

Photo-Dimerization Characteristics of Coumarin Pendants within Amphiphilic Random Copolymer Micelles^{*}

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Abstract The photo-dimerization characteristics of coumarin pendants within amphiphilic random copolymer micelles in aqueous solution was comprehensively investigated using various selected wavelength light in the UV-Vis-NIR region. The time-dependent photo-dimerization degree (PD) changes in the photo-dimerization experiments showed saturating behaviors with intensity-independent of PD_{max} values at 28%, 44%, 92%, 85%, 36%, 35%, 32% and 31% for 254, 288, 320, 360, 400, 500, 650 and 900 nm irradiations, respectively. The irradiation experiments at 254 and 288 nm announced the occurring of an asymmetric equilibrium of photo-dimerization and photo-cleavage at the used conditions. Both the alternative irradiation cycles of 360 and 254 nm, 650 and 254 nm showed a partially, but evidently reversible photo-dimerization tendency.

Keywords: Polymer micelles; Coumarin; UV-Vis-NIR; Photo-dimerization; Photo-cleavage.

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INTRODUCTION

Coumarin and its derivatives have attracted considerable attention because of their diverse photophysical and photochemical properties^[1–3]. In addition, coumarins can undergo a 2 + 2 photo-dimerization upon irradiations at $\lambda > 300$ nm, whereas the reverse photo-scission reaction occurs under irradiation at $\lambda < 300$ nm^[4]. Since this reversible photo-dimerization was first disclosed in 1902^[4], enormous studies concerning coumarins have been published due to their unique photochemistry^[5–11]. Especially, in recent years, the dimerization of coumarins has been accomplished with near-infrared (NIR) or two photon light for the applications of NIR responsive materials^[12, 13]. However, these previous works have always been seeking the photo-induced physical and chemical changes of coumarin-containing materials derived from the photo-dimerization of coumarins, few examples related to the comprehensive photo-dimerization characteristics upon irradiations in the UV-Vis-NIR region, which, apparently, will help further understanding on the photo-dimerization mechanism of coumarins and provide more choice for materials with tunable properties in the applications of nano-reactors, biological functional models and *etc*^[14–18].

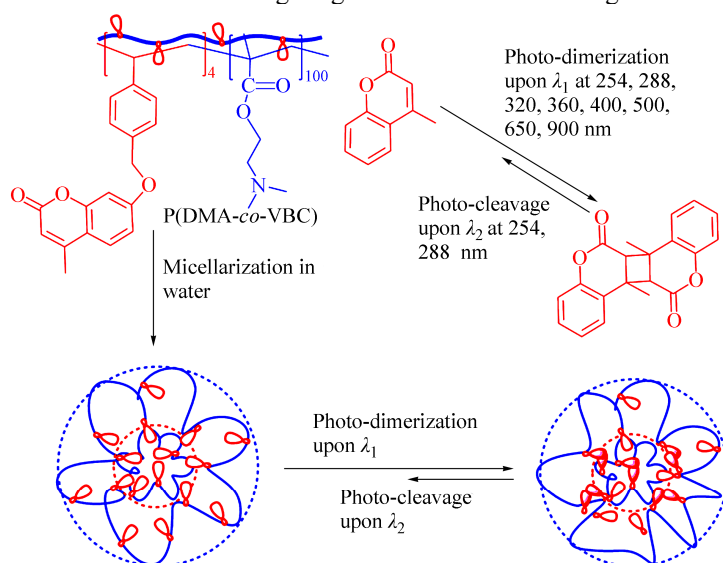
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Recently, we reported the photo-dimerization characteristics of anthracene pendants within amphiphilic block copolymer micelles based on poly(ethylene oxide)-*b*-poly(anthracene methyl methacrylate) (PEO-*b*-PAM)^[19]. By irradiation with selected narrow band wavelength light in the UV-Vis-NIR region, *i.e.* 261, 300, 338, 353, 371, 392, 416, 550, 700 and 900 nm, respectively, the photo-dimerization of anthracene was comprehensively studied. It was found that for the dimerization UV light was favorable than the Vis-NIR light and the maximum dimerization extent upon a certain wavelength light was always independent of irradiation intensities at the used conditions. In this study, as shown in Scheme 1, we seek to find the comprehensive photo-dimerization characteristics of coumarin pendants within amphiphilic random copolymer micelles of poly[2-(dimethylamino)ethyl methacrylate-*co*-7-(4-vinyl-benzyloxy)-4-methyl coumarin] (P(DMA-*co*-VBC)) in aqueous solutions upon several narrow wavelength light in the UV-Vis-NIR region.



Scheme 1 The structure of the amphiphilic random copolymer of P(DMA-*co*-VBC) and the reversible photo-dimerization of coumarin pendants upon selected irradiations in aqueous solutions

EXPERIMENTAL

Materials

Ethyl-2-bromo-2-methylpropionate (EBM-Br), Cu(I)Br, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), 4-vinylbenzyl chloride (90%), 7-hydroxy-4-methylcoumarin, 4-methoxyphenol (99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA), anhydrous potassium carbonate and alumina were purchased from Aladdin. DMAEMA was passed through a neutral Al₂O₃ column to remove the inhibitor before the polymerization. The coumarin containing monomer of 7-(4-vinyl-benzyloxy)-4-methylcoumarin (VBC) was prepared according to previous works^[20, 21].

Characterization

¹H-NMR spectrum (400 MHz) was investigated by a Bruker spectrometer with CDCl₃ as solvent. Gel permeation chromatography (GPC) was performed using a Waters system equipped with a refractive index and a photodiode array detector, using THF as eluent (0.5 mL/min) and polystyrene as calibration standard.

DLS measurements were performed at 25 °C with a Malvern Nano-ZS90 instrument (Malvern, U.K.) to determine the average diameter and size distribution of polymer micelles. UV-Vis absorbance spectra were recorded on a UV-6100s Double Beam Spectrophotometer (Meipuda, China) at 25 °C. AFM images of polymer micelles were obtained in tapping mode on a CSPM5500A scanning probe microscope system (Benyuan, China). The samples were prepared by dropping the micellar aqueous solution (0.05 mg/mL) onto mica sheets, and dried at room temperature overnight.

Synthesis of P(DMA-co-VBC)

In the polymerization^[22, 23], EBM-Br initiator (0.058 g, 0.3 mmol), Cu(I)Br (0.086 g, 0.6 mmol), DMAEMA (5.030 g, 32 mmol), VBC (0.750 g, 2.5 mmol), PMDETA (0.110 g, 0.6 mmol) and dioxane (10 mL) were quickly added into a 50 mL ampoule. Then, the mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the ampoule was placed in a preheated oil bath (60 °C) for 24 h. Then, the solution was passed through a neutral Al₂O₃ column with chloroform as eluent to remove all the catalyst. The amphiphilic random copolymer of P(DMA-co-VBC) was collected by precipitation twice into ethyl ether. The pale powder was dried under vacuum at 30 °C overnight. Yield: 70%. $M_n = 1.67 \times 10^4$ g/mol. $M_w/M_n = 1.20$ (GPC). P(DMA-co-VBC) was further estimated to compose of 100 DMAEMA and 4 VBC units according to the calibration curve of VBC in DMF (see Fig. S1 in the Supporting Information).

The Photo-Reaction with Selected Narrow Band of Wavelength Light

Irradiation experiments of coumarin pendants within polymer micelles in aqueous solutions were carried out at 25 °C by an adjustable double grating monochromator of Omni- λ 1805i equipped with a broadband laser-driven light source of EQ-1500 LDLSTM and a set of six optical filters, which can afford narrow band wavelength of light between 250–1500 nm intervals. Light within 100–600 nm and 550–1500 nm intervals were generated by grating one and grating two, respectively. And the different optical filter was applied to the selected narrow band of light in order to eliminate the influence of other stray light, as shown in Table 1.

Table 1. The optical filters used for narrow selected wavelength light

Filter type	Wavelength range (nm)	Transmission (%)
No filter	Full band	100
ZJB280	350–440	89.5
ZJB360	440–650	87
CB550	650–800	88.7
HB720	800–1100	80
HWB3	1100–1500	75

Two narrow band UV light of 320, 360 nm and four Vis-NIR light of 400, 500, 650 and 900 nm were chosen as the photo-dimerization light, and 254 and 288 nm were chosen as the photo-cleavage light. And the bandwidth for the selected irradiation light was 5 nm.

The calculated amount of P(DMA-co-VBC) was directly dissolved in deionized water to a concentration of 0.25 mg/mL. For the photo-dimerization experiment, 1 mL of polymer aqueous solution was sealed in the fluorescence cuvette and irradiated directly with the selected photo-dimerization light; and for the photo-cleavage procedure, the polymer aqueous solution was first photo-dimerized to the given dimerization extent (88.31%) with 320 nm light (0.86 mW/cm²), then irradiated by 254 and 288 nm light with different intensities, respectively. The distance between the quartz wall and the spot light was 0.2 cm and the illumination intensities were measured by a CEL-NP 2000 optical power meter. The irradiation experiment procedures were monitored with UV-Vis absorbance spectra instrument at 25 °C.

For the reversible photo-dimerization procedure, the polymer aqueous solution (0.25 mg/mL $\times$ 1 mL) was alternatively irradiated by 360 nm (0.65 mW/cm², 80 min) and 254 nm (0.16 mW/cm², 90 min), and 650 nm (1.66 mW/cm², 80 min) and 254 nm (0.16 mW/cm², 90 min) for four cycles to evaluate their reversibility, respectively.

The photo-dimerization degree (PD) was calculated from the UV-Vis spectra by comparing the peak absorption at 320 nm assigned to the coumarin group by the following equation:

$$\text{PD}(\%) = 100 \times (A_0 - A_t) / A_0 \quad (1)$$

Here, A_0 and A_t were the peak absorptions centered at 320 nm before irradiation and after irradiation, respectively.

RESULTS AND DISCUSSION

Micellization of P(DMA-co-VBC) in Aqueous Solution

Water-soluble amphiphilic copolymers (WSAPs) have attracted much attention in the past years due to their unique self-assembly behaviors under various chemical and physical stimuli, such as pH, temperature, light and redox^[24–27]. A simple design of WSAPs is to introduce some hydrophobic comonomers into water-soluble polymers. Like amphiphilic block copolymers, this kind of polymers can also self-assemble into various forms of micellar aggregates, which can be exploited for applications in nano-carriers, nano-reactors, *etc.* As designed, the objected polymer of P(DMA-co-VBC) was prepared by ATRP using DMAEMA as the water-soluble main monomer and VBC as the hydrophobic and photo-crosslinkable comonomer, which would afford P(DMA-co-VBC) the hydrophobic association to assemble into micelles in aqueous solutions in the case of exceeding the CMC value and the reversible photo-dimerization ability^[28].

In order to verify the micellization of P(DMA-co-VBC) in aqueous solutions, the polymer was dissolved in previously pyrene saturated aqueous solution and monitored with pyrene probe technique. As shown in Fig. 1(a), the emission spectra ($\lambda_{\text{ex}} = 334 \text{ nm}$) exhibited a vibrational fine five peaks emission of pyrene at the beginning ($< 1.25 \times 10^{-1} \text{ mg/mL}$), which was then suppressed to a broad emission band covering 350–550 nm interval with the increasing polymer concentration. Figure 1(b) showed the intensity ratio changes between the first peak (I_1 at 373 nm) and the third one (I_3 at 384 nm) as a function of polymer concentration, the ratio I_1/I_3 for polymer concentrations below $4.70 \times 10^{-3} \text{ mg/mL}$ remained constant and decreased progressively above it, which reflected the onset of micelle formation and the partitioning of the pyrene between the aqueous and micellar phases^[29–31]. Therefore, the CMC value for P(DMA-co-VBC) in aqueous solutions could be determined as $4.70 \times 10^{-3} \text{ mg/mL}$. Taking both the micellar stability and the demands of the real-time UV-Vis spectroscopy into consideration, the polymer concentration used in the irradiation experiment was kept at 0.25 mg/mL . The dynamic light scattering analysis (see Fig. S4 in supporting information) showed that the average size of P(DMA-co-VBC) (0.25 mg/mL) was about 300 nm, and the polymer micelle was also visualized as nano spheres by AFM observation (see the inset of Fig. 1b).

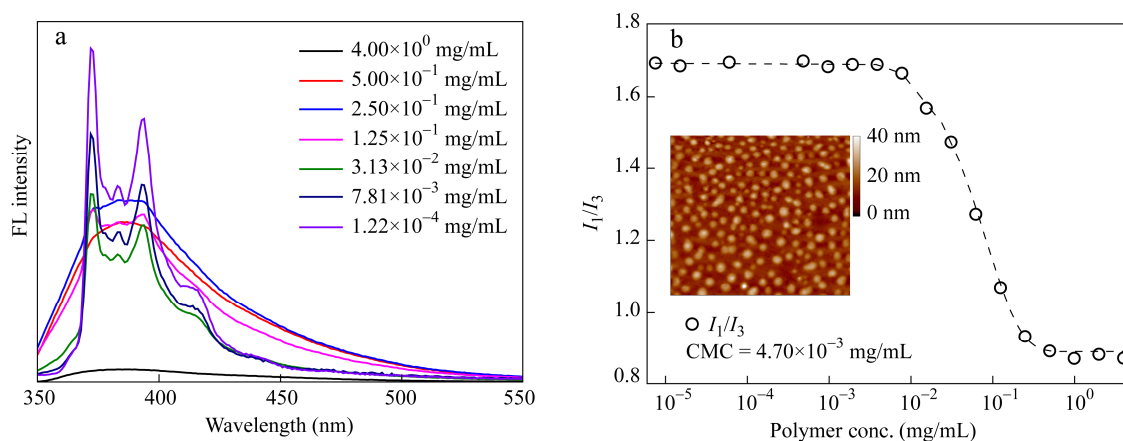


Fig. 1 (a) The fluorescence spectra ($\lambda_{\text{ex}} = 334 \text{ nm}$) of polymer in previously pyrene saturated aqueous solutions and (b) The dependence of I_1/I_3 as a function of polymer concentration and the AFM image ($2 \mu\text{m} \times 2 \mu\text{m}$) of polymer micelles

The Photo-Reaction upon Selected Bands of Light at $\lambda > 300 \text{ nm}$

Coumarin can be photo-dimerized upon irradiation at $\lambda > 300 \text{ nm}$. Thus, in order to comprehensively investigate the photo-dimerization kinetics dependency of irradiation conditions, and according to the characteristic absorbance band of coumarin pendants in aqueous solution, polymer micellar solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) sealed in the fluorescence cuvette was first irradiated by two narrow band UV light of 320, 360 nm and then by four Vis-NIR light of 400, 500, 650 and 900 nm, respectively.

As shown in Fig. 2(a), irradiation of polymer aqueous solution by 360 nm wavelength light (0.35 mW/cm^2) induced the photo-dimerization of coumarins and thus resulted in a gradual decrease in the absorption band at 320 nm. Figure 2(b) shows the estimated PD values based on the absorbance changes at 320 nm upon different intensity irradiations of 360 nm. The time-dependent PD values for coumarins showed saturating behavior and synchronously decreased with the lowering of irradiation intensities. And these observed PD changes can be fitted well with a biexponential equation:

$$\text{PD}(t) = X_1(1 - e^{-k_1 t}) + X_2(1 - e^{-k_2 t}) \quad (2)$$

where $\text{PD}(t)$ corresponded to the time-dependent photo-dimerization degree, k_1 and k_2 were rate constants, X_1 and X_2 were the relative weight fractions^[19, 32]. And as shown in the Fig. 2(c), k_1 and k_2 obtained upon 360 nm irradiations increased linearly as a function of light intensity, respectively. On the contrary, the relative weight fractions of X_1 and X_2 showed no obvious intensity-dependence. However, it was interesting that the obtained sum of X_1 and X_2 , which decided the maximum photo-dimerization extent ($\text{PD}_{\max}$) that the coumarins could reach after long enough irradiation time of 360 nm light with different irradiation intensities, fluctuated weakly around 85% and afforded a good zero-order linear fit, indicating that $\text{PD}_{\max}$ was always intensity-independent at used conditions^[19].

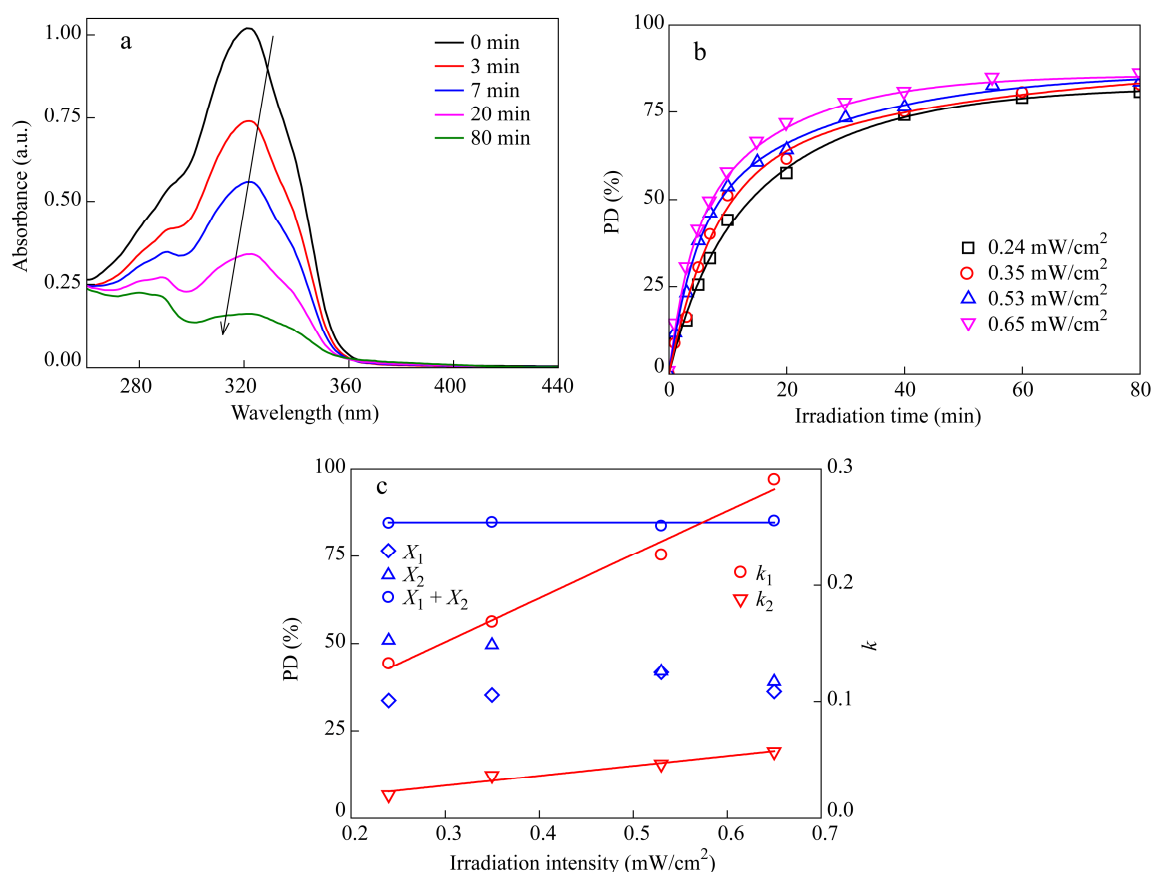


Fig. 2 (a) Absorbance spectra changes of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon 360 nm irradiation (0.35 mW/cm^2); (b) The time-dependent PD values of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon different intensity irradiations of 360 nm fitted with Eq. (2); (c) The intensity-dependences of k_1 and k_2 and the obtained $X_1 + X_2$ values as a function of irradiation intensity, respectively

Figure 3 shows the photo-dimerization kinetics of coumarin pendants irradiated by light of various wavelengths at $\lambda > 300$ nm from the double grating monochromator with the same slits (their irradiation intensities corresponding to the highest in Fig. 3b, respectively). As shown in Fig. 3(a), the obtained time dependences of PD are fit very well to the four parameter biexponential Eq. (2), and the UV light irradiations gave faster dimerization rates and higher extents than the Vis-NIR light at the same time. The solid linear lines in Fig. 3(b) are zero-order linear fits of $X_1 + X_2$ values obtained by changing the irradiation intensities of the above selected light. The $X_1 + X_2$ value obtained by 320 nm irradiation was about 92%, which was a little greater than that of 360 nm irradiation. While for the latter four Vis-NIR light irradiations, in which region coumarins have almost no absorptions, considerable photo-dimerization efficiencies could still be found with the $PD_{\max}$ values of 36%, 35%, 32% and 31% for 400, 500, 650 and 900 nm light irradiations, respectively. These results strongly gave the fact that the photo-dimerization extent ($PD_{\max}$) of coumarins under UV irradiations was always much higher than that under Vis-NIR ones and independent to the irradiation intensities of a certain light at used conditions. Furthermore, the evidential $PD_{\max}$ values of coumarins upon NIR light announced the applications of NIR responsive materials.

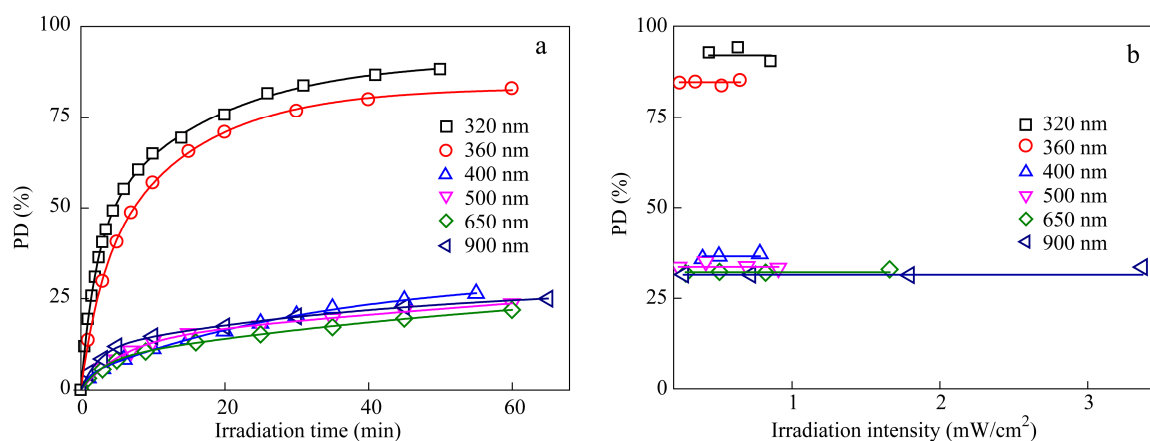


Fig. 3 (a) The time-dependences of PD values of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon selected narrow band light irradiations at $\lambda > 300$ nm fitted with Eq. (2); (b) The zero-order intensity dependence of $X_1 + X_2$ values for the selected light irradiations, respectively

The Photo-Reaction upon Selected Narrow Band of Light at $\lambda < 300$ nm

The coumarin photo-dimers can also revert to the starting compound upon irradiation with shorter wavelength ($\lambda < 300$ nm)^[33, 34]. However, it is found that only about 40%–60% of dimers can be photo-dissociated^[34]. Thus, the polymer aqueous solution was first irradiated by 254 and 288 nm light to check the photo-dimerization possibility at $\lambda < 300$ nm, respectively. As shown in Fig. 4(a), irradiation of polymer micelles by 254 nm wavelength light (0.31 mW/cm^2) also induced a gradual decrease in the absorption band at 320 nm; the reasonable biexponential fits with Eq. (2) for 254 nm irradiations in Fig. 4(b) indicated that coumarins upon short wavelength light at $\lambda < 300$ nm also underwent a considerable photo-dimerization speed, which synchronously decreased with the lowering of irradiation intensities. And as shown in the inset of Fig. 4(b), the photo-dimerization extent of $X_1 + X_2$ for 254 and 288 nm irradiations was about 28% and 44%, respectively, which were much lower than those for 320 and 360 nm irradiations, and at the same level with those for four Vis-NIR light irradiations.

The above photo-dimerization procedures upon 254 and 288 nm irradiations were further studied with long-and-short time irradiation method to investigate the possible simultaneous photo-scission of coumarin dimers during the photo-dimerization. As shown in Fig. 5, under 254 nm irradiation, the photo-dimerization degree of coumarin pendants increased to 17.5% within the first 10 min, and decreased to 16.1% after the subsequent 60 s irradiation; and for 288 nm irradiation, it increased to 26.8% in the initial stage, then decreased to 26.1% after

20 s and increased to 26.9% in the remaining 40 s. The remaining long-and-short cycles of 254 and 288 nm irradiations showed similar features of photo-dimerization and photo-cleavage, indicating the asymmetric equilibrium of photo-dimerization and photo-cleavage occurring at $\lambda < 300$ nm and the faster photo-cleavage reaction of coumarin dimers upon 254 nm irradiation than the 288 nm one. And this long-and-short time irradiation method was also applied to 360 and 650 nm irradiations, however, no photo-cleavage stages were found during the irradiations (Figs. S8 and S18 in the Supporting Information, respectively).

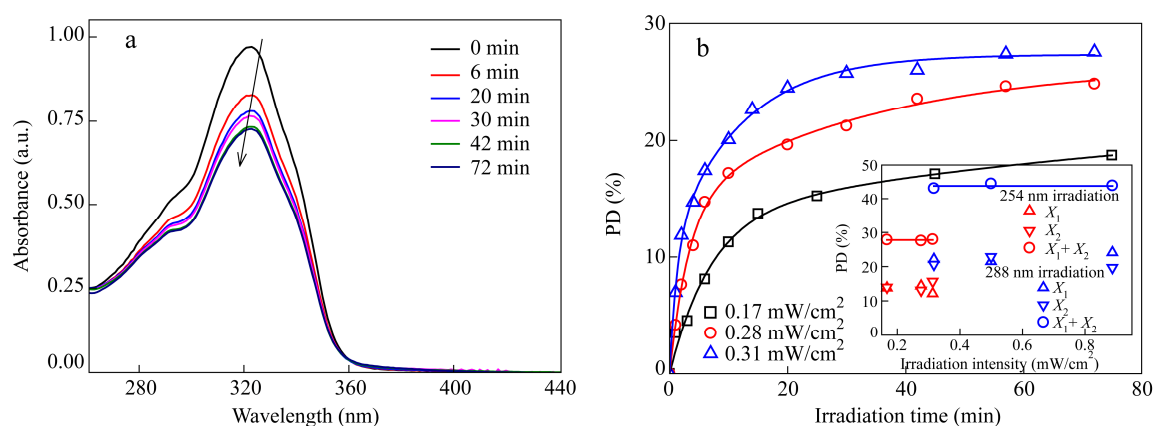


Fig. 4 (a) Absorbance spectra changes of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon 254 nm irradiation (0.31 mW/cm^2); (b) The time-dependent PD values of coumarins upon different intensity irradiations of 254 nm filled with Eq. (2) (The inset shows the zero-order intensity dependence of $X_1 + X_2$ values for 254 and 288 nm irradiations, respectively.)

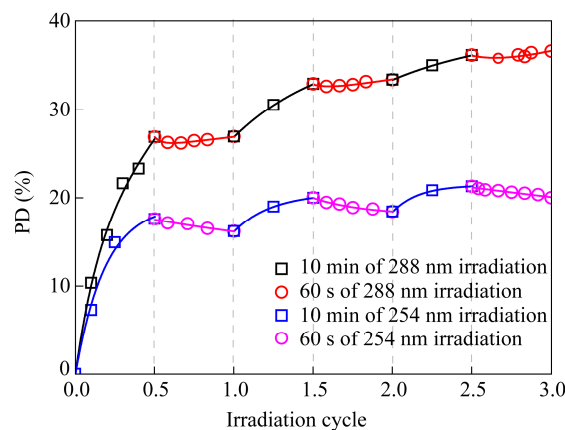


Fig. 5 PD changes of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon 254 (0.24 mW/cm^2) and 288 nm (0.50 mW/cm^2) light using long-and-short time irradiation method, respectively

To further investigate the photo-reaction of coumarin at short wavelength light, the micellar solution with given photo-dimerization degree was photo-dissociated by 254 and 288 nm light, respectively. As shown in Fig. 6(a), the absorption at 320 nm recovered along with 254 nm irradiation (0.24 mW/cm^2), indicating the ongoing scission of the coumarin photo-dimers and resulting in the decline of PD values along with the irradiation time. The time-dependences of these observed PD changes upon various intensity irradiations were fitted reasonably with a biexponential equation:

$$\text{PD}(t) = \text{PD}(0) - X_a(1 - e^{-k_3 t}) + X_4(1 - e^{-k_4 t}) \quad (3)$$

where $PD(t)$ corresponded to the PD value after t time of photo-cleavage, $PD(0)$ was the given PD value (88.31%) of the photo-dimerized coumarin solution, k_3 and k_4 were rate constants, X_3 and X_4 were the relative weight fractions. It is understandable that Eqs. (2) and (3) are opposite each other since these two fitting equations are derived from the reversible photo-dimerization process. Furthermore, $X_3 + X_4$ determined the maximum photo-scission ($PS_{\max}$) that the system could reach after long enough photo-dissociation time. As shown in the inset of Fig. 6(b), the obtained $X_3 + X_4$ values at different irradiation intensities of 254 nm and 288 nm light declined linearly with a linear fit slope of -70.55 and -16.14 , respectively, and the linear fit line for 288 nm irradiation was always below that for 254 nm light. These results indicated that the photo-dissociation of coumarin dimers was favorable for the 254 nm light than for the 288 nm one, and a more thorough photo-scission of coumarin dimers could be achieved with long enough time of lower intensity irradiation light ($\lambda < 300$ nm) at used conditions.

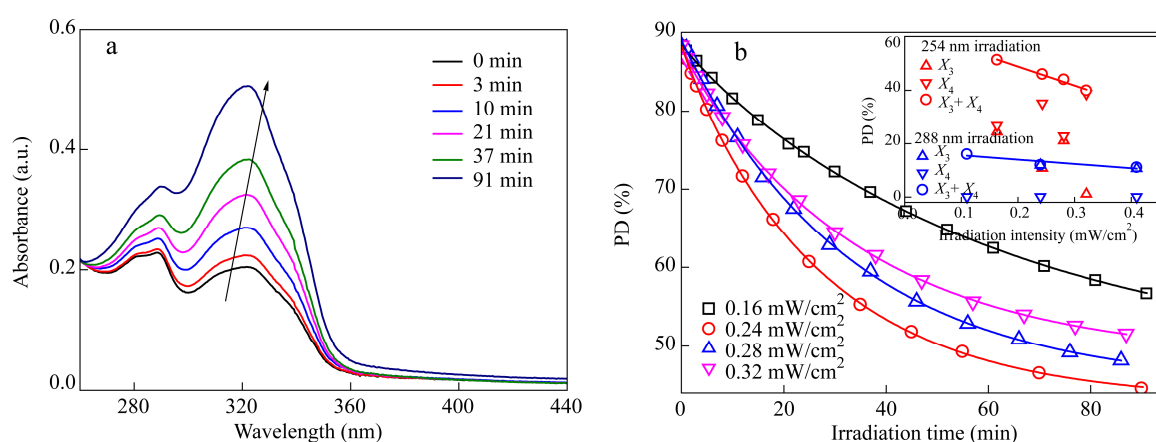


Fig. 6 (a) Absorbance spectra changes of photo-crosslinked polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$, $PD(0) = 88.31\%$) upon 254 nm irradiation (0.16 mW/cm^2); (b) The time-dependent PD values upon different intensity irradiations of 254 nm fitted with Eq. (3) (The inset shows the intensity dependence of $X_3 + X_4$ values according to Eq. (3) for 254 and 288 nm light irradiations, respectively.)

The Reversible Photo-Dimerization Cycles upon Alternative Irradiations

To further investigate the reversible photo-dimerization of coumarin pendants within polymer micelles, polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) was irradiated with two sets of alternative light of 360 and 254 nm, and 650 and 254 nm, respectively. As shown in Fig. 7, when polymer solution was exposed upon alternative irradiation of 360 and 254 nm for four cycles, the final photo-dimerization degree in four photo-dimerization stages dropped weakly from 88.3% to 84.3%, 82.8% and 82.6%, respectively; however those final PD values for photo-cleavage stages increased progressively from 44.0% to 59.5%, 68.3% and 73.0% along with the irradiation cycle, respectively. And the irradiation cycles of 650 and 254 nm also afforded the similar tendency with a decreasing PD value from 21.89% to 20.63%, 18.23% and 17.23% at the end of four photo-dimerization stages and an constant PD value around 13.00% after each photo-dissociation stage, respectively. These results indicated that the reversible photo-dimerization of coumarins within polymer micelles could be partially achieved upon alternative irradiations. However, this partially reversible change in the dimerization degree can still be evidently observed, indicating that alternating irradiation can be used as a trigger to predictably alter the physicochemical properties of the coumarin containing materials. And since NIR light with wavelengths in the range of about 700–1000 nm is more suitable for biomedical applications than UV light, the partially reversible photo-dimerization upon alternative 650 and 254 nm irradiations announced their applications in biological functional materials.

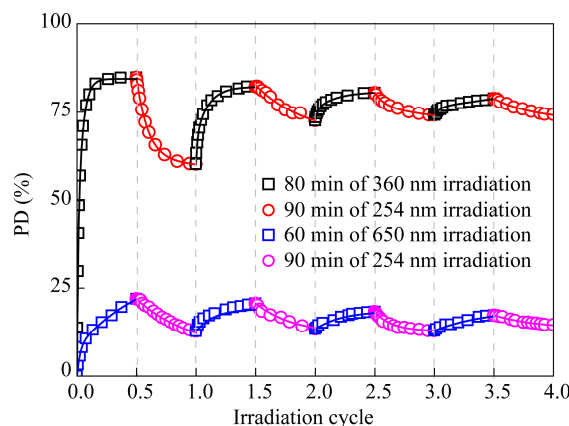


Fig. 7 Plots of PD changes of polymer aqueous solution ($0.25 \text{ mg/mL} \times 1 \text{ mL}$) upon alternative irradiations of 360 nm (0.65 mW/cm^2) and 254 nm (0.16 mW/cm^2), and 650 nm (1.66 mW/cm^2) and 254 nm (0.16 mW/cm^2), respectively

CONCLUSIONS

To summarize, a water-soluble amphiphilic random copolymer of P(DMA-*co*-VBC) containing coumarin pendants was chosen to comprehensively investigate the photo-reaction characteristics of coumarin pendants in aqueous solution using various narrow band wavelength light in the UV-Vis-NIR region. The result shows that the photo-dimerization of coumarins was favorable for UV irradiations at $\lambda > 300 \text{ nm}$ than the Vis-NIR light between 400–900 nm intervals. The irradiation experiments at 254 and 288 nm announced the occurring of an asymmetric equilibrium of photo-dimerization and photo-cleavage at the used conditions. And the alternative irradiation cycles showed a partially, but evidently reversible photo-dimerization tendency.

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