synthesize well-defined side chain coumarin-containing polymers, the RAFT polymerization of 7AC was carried out in DMF solution using AIBN as the initiator and CPDB as the RAFT agent at 60 °C (molar ratio – [7AC]$_0$:[CPDB]$_0$:[AIBN]$_0$ = 100:3:1). As shown in Fig. 1, the corresponding plot of ln([M]$_0$/[M]) versus the polymerization time was linear, which indicated that the propagating radical concentrations were almost constant during the process of polymerization. The result also showed that there was an inhibition period of about 6.5 h at 60 °C. The reason for the inhibition period could be contributed to the low reactivity between the reinitiating group and the monomer or a slow fragmentation rate of a pre-equilibrium RAFT radical [15–18]. Similar inhibition period was found in the RAFT polymerization of 2-naphthyl acrylate [23]. Thus, the monomer structure may also cause inhibition in RAFT polymerization. The dependence of the number-average molecular weights (M_ns) and polydispersity indices (PDIs) of the polymers on the monomer conversions is shown in Fig. 2. The molecular

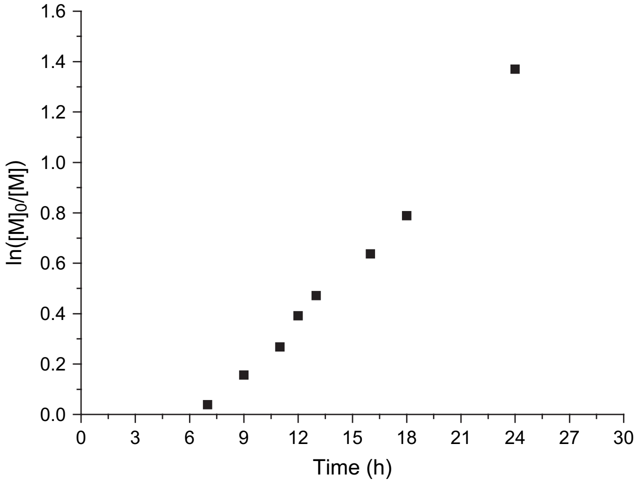


Fig. 1. Kinetic plot for RAFT polymerization of 7AC in DMF solution at 60 °C. Polymerization conditions: [7AC]$_0$:[CPDB]$_0$:[AIBN]$_0$ = 100:3:1, [7AC]$_0$ = 1.16 mol L^{-1}.

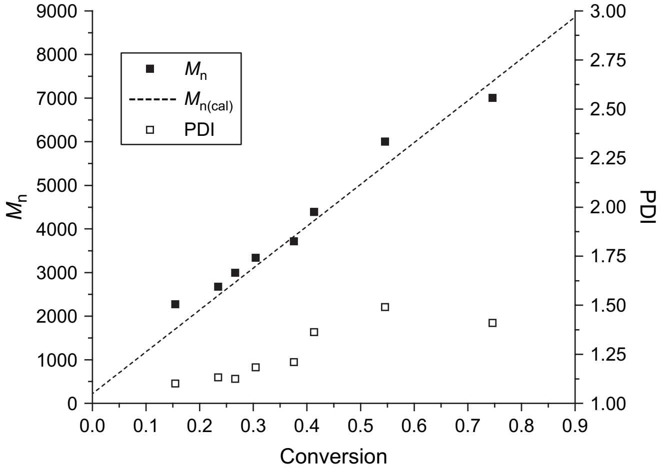


Fig. 2. Dependence of the number-average molecular weight and polydispersity on the monomer conversion for the RAFT polymerization of 7AC. Polymerization conditions are same as in Fig. 1.

weights of the polymers increased linearly with the monomer conversions and were close to the values calculated from the following equation in the early stage of polymerization:

$$M_{n(cal)} = M_{CPDB} + \frac{[7AC]_0}{[CPDB]_0} M_{7AC} \times \text{conversion}$$

where $M_{n(cal)}$ is the calculated number-average molecular weight; $[7AC]_0$ and $[CPDB]_0$ are the starting concentrations of the monomer and RAFT agent, respectively; M_{CPDB} and M_{7AC} are the molecular weights of the RAFT agent and monomer, respectively.

Fig. 2 shows that PDIs of the polymers increased with increasing monomer conversion, and the PDIs were narrow at low conversion, ranging from 1.1 (15.4% conversion) to 1.21 (37.6% conversion). However, when the conversion further increased, the PDI increased to a large value, 1.41 at 74.6% conversion, which indicated that some side reactions occurred. Furthermore, in Fig. 3, a large shoulder peak appeared at a high molecular weight position when the monomer conversion was 54.0%, which demonstrated the existence of uncontrollable side reaction in this polymerization process. These results may be partly attributed to a product formed by bimolecular termination between propagating radicals [32]. Another reason was that cross-termination reaction may exist between coumarin units.

3.2. Chain extension and structure analysis of the polymer

The chain-extension polymerization of obtained P7AC ($M_n = 3400$ g/mol, PDI = 1.18) as the macro-RAFT agent with St was performed. Gel permeation chromatographic (GPC) curves (Fig. 4) demonstrated that there was an increase in the molecular weights (from 3400 g/mol to 5500 g/mol) after chain extension. However, a shoulder peak at high molecular weight region was found in the GPC spectrum of the block copolymer, which resulted in an increase of the PDI of block copolymer (from 1.18 to 1.38). The shoulder peak at a high molecular weight could be due to the bimolecular termination in the polymerization reaction [32,33].

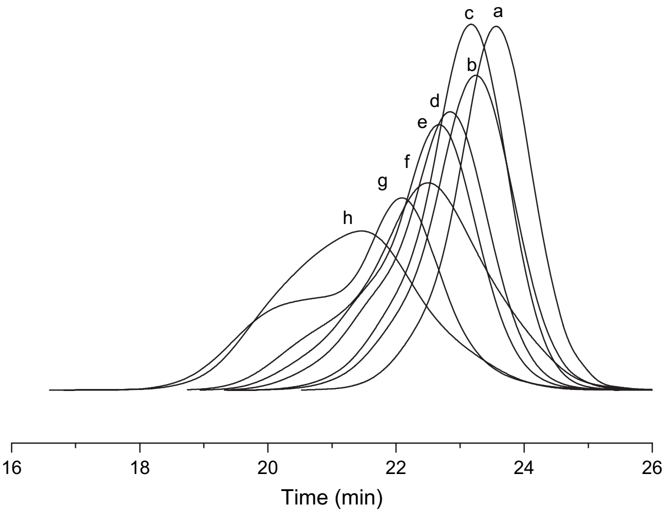


Fig. 3. GPC traces of the polymers obtained from the RAFT polymerization of 7AC using CPDB as the RAFT agent in DMF solution ($[7AC]_0$:$[CPDB]_0$:$[AIBN]_0$ = 100:3:1, $T = 60$ °C, $[7AC]_0 = 1.16$ mol L^{-1}). (a) $M_n = 2300$ g/mol, PDI = 1.10, conversion = 15.5%; (b) $M_n = 2700$ g/mol, PDI = 1.10, conversion = 23.5%; (c) $M_n = 3000$ g/mol, PDI = 1.10, conversion = 26.6%; (d) $M_n = 3400$ g/mol, PDI = 1.20, conversion = 30.5%; (e) $M_n = 3700$ g/mol, PDI = 1.20, conversion = 37.6%; (f) $M_n = 4400$ g/mol, PDI = 1.36, conversion = 47.1%; (g) $M_n = 6000$ g/mol, PDI = 1.49, conversion = 54.0%; (h) $M_n = 7010$ g/mol, PDI = 1.42, conversion = 74.6%.

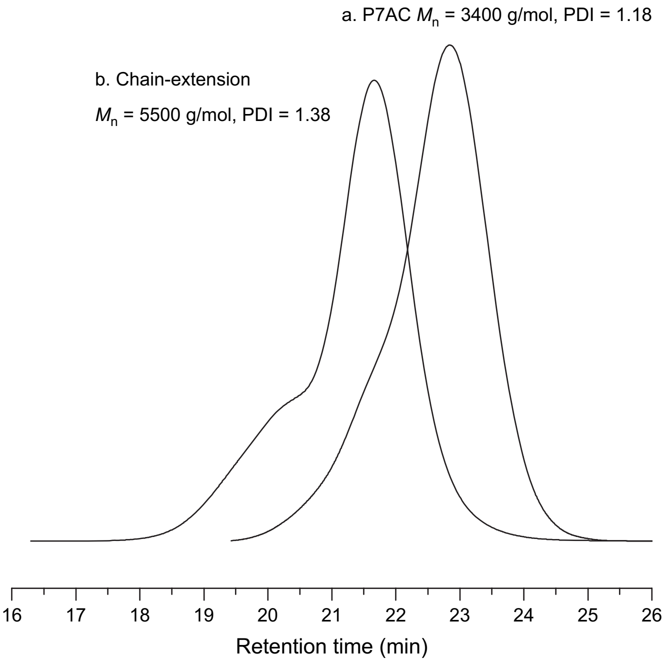


Fig. 4. GPC curves of the original macro-RAFT agent (P7AC) and chain extended block copolymer (P7AC-*b*-PS) in THF solution. Polymerization conditions: $[St]_0$:$[P7AC]_0$:$[AIBN]_0$ = 1000:3:1, $[St]_0 = 4.54$ mol L^{-1}, time = 24 h, $T = 60$ °C and conversion = 7.2%.

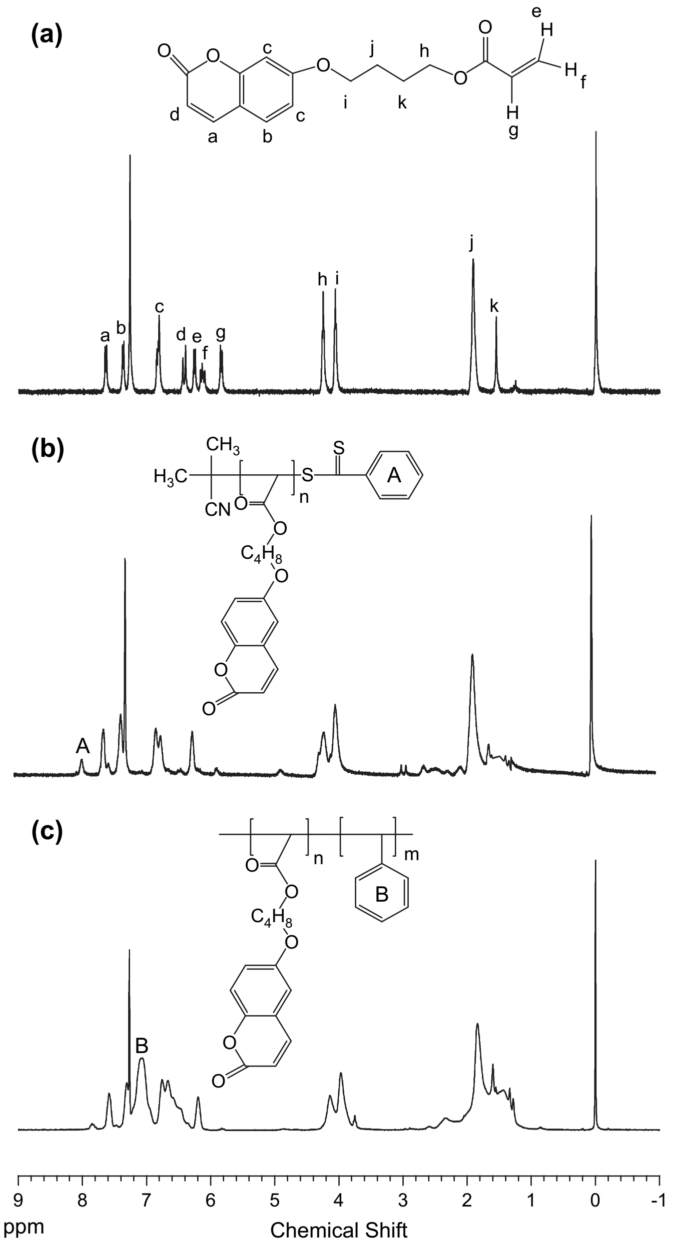


Fig. 5. ^{1}H NMR spectra of 7AC, P7AC and P7AC-*b*-PS. (a) 7AC; (b) P7AC ($M_n = 3400$ g/mol, PDI = 1.18); (c) P7AC-*b*-PS ($M_n = 5500$ g/mol, PDI = 1.38).

The structures of 7AC, P7AC and P7AC-*b*-PS were characterized by ^{1}H NMR. The spectra of the 7AC, P7AC and P7AC-*b*-PS are shown in Fig. 5(a)–(c), respectively. Compared with Fig. 5(a), a new signal (7.94 ppm (A)) appeared in Fig. 5(b) and (c), which could be assigned to the end-capped phenyl group of CPDB on the polymer chain. This result confirmed the RAFT mechanism of the polymerization. In Fig. 5(c), the new signals (around 7.0–7.2 ppm (B)) could be assigned to the phenyl group in the repeat unit of PS structure introduced into the P7AC-*b*-PS diblock copolymer. Other signals were almost same, which were attributed to the 7AC group in 7AC, P7AC and P7AC-*b*-PS. These results indicated that PS segment was present in the diblock copolymer.

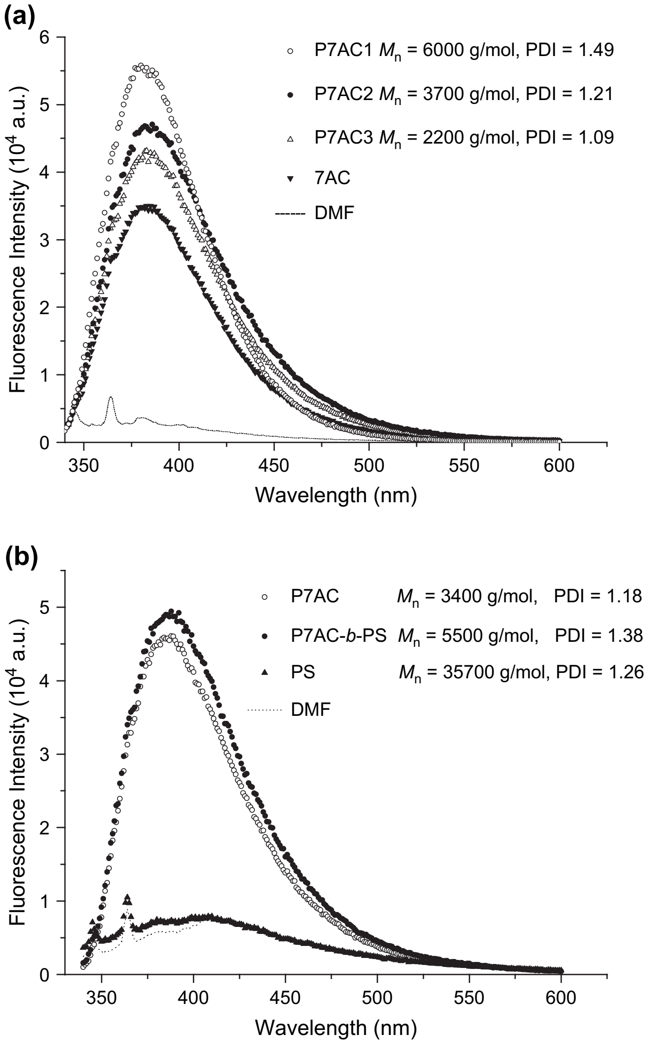


Fig. 6. Fluorescence spectrum of polymer in DMF solution at room temperature. The concentration of coumarin moieties was 5.0×10^{-5} mol L^{-1} and excitation wavelength was 329 nm. (a) P7AC and 7AC; (b) P7AC, P7AC-*b*-PS and PS.

3.3. Fluorescence properties of the polymers

The fluorescence spectra of monomer (7AC) and polymers (P7AC) with different molecular weights are shown in Fig. 6(a), and showed a strong fluorescence peak at about 390 nm, which was the characteristic fluorescence peak of the coumarin chromophore [34]. Furthermore, it showed that there was an apparent increase in the fluorescence intensity from the monomer (7AC) to the polymer (P7AC). The fluorescence intensity of P7AC increased with the increasing molecular weight of P7AC with the same coumarin moieties' concentrations. The reason could be attributed to the structural self-quenching effect with the interaction between the electron-donating chromophore and the electron-accepting carbon–carbon double bond existing in the monomer [35–38]. On the other hand, the increase in the fluorescence intensity with an increasing molecular weight of P7AC could be assigned to the increase of chain length, which played an important role in providing sufficient numbers of chromophore−chromophore interactions in the intramolecular system [39,40]. The fluorescence spectra of P7AC-*b*-PS diblock copolymer and P7AC in the same concentration of coumarin moieties are shown in Fig. 6(b). It showed that the fluorescence intensity of P7AC was slightly lower than that of P7AC-*b*-PS diblock copolymer. Very weak fluorescence of PS was observed in the same condition. The introduction of PS block into the polymer chain separated the coumarin group from dithiobenzoyl moieties. The dithiobenzoyl moiety was considered as a fluorescence quenching agent for the excited coumarin chromophores. Moreover, the interactions between the chromophore moieties and the phenyl moieties might be another reason for this phenomenon [23].

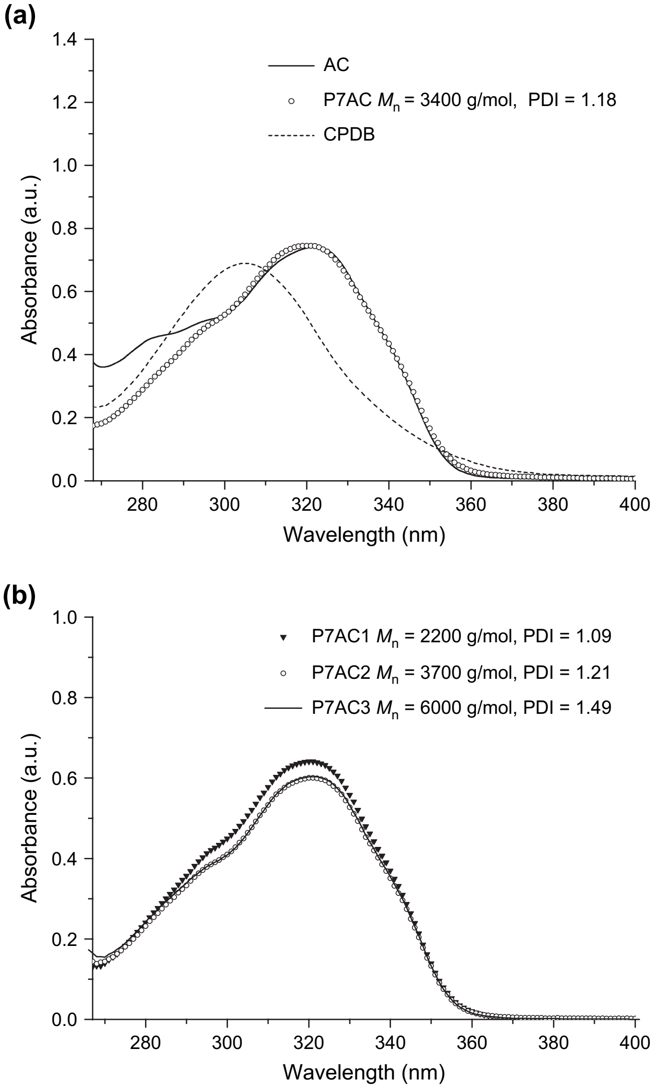


Fig. 7. (a) UV−vis spectra of P7AC, 7AC and CPDB in DMF at room temperature. For P7AC and 7AC, the initial concentration of chromophore moieties was 5.3×10^{-5} M for all cases. (b) UV−vis spectra of P7AC in DMF at room temperature. The concentration of coumarin moieties was 5.0×10^{-5} mol L^{-1} for all cases.

3.4. UV−vis absorption of the polymers

Fig. 7(a) shows the UV−vis spectra of polymer, monomer and RAFT agent, and that both the monomer and the polymer had a strong UV−vis absorption at 322 nm. However, the weaker UV−vis absorption intensities of the polymer from 268 nm to 300 nm wavelength could be attributed to the disappearance of intermolecular or intramolecular exciplex between the electron-donating chromophore and the electron-deficient acrylic carbon−carbon double bonds [41], and was not the influence of CPDB (the RAFT agent). Furthermore, the UV−vis spectra of P7AC with different molecular weights were measured and are shown in Fig. 7(b). The results in Fig. 7(b) show that the molecular weight of polymer had no obvious effect on the UV−vis spectra, which was due to the same concentration of chromophore concentration (5.0×10^{-5} mol L^{-1}).

3.5. Photodimerization reaction

The photodimerization reaction of P7AC ($M_n = 2600$ g/mol, PDI = 1.10) was carried out under the irradiation of UV spot light source. The evolution of the reaction was monitored by UV−vis−NIR spectrophotometer in THF solution. The concentration of coumarin units was set to 5×10^{-4} mol L^{-1}. The typical UV−vis absorption spectral change of P7AC during irradiation is shown in Fig. 8. The peak intensity of UV−vis absorption at 322 nm decreased during the irradiation due to the disruption of aromaticity of the coumarin [42].

Table 1 shows the GPC results of P7AC before and after different irradiation times. The molecular weight and PDI of

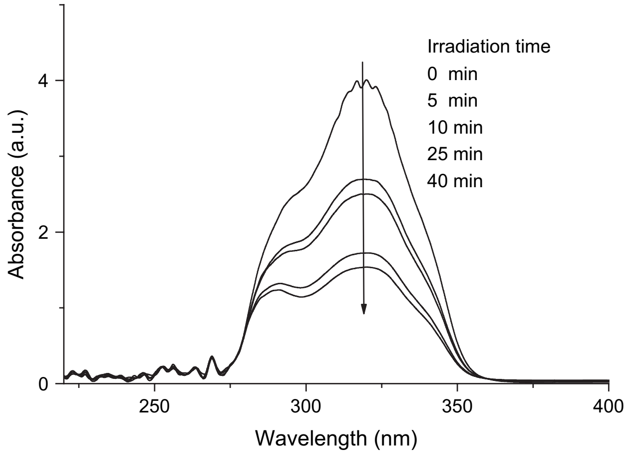


Fig. 8. UV−vis absorption spectral change of P7AC during irradiation.

Table 1
Effect of irradiation time on molecular weight and PDI changes of P7AC

Irradiation time (min)	0	10	20	30	45
M_n (g/mol)	2600	2690	2820	2780	Gel
PDI	1.10	1.17	1.21	1.31	−

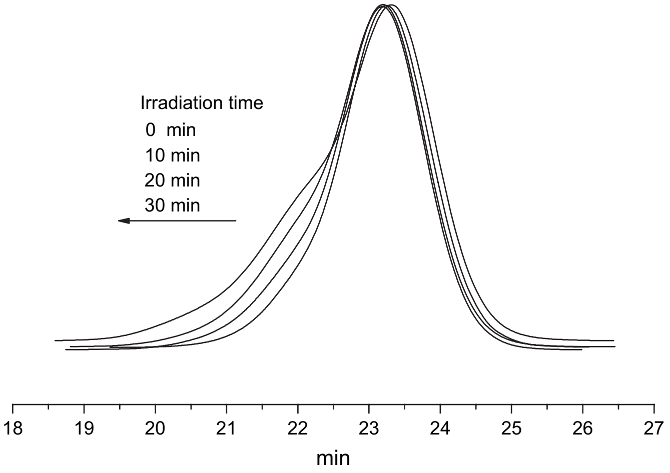


Fig. 9. GPC curves of P7AC during irradiation.

P7AC increased after irradiation by UV. The GPC curves of P7AC showed trails in high molecular weight region after irradiation (Fig. 9), which suggested that the photodimerization reaction between coumarin groups occurred. The molecular weight of P7AC after UV irradiation had a very little increase with increase of irradiation time from 10 min to 30 min, which indicated that the photodimerization reaction took place mainly between the coumarin groups on the same P7AC chain. By further prolonging the irradiation time to 45 min, P7AC was hardly dissolved in THF, which could be caused by the crosslink among coumarin groups of different P7AC chains.

4. Conclusion

The well-defined fluorescence polymer, poly(7-(4-(acryloyloxy)butoxy)coumarin) (P7AC), with coumarin units was prepared via RAFT polymerization. Polymerization showed controlled/'living' polymerization characteristics: the first-order kinetics, the linear dependence of the molecular weights on the monomer conversions and obtained polymers with narrow polydispersities. The results of end-group analysis by ^{1}H NMR spectroscopy showed that the obtained polymer was end-capped with moiety of RAFT agent. The polymer was active enough for carrying out the chain-extension reactions. The fluorescence intensity of P7AC increased with increasing the molecular weight of polymer and was higher than that of the monomer. The photodimerization reaction of P7AC was carried out in THF solution. The UV−vis absorption of P7AC ($\lambda_{max} = 322$ nm) decreased after irradiation under UV light. The molecular weight and PDI of the polymer after irradiation were larger than those before irradiation.

Acknowledgments

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