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COMMUNICATION

The Photodimerization Characteristics of Anthracene Pendants within Amphiphilic Polymer Micelles in Aqueous Solution

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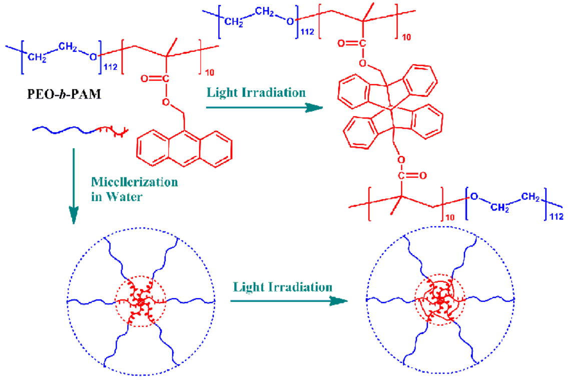
An amphiphilic polymer with anthracene pendants of PEO-*b*-PAM has been applied to comprehensively investigate the photodimerization characteristics of anthracene in aqueous solution upon various selected narrow band of light irradiations in the UV-Vis-NIR region.

Anthracene and its derivatives are interesting compounds because of their versatile photochemical applications.[1] Owing to their diverse photophysical and photochemical properties, anthracenes have been used in many systems such as functional polymers, triplet sensitizers and molecular fluorosensors.[1-5] Another well-known facet of anthracenes is their typically photodimerization reaction, which is of favorable UV light irradiations (250-400 nm) and has widely been investigated for the application of photoresponsive materials.[6-15] Furthermore, the dimerization has been recently accomplished with the visible light (400-700 nm) or multiphoton light in order to weaken some side effects during irradiations.[16-18] It is widely accepted that the photodimerization efficiency always depends on the photochemical absorbency of anthracenes upon the light. Thus, the photodimerization efficiency can be anticipated according to the characteristic UV-vis absorbance of anthracenes and easily controlled by adjusting the photon flux.[6] However, to date, reports that comprehensively describe the photodimerization characteristics of anthracene upon various light irradiations in the UV-Vis-NIR region are seldom. Which, apparently, will help further understanding on the photodimerization mechanism of anthracenes and also other photo-crosslinkable chromophores and may improve their opportunities in potential applications, such as nanofabrication, nano-reactors and biological functional models, especially when they are demanded to be controlled sophisticatedly.[19-22]

Herein, based on our ongoing study of the photoresponsive amphiphilic polymers, our attention was drawn to the photodimerization characteristics of anthracene pendants within the polymer micelles of poly(ethylene oxide)-*b*-poly(anthracene methyl methacrylate) (**PEO-*b*-PAM**), which was concisely synthesized by ATRP. Figure 1 schematically illustrates the amphiphilic structure of such block copolymer and its photodimerization upon light irradiation in aqueous solution. To be emphasized, the photodimerization efficiency of anthracene always depends on its concentration and molecule mobility.[23] And the typical amphiphilic block copolymer of **PEO-*b*-PAM** can spontaneously form aggregated micelles. Thus, anthracene pendants would be entangled into the confined micelle core with high local concentration and restricted mobility, which may facilitate the dimerization in the beginning period of irradiation and result in the maximum equilibrium extent in the late.



Scheme 1. Schematic illustration of the amphiphilic polymer with anthracene pendants (**PEO-*b*-PAM**) and its photodimerization upon light irradiation in aqueous solution.

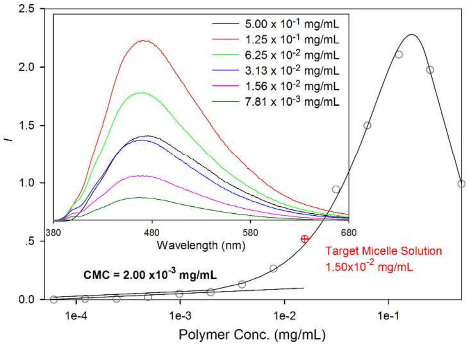


Figure 1. Normalized fluorescence emission intensity of anthracene at 470 nm (λ_{exc} = 353 nm). Inset: fluorescence emission spectra of **PEO-*b*-PAM** in aqueous solution.

We first focused on the micellization of **PEO-*b*-PAM** in aqueous solution. The obtained polymer micelle aqueous solution was first diluted gradually to evaluate its stability and the dilution process was traced by fluorescent spectroscopy and DLS instrument. As shown in the inset of Figure 1, the anthracene emission spectra in aqueous solution are easily detected with broad fluorescence emission covering 380-680 nm intervals. And the maximum emission peak around 470 nm is not always weakening during the dilution, which is strengthened at the beginning and then becomes weak upon the further dilution. This phenomenon can be often found in the assemblies of anthracene-containing polymers.[13] The self-quenching effect of anthracene decreases with the decreasing concentration of anthracene pendants first, then the fluorescence decreases with the further decreasing concentration of anthracene.[24-25] Furthermore, as shown in Figure 1, the plot of normalized maximum emission below polymer concentration of 2.00×10^{-3} mg/mL show a relatively gentle and lineal decrease along with the dilution. While the DLS examinations (S2 in Supporting Information) show narrow size distributions around 50 nm above 2.00×10^{-3} mg/mL and huge fluctuations below this concentration. Thus, we assigned this value as the critical micelle concentration (CMC) of **PEO-*b*-PAM** in aqueous solution. The nanostructures of polymer micelles before and after photodimerization were also visualized by AFM images with uniformly spherical micelles (S3 in Supporting Information). And taking both the micelle stability and the demands of the real-time UV-vis spectroscopy into consideration, the polymer concentration used in photodimerization were kept on 0.015 mg/mL.

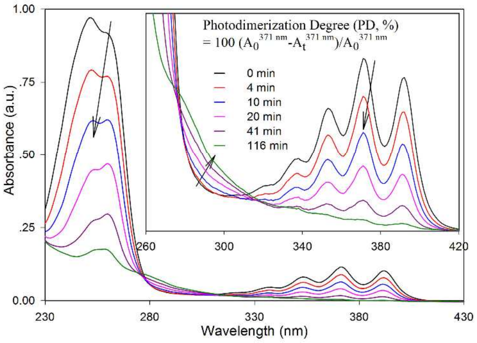


Figure 2. UV-vis spectra changes (0.015 mg/mL×1 mL) upon the 371±5 nm (1.20 mW/cm^2) light irradiation. Inset: enlarged view from 260 to 420 nm and the definition of photodimerization degree (PD) by comparing the absorption at 371 nm before and after irradiation.

In order to comprehensively investigate the photodimerization characteristics of anthracene pendants in polymer micelle, an adjustable double grating monochromator of Omni-λ1805i equipped with a broadband laser-driven light source of EQ-1500 LDLS™ and a set of six optical filters was assembled to afford the adjustable narrow band wavelength of light between 250-950 nm intervals. Under the used conditions, 1 mL of polymer micelle solution (0.015 mg/mL) was sealed in the fluorescence cuvette and photodimerization of anthracene pendants was performed directly on an optical bench at 25 °C while mild stirring. As designed, the anthracene micelle solution was first photodimerized with 371±5 nm (1.20 mW/cm^2) wavelength light, which corresponded to one of the characteristic absorbance bands of anthracene pendants in aqueous solution. As shown in Figure 2, the UV-vis spectrum before irradiation showed a broad absorption band around 260 nm and a series of vibrationally spaced absorption structures at 320, 338, 353, 371 and 392 nm (finger like absorption bands), which are typical for anthracenes.[9] During irradiation, accompanied with the weak ascending between 280-310 nm intervals, all the absorbance bands decreases significantly, strongly indicating the ongoing photodimerization of anthracene in the polymer micelle core.[9] And because of its linear degradation and higher signal-to-noise ratio, the absorption band intensity at 371 nm was used as the baseline to measure the time-dependent photodimerization changes, resulting in the definition of photodimerization degree (PD) by comparing the peak absorption at 371 nm.

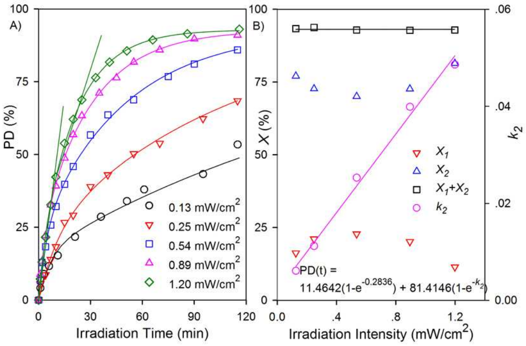


Figure 3. a) The time-dependent PD of anthracenes upon 371±5 nm light irradiation with different intensities. The solid curves are four parameter biexponential fits to eq 1. b) The intensity dependence of X_1, X_2, X_1+X_2 values according to the four parameters biexponential fitting, and the linear dependence of k_2 according to the one parameter biexponential fitting.

As shown in Figure 3a, when upon 371±5 nm light irradiations, the time-dependant PD values for anthracene pendants synchronously decreased with the lowering of irradiation intensities. And for 1.20 mW/cm^2 irradiation, it showed saturating behaviour, affording a linear quick increase in the initial stage (up to 40%), a relatively slow increase thereafter (from 40% to 70%), and finally levelled off above 90%. The time-dependences of these observed PD changes upon various irradiation intensities are fit reasonably with a biexponential equation:

$$\mathrm{PD}(t) = X_1(1-e^{-k_1 t}) + X_2(1-e^{-k_2 t}) \qquad (1)$$

where PD(t) corresponds to the time-dependent photodimerization degree, k_1 and k_2 are rate constants, X_1 and X_2 are the relative weighting fractions. To be emphasized, the sum of X_1 and X_2 determines the maximum photodimerization extent (PD_{max}) that the anthracene pendants could reach after long enough irradiation time. Figure 3b show the obtained fractions of X_1 and X_2 at different irradiation intensities, whose sum fluctuated weakly around 93% and afforded a good zero-order linear fit, indicating that PD_{max} of anthracenes upon 371±5 nm light irradiation is always intensity-independent. Thus, in order to better verify the intensity-dependence of the photodimerization kinetics, X_1 = 11.4642, k_1 = 0.2836 min^{-1} and X_2 = 81.4146 obtained from the biexponential fitting of 1.20 mW/cm^2 irradiation were used as constants to give an one parameter biexponential fit of eq 1 for another four intensity irradiations. As shown in Figure 3b, with these constraints, the obtained k_2 ranged from 0.0061 min^{-1} at 0.13 mW/cm^2 to 0.0486 min^{-1} at 1.20 mW/cm^2 and increased linearly as a function of 371±5 nm light intensity, implying the existence of two different populations of anthracene pendants, one that is insensitive to irradiation intensity and reacts with rate k_1 = 0.2836 min^{-1}, and another that is sensitive to intensity, corresponding to k_2.[11]

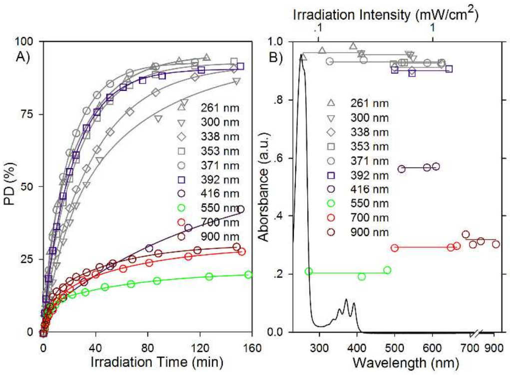


Figure 4. a) The time-dependence of PD upon selected narrow band light irradiations derived from the monochromator with the same slits. The solid curves are four parameter biexponential fits to eq 1. b) The UV-Vis-NIR absorbance spectrum of polymer micelles (0.015 mg/mL) and the zero-order intensity dependence of X_1+X_2 values for the selected light irradiations.

In order to better understand the photodimerization kinetics dependency of irradiation conditions, and according to the characteristic absorbance bands of anthracene pendants in aqueous solution, another five narrow band UV light of 261, 300, 338, 353, 392±5 nm and four Vis-NIR light of 416, 550, 700 and 900±5 nm were chosen as the irradiation light. As shown in Figure 4a, when irradiated by these various wavelength light from the double grating monochromator with the same slits (their irradiation intensities corresponding to the highest values in Figure 4b respectively), the obtained time dependences of PD are fit very well to the four parameter biexponential of eq 1, and all 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 Figure 4b are zero-order linear fits of X_1+X_2 values obtained by changing the irradiation intensities of the above selected light. All the X_1+X_2 values obtained by the UV light irradiations were above 90%, despite that there are huge gaps in light absorbency of the selected UV light according to the characteristic absorbance bands of anthracenes (see the curve line in Figure 4b). Even for the latter four Vis-NIR light irradiations, in which region anthracenes have nearly no absorptions, they still afforded considerable efficiencies with PD_{max} values of 55%, 35%, 25% and 32% for 416, 550, 700 and 900±5 nm light irradiations, respectively. Which can ascribe to the multi-photon effect. These results strongly give the facts that the photodimerization extent (PD_{max}) of anthracenes is always of favourable UV light than Vis-NIR light and independent to the intensities of a certain light irradiation.

To summarize, we have synthesized an amphiphilic block copolymer of **PEO-*b*-PAM** with anthracene pendants, which can afford the high local concentration and restricted mobility of anthracene pendants in the confined micelle core and thus facilitate the dimerization of anthracenes upon light irradiations. Most efforts have been dedicated to the photodimerization of anthracenes, but to our knowledge, our study is the first attempt to comprehensively describe it using various narrow band wavelength light in the UV-Vis-NIR region. The result shows that the photodimerization of anthracene pendants is of favourable UV light than the Vis-NIR light. And for a certain light irradiation, the dimerization extent that anthracenes can reach is always independent to light intensities, indicating that anthracenes can not afford the similar photodimerization efficiencies of UV light if simply strengthen the power of Vis-NIR light.

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Notes and references

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