PEG-Based Hydrogel Synthesis via the Photodimerization of Anthracene Groups

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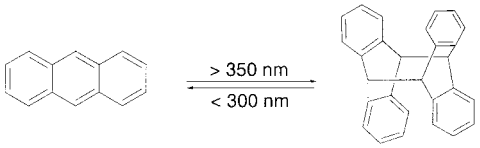
ABSTRACT: Photo-cross-linking has received a considerable attention for the design of intelligent materials in biochemical and biomedical applications. In this report, we describe the synthesis and properties of a novel photoreversible poly(ethylene glycol)- (PEG-) based hydrogel system. 9-Anthracenecarboxylic acid was used to modify the hydroxyl groups of an eight-armed PEG polymer (molecular weight 20 000) and the degree of substitution was determined to be 87.4%. The PEG−anthracene macromers (PEG−AN) exhibited high photosensitivity at wavelengths close to visible light (absorption maxima at 366 and 380 nm) and underwent rapid and reversible photo-cross-linking upon exposure to alternating wavelengths of irradiation (365/254 nm) in the absence of photoinitiators or catalysts. Changes in light exposure and wavelength of irradiation reversibly altered the physicochemical properties of the PEG−AN hydrogel, including swellability, absorption spectrum, and topography.

Introduction

Over the past decade, numerous studies are focused on the construction of novel polymeric networks by means of photo-cross-linking.[1] Photo-cross-linking exhibits special advantages over conventional physical or chemical methods of network formation: mild reaction conditions, minimum side-product formation, fast curing times, and spatial control of the polymerization reaction. The physicochemical properties of the photo-cross-linked polymer network can be easily modulated by adjusting the sequence of illumination; the swelling ability of photo-cross-linked hydrogels can be tailored by merely changing the irradiation time.[1,2] Photo-cross-linking reactions usually involve (a) the free radical polymerization of pendant acrylate or methacrylate groups along the polymeric backbone of hydrophilic polymers in the presence of an initiator or catalyst[3] or (b) the photodimerization of cinnamates attached as end groups in multiarmed polymers.[4]

We are interested in developing highly efficient photoresponsive materials with tunable properties. We envision these materials to have potential applications in developing optical switches, controlled delivery carriers or biosensors. Current photoinduced systems are associated with various shortcomings. For example, acrylate-based polymers, even though they demonstrate fast curing times, the rate of polymerization usually depends on the nature and concentration of potentially toxic initiators, the photopolymerization leads to irreversible cross-links, and the polymers are unstable for storage. On the other hand, cinnamates-based photo-cross-linking systems (e.g., photodimerization reactions) are intrinsically competed by *E*/*Z* isomerization, which greatly compromises the efficiency of photodimerization. Photosensitive groups such as coumarin,[5] stilbazolium,[6] thymine,[7] cinnamylidene,[1d,8] etc. have been used to prepare photo-cross-linked networks which exhibited superior photostability and photoefficiency but minimum reversibility. Andreopoulos et al.[1d,9] developed a photoswichable PEG-based hydrogel (PEG−cinnamylidene) and demonstrated that the physical properties (mesh size and swellability) of the hydrogel membrane were controlled in a predictable fashion by alternating the wavelength (>300/254 nm) and sequence of irradiation. The photoreversibility of the PEG−cinnamylidene hydrogel however was reported later to be strongly limited due to photoscissive light inefficiency, cinnamylidene photodegradation, and side polymerization reactions.[10] Our group has recently reported the synthesis of a photo-cross-linked poly(ethylene glycol)−nitrocinnamate (PEG−NC) hydrogel which demonstrates a photoscissile behavior upon shortwave UV irradiation.[11] The PEG−NC macromers exhibited fast gelation times and superior storage stability over their cinnamylidene and acrylate analogues.

Our continuous research effort is targeted toward the development of novel, highly photosensitive polymers that undergo rapid reversible transitions. In the present work, we report the synthesis of a novel PEG-based hydrogel based on the reversible photodimerization of the anthracene functionality. Anthracene and its derivatives undergo [4 + 4] dimerization upon longwave



UV irradiation (>350 nm).[12] The dimer can be restored

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to the original monomers upon exposure to shortwave UV light. This photochromism has been extensively applied to study many intermolecular and intramolecular processes.[13] The incorporation of anthracene and its derivatives within a polymer matrix is not a new topic.[14] For example, Horie and co-workers[14b,14c] utilized the anthracene functionality to produce photoemissive probes. Coursan and Desvergne[14d] reported the synthesis of anthracene modified polystyrene polymers that exhibited excellent photoreversibility. Despite these studies, the use of anthracene moieties as cross-linking sites to produce photoreversible hydrophilic biomaterials has rarely been reported.[15] Herein we modified a branched poly(ethylene glycol) polymer with 9-anthracenecarboxylic acid to obtain photoreactive poly(ethylene glycol)-anthracene macromers (PEG−AN). The PEG−AN macromers underwent reversible photo-cross-linking when exposed to alternating wavelengths of irradiations (365/254 nm).

Experimental Section

Materials. Poly(ethylene glycol) (b-PEG, MW = 20 000, eight arms) was purchased from Shearwater Polymers Inc. (Huntsville, AL). It was fully crushed and dried under high vacuum before use. All other chemicals and organic solvents were purchased from Sigma-Aldrich (St. Louis, MO) at their highest purity. The deionized water used was purified by a Modulab 2020 water purification system (Continental Water Systems Corp., San Antonio, TX).

Synthesis of 9-Anthracenecarbonyl Chloride. A 15 mL aliquot of $SOCl_2$ (0.21 mol) was placed in a N_2-purged flask followed by the addition of 3.0 g of 9-anthracenecarboxylic acid (13.5 mmol). One drop of anhydrous DMF was added to start the reaction. After 5 min, the solid dissolved completely. Temperature was increased to 60 °C, and the reaction mixture was kept overnight under stirring. Upon reaction completion, unreacted $SOCl_2$ was evaporated under reduced pressure. The final product (3.0 g, 93% yield) was used without further characterization.

Synthesis of the Anthracene-Modified PEG Macromer (PEG−AN). The synthesis was achieved by reacting PEG with 9-anthracenecarbonyl chloride. In a typical experiment, 1.4 g (0.56 mmol OH's) of an eight-branched PEG was dissolved in 10 mL of anhydrous THF. 9-Anthracenecarbonyl chloride (1.35 g, 5.6 mmol) was dissolved in 10 mL of THF and then added to the PEG solution. The mixture reacted for 20 h at 60 °C. N_2 atmosphere was used at all times. After the reaction was over, the solution was concentrated by evaporation, and 20 mL of water was added to the residue. The mixture was filtered and lyophilized in a vacuum. The dried solid was washed with ether two times and dried in a vacuum. The final yield of the PEG−AN was 0.43 g (28%). ^{1}H NMR showed that the hydroxyl groups were converted to ester to the extent of 87.4%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.53 (s, 7H), 8.12 (d, 14H), 8.02 (d, 14H), 7.51 (m, 28H), 4.78 (d, 14H) and 3.96−3.39 (m, 1802H). FT-IR (NaCl, film): 772.2, 945.9, 1061.1, 1113.7, 1147.8, 1219.2, 1241.9, 1280.5, 1344.9, 1359.7, 1466.8, 1721.4 (C═O), 2883.2 cm^{-1}. UV−vis (in water): $\epsilon_{365\,nm} = 3.61 \times 10^4$ L·mol^{-1}·cm^{-1}. $\epsilon_{254\,nm} = 6.83 \times 10^5$ L·mol^{-1}·cm^{-1}.

Methods and Instrumentation. A concentrated 10% w/v aqueous solution of PEG−AN macromer was used for the photochemical studies. Unless indicated otherwise, the sample was prepared by spreading drops of the aqueous solution to form a film of 0.1 mm thickness between two quartz slides (detachable quartz cells, Hellma Worldwide, Inc., USA, Plainview, NY).

Photo-cross-linking was performed using a 4-W 365-nm UV lamp and photocleavage was performed using a 4-W 254-nm UV lamp (Spectronics Corp., Westbury, NY). In either case, the lamp was placed above the sample at a distance of 3 cm.

In the swelling experiments, a 10% w/v aqueous solution of PEG−AN in a detachable cell (one slide is precoated with SigmaCote to avoid sample adhering) was treated with light irradiation (10 min of 365-nm light and 5 min of 254-nm light, respectively) and then washed with water to remove any uncross-linked PEG−AN. The gel was allowed to equilibrate in water for 1 h. Following equilibration the hydrogel was removed from water and the exposed surface was carefully blotted with a Kimwipe (Aldrich, St. Louis, MO). The degree of swelling (DS) was determined from $(W_s - W_d)/W_d$, where W_s is the weight of the swollen gel following 1 h equilibrium in water and W_d is the weight of the dry gel (air-dried for 24 h). All measurements were performed in triplicates and the standard deviation is reported (average ± SD).

UV−vis spectra of PEG−AN films were recorded on a Lambda 900 UV/vis spectrometer (Perkin-Elmer, Inc., Shelton, CT). For the UV−vis measurement of solid-state PEG−AN, the sample was prepared by spreading a dilute dichloromethane solution of PEG−AN (1 mg/mL) on a quartz slide. After solvent evaporation, a thin solid PEG−AN film was left on the quartz slide.

^{1}H NMR was measured on a Bruker 300 MHz instrument. A 5 mm quartz NMR tube was purchased from Wilmad-Glass, Inc., Buena, NJ. PEG−AN solution in D_2O (5% w/v) was placed in the quartz tube, and the sample was irradiated with high power UV lamps (100-W 365 nm and 50-W 254 nm, both from UVP, Inc., Upland, CA).

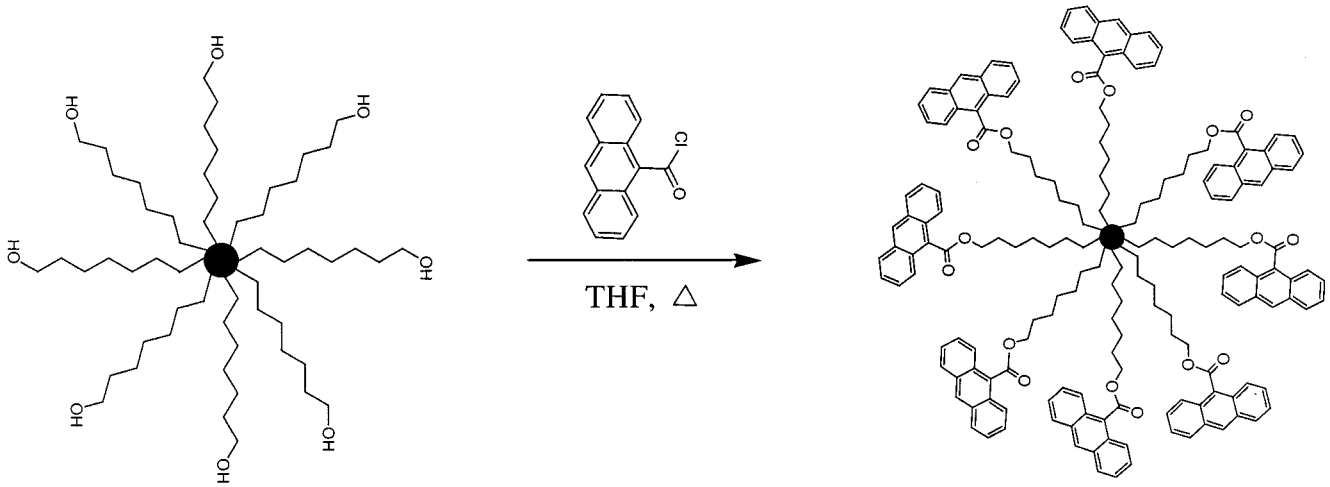
Environmental scanning electron microscopy (ESEM) images were recorded with a FeiCo Phillips-Electroscan FEG XL-30 field emission gun ESEM microscope. A drop of aqueous PEG−AN solution (10% w/v) was placed on a specimen holder and exposed to the indicated irradiation sequence. No additional sample treatment was performed, thus avoiding introduction of possible coating artifacts. All the micrographs were obtained in the environmental wet mode and collected with a large-field gaseous secondary electron (GSE) detector. As a protective atmosphere and imaging gas, a water vapor pressure of 0.9 Torr was present in the chamber at all times. To further prevent the sample from dehydration, we kept water vapor in the saturated condition within the microscope chamber by cooling the sample down using the Pertiler cold stage. The sample was kept at a working distance of 7.7 mm from the large field GSE detector. Images were acquired at a magnification of 1000× and optimized for maximum sharpness and contrast, using the charge contrasting technique.

Atomic force microscopy (AFM) images were taken with a PicoSPM microscope (Molecular Imaging Inc., Phoenix, AZ). Samples of 10% w/v aqueous solution of PEG−AN were spin-coated on a mica substrate to form a thin film. The film was then submitted to UV exposure. Following irradiation, the sample was scanned in air using the constant force mode with microfabricated Si_3N_4 tips attached to rectangular beams (spring rate 0.09 N/m). The setting point was adjusted to minimize the force between the tip and the sample. This force was maintained constant between 1 and 5 nN.

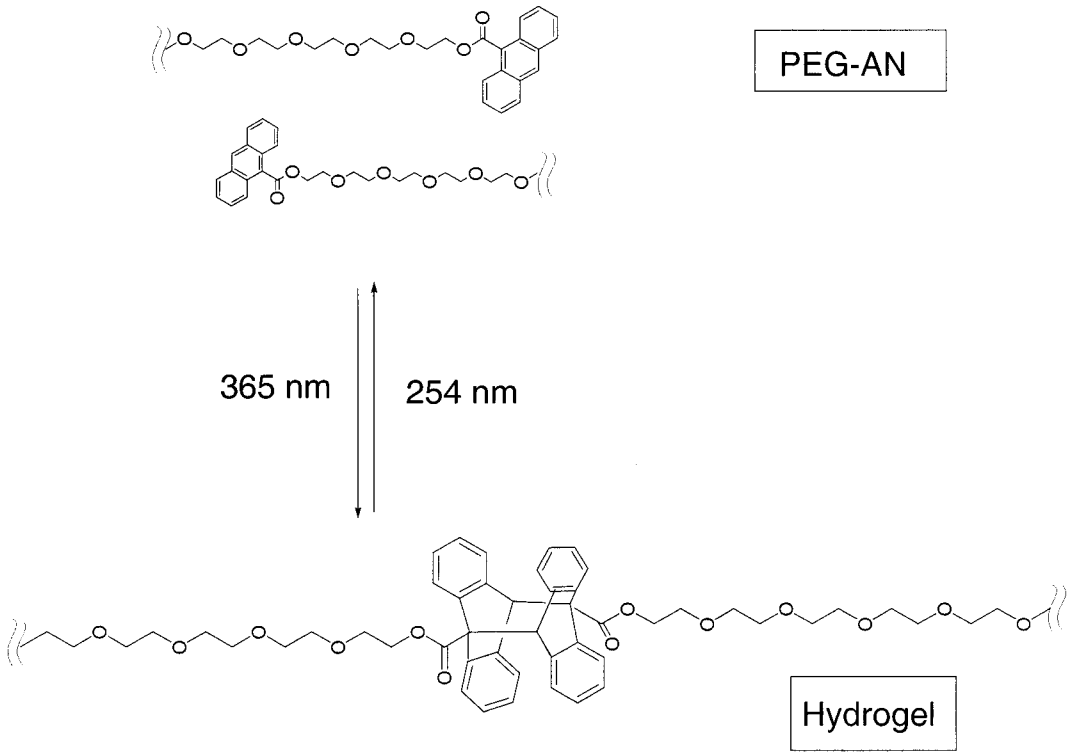
Results and Discussion

Synthesis of Poly(ethylene glycol)−Anthracene (PEG−AN). The synthesis of the photosensitive PEG macromer (PEG−AN) is diagrammatically represented in Scheme 1. Commonly, esterification reactions are assisted by HCl scavengers such as tertiary amines. However, the esterification of 9-anthracenecarboxylic acid is carried out at efficient yields only in the absence of bases.[16] In the presence of triethylamine or pyridine, only 20% hydroxyl groups in the PEG was acylated. In contrast, in the absence of amines, the degree of modification was greatly improved, i.e., by 87%. In addition, coupling reagents such as diisopropylcarbodiimide, 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide, bis(2-oxo-3-oxazolidinyl)-phosphinic chloride, etc, were also used to catalyze the reaction between PEG and

Scheme 1. Synthesis of PEG−Anthracene Macromer (PEG−AN)



Scheme 2. Photo-Cross-Linking/Photoscission of PEG−AN Macromers



9-anthracenecarboxylic acid, but none of these reactions were successful. The reason is probably due to the steric hindrance of two adjacent α-protons and the poor solubility of the reactive intermediates in the reaction system.

Gelation by Photo-Cross-Linking. The synthesized PEG−AN macromer underwent photo-cross-linking to form a three-dimensional hydrogel network due to the [4 + 4] dimerization of anthracene groups (Scheme 2). A solution of PEG−AN macromer (10% w/v in water) was cast within a thin quartz cell (0.1 mm thick). The macromer solution underwent rapid photo-cross-linking upon irradiation at 365 nm for 1 min and formed a transparent water-insoluble gel sheet. The gelation speed was comparable to that of the poly(ethylene glycol)−nitrocinnamate (PEG−NC) macromer that our group has recently demonstrated[11] and is much faster than those for previously reported hydrophilic photosensitive systems.[1d,15] The main reasons for such fast photogelation are summarized as follows: (i) High modification of PEG with anthracene groups provides sufficient photosensitive groups for cross-linking. In our study, we found that 20% modified PEG of the same type did not induce gelation even after hours of irradiation. (ii) The flexibility of the PEG polymer chains allows for optimal aligning of the anthracene groups to undergo efficient photodimerization reactions.[17] (iii) The hydrophobic nature of the anthracene groups of the PEG−AN macromers in an aqueous solution favors their aggregation in the polymer matrix, which is a prerequisite for [4 + 4] dimerization. Similar hydrophobic effect was also observed in previous studies.[18]

The degree of swelling (DS) of the PEG−AN gel was significantly changed following exposure to alternating wavelengths of irradiation (Figure 1). After cross-linking with 365-nm irradiation for 5 min, DS was determined to be 10.5 ± 2.1. However, if 254-nm irradiation (5 min) was subsequently applied, the DS increased to 17.0 ±

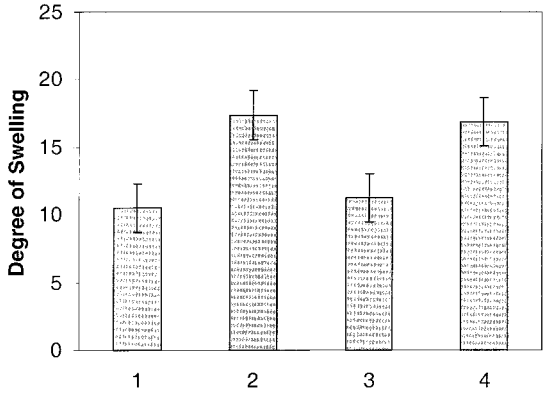


Figure 1. Degrees of swelling of PEG−AN hydrogel at different irradiation stages: (1) 365 nm (15 min), (2) 365 nm (15 min) + 254 nm (5 min), (3) 365 nm (15 min) + 254 nm (5 min) + 365 nm (15 min), and (4) 365 nm (15 min) + 254 nm (5 min) + 365 nm (15 min) + 254 nm (5 min). The degree of swelling was calculated from the equation $(W_s - W_d)/W_d$, where W_s is the weight of the swollen gel following 1 h of equilibration in H_2O and W_d is the weight of the dry gel (air-dried for 24 h at room temperature).

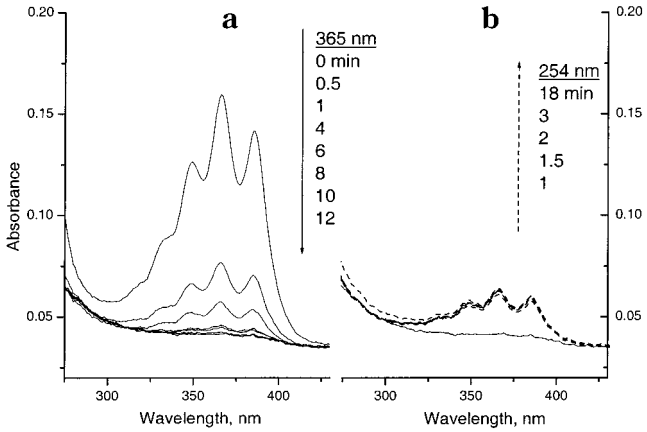


Figure 2. UV−vis spectra of an aqueous PEG−AN solution as a function of irradiation conditions. The initial concentration of PEG−AN macromers is 10% w/v in H_2O. Cuvette path = 0.1 mm. The PEG−AN solution was first exposed to 365-nm irradiation (0, 0.5, 1, 4, 6, 8, 10, 12 min (a)) followed by 254-nm irradiation (1, 1.5, 2, 3, 18 min (b)).

2.2. Continuous irradiation at 365 and/or 254 nm changed the DS in a similar way. These results indicate that different irradiation sequences have an enormous impact on the backbone structure of the formed hydrogel. The DS is strongly related to the mesh size of the polymer network; as the mesh size increases, the DS of the PEG−AN gel also increases. Here, 365-nm light led to the formation of a tightly interconnected three-dimensional gel network with a small mesh size, while 254-nm UV irradiation significantly photocleaved the gel network, thus increasing its mesh size and degree of swelling.

UV−Vis Absorption. The photochemical process of PEG−AN can be conveniently monitored by its electronic absorption spectroscopy. Figure 2 shows the UV−vis absorption of a 10% w/v aqueous solution of PEG−AN (optical path length = 0.1 mm). Upon irradiation with 365-nm light, the absorption maximum at 366 nm decreased with the irradiation time, indicating the undergoing [4 + 4] dimerization of anthracene groups in the polymer. After 12 min of irradiation, there was no further decrease in the spectral intensity that suggested the complete conversion of anthracene group

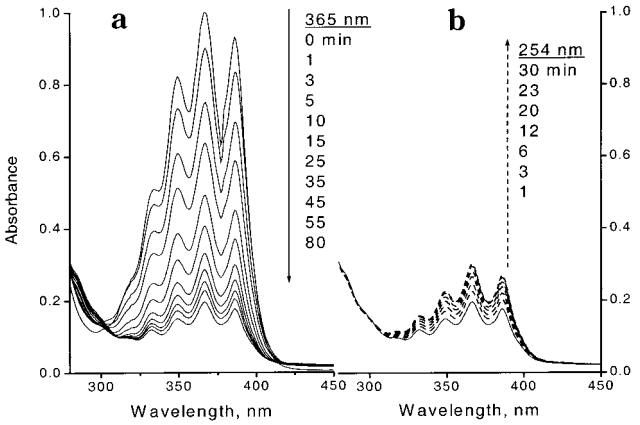


Figure 3. UV−vis spectra of a PEG−AN solid film as a function of irradiation conditions. The polymer film was first exposed to 365-nm irradiation (0, 1, 3, 5, 10, 15, 25, 35, 45, 55, 80 min (a)) followed by 254-nm irradiation (1, 3, 6, 12, 20, 23, 30 min (b)).

to its dimers. The PEG−AN gel was then exposed to 254-nm light. Very quickly the absorption increased due to the regeneration of anthracene groups. At 3 min of irradiation, the spectral intensity reached its maximum. Further irradiation with 254 nm changed the spectra at a negligible level. This indicated that a photostationary state was reached in a short period of time.

The effects of irradiation on the UV−vis absorption spectra of PEG−AN were also determined in the form of solid thin films (Figure 3). The results showed a big difference from the aqueous solution. Upon irradiation at 365 nm, the rate of decrease of the absorption intensity is much slower than that in the solution phase. For the aqueous PEG−AN solution (10% w/v), after 12 min of 365-nm irradiation the absorption reached its minimum. However, for the solid sample, even after 15 min of irradiation (365 nm), the absorption maximum at 366 nm is still as high as 40% of the original value. The photo-cross-linking reaction is not completed even after 80 min of irradiation. As aforementioned, PEG exhibits its full flexibility in aqueous solution that allows the optimal alignment of the anthracene groups for photodimerization. On the other hand, for the solid sample of PEG−AN, the solvent-induced advantage does not exist, and therefore, it takes a longer time of irradiation to achieve complete gelation. The photoscission process of the solid PEG−AN film induced by 254-nm irradiation also demonstrates a slower kinetic than the dissociation process of PEG−AN in aqueous solution possibly due to the stability of the 4,4′-photocycloadduct under different media (Figure 3b). Without the polar aqueous environment, the 4,4′- photocycloadduct in the solid state becomes more stable to photoscission.

NMR Studies. ^{1}H NMR spectroscopy was used to delineate the effect of UV wavelength on the gel structure. There are two characteristic regions in the ^{1}H NMR spectrum of PEG−AN, one representing the PEG backbone chain protons (3−5 ppm) and the other corresponding to the anthracene moiety (7−9 ppm) (Figure 4a). The 365-nm irradiation has no obvious effect on the PEG backbone proton peaks (spectral region not shown). On the other hand, however, 365-nm exposure causes the peaks of the anthracene protons to decrease in intensity and their chemical shifts to move to a lower field (Figure 4b). These changes are attributed to the disappearance of the anthracene groups and the formation of [4 + 4] dimers. The

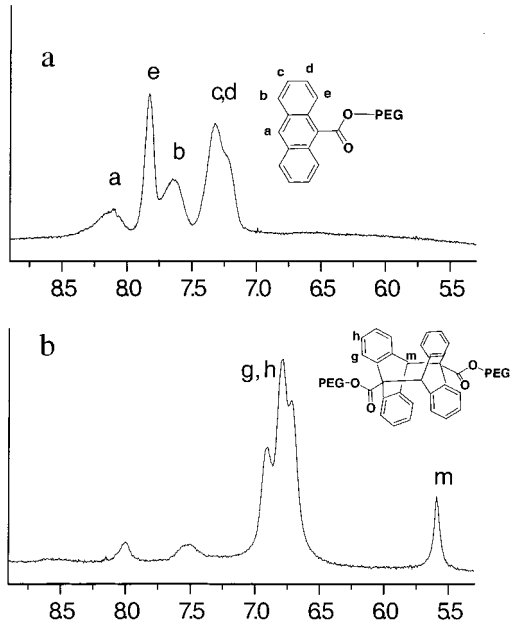
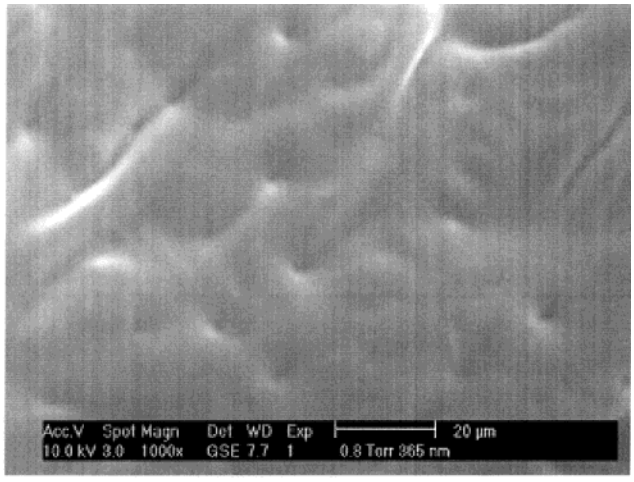


Figure 4. Changes in ^{1}H NMR spectra of PEG−AN (in D_2O) at different irradiation conditions: (a) no irradiation; (b) 365 nm (30 min). Lamp power: 365 nm, 100 W; 254 nm, 50 W.

appearance of new proton peaks at $\delta = 6.8$ and 5.6, further validates the formation of 4,4′-cycloadduct caused by photo-cross-linking. Further exposure of the PEG−AN gel to 254-nm UV does not change the basic shape of Figure 4b but causes the area under the anthracene peaks to increase with respect to the area of the 4,4′-cycloadduct, illustrating the partial photoscission of the 4,4′-cycloadducts to monomers.

Environmental Scanning Electron Microscopy (ESEM). Microscopic techniques were utilized to provide a direct method of monitoring the changes on the topography of the PEG−AN surface caused by photo-cross-linking and photocleavage. Previously, we have shown that ESEM and field emission SEM could be used to image fragile structures, such as Langmuir−Blodgett films, polymeric self-assembled films, protein coatings, and hydrogels.[11,19] Parts a−c of Figure 5 present typical topographies of the hydrogel at three different irradiation stages.

PEG−AN gel (prepared by 10 min of 365-nm irradiation, Figure 5a) shows an essentially smooth surface, with randomly distributed pores of less than 1 μm in size. These pores are probably caused by a process of heterogeneous congregation and redistribution during light irradiation (see the AFM images in next section). After the gel sample was further irradiated with 254-nm UV light (5 min), the topography of the gel surface was significantly altered from smooth to coarse (Figure 5b). The smooth surface was cleaved into many divided domains with size of 10 μm. These micrographic changes strongly demonstrated the photoscissive behavior of 254-nm irradiation. Figure 5c depicts the topography of a PEG−AN hydrogel being treated with alternating wavelengths of irradiation (365 nm + 254 nm + 365 nm, 10 min of 365 nm, and 5 min of 254 nm, respectively). The gel surface was smooth in nature and only a minimum amount of coarseness was detected. It highly resembles the topography of the PEG−AN gel, which was prepared under only 365-nm irradiation. Therefore, the final dose of 365 nm exposure restored the topography of the photocleaved hydrogel. These



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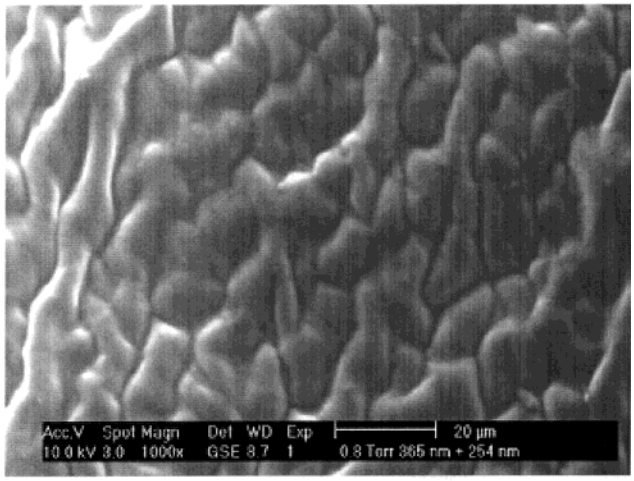

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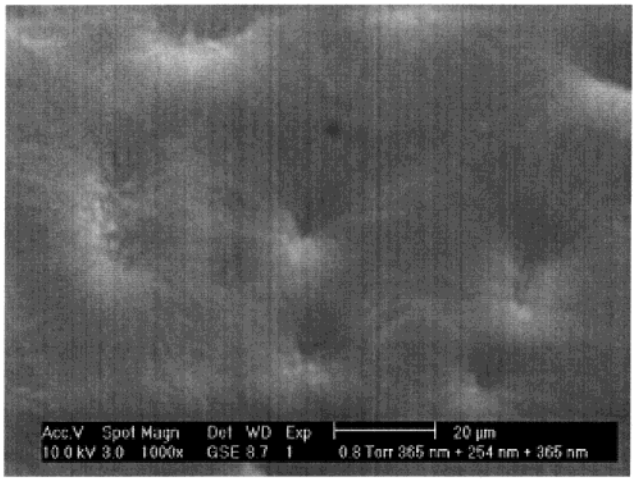

c

Figure 5. ESEM micrographs of PEG−AN hydrogel under different irradiation conditions: (a) 365 nm (10 min), (b) 365 nm (10 min) + 254 nm (5 min), and (c) 365 nm (10 min) + 254 nm (5 min) + 365 nm (10 min). ESEM conditions: wet mode, 0.9 Torr of H_2O vapor, and gaseous secondary electron (GSE) image.

ESEM images clearly demonstrate that the wavelength of irradiation (365/254 nm) can significantly alter the physical properties of the PEG−AN gel in a periodic manner.

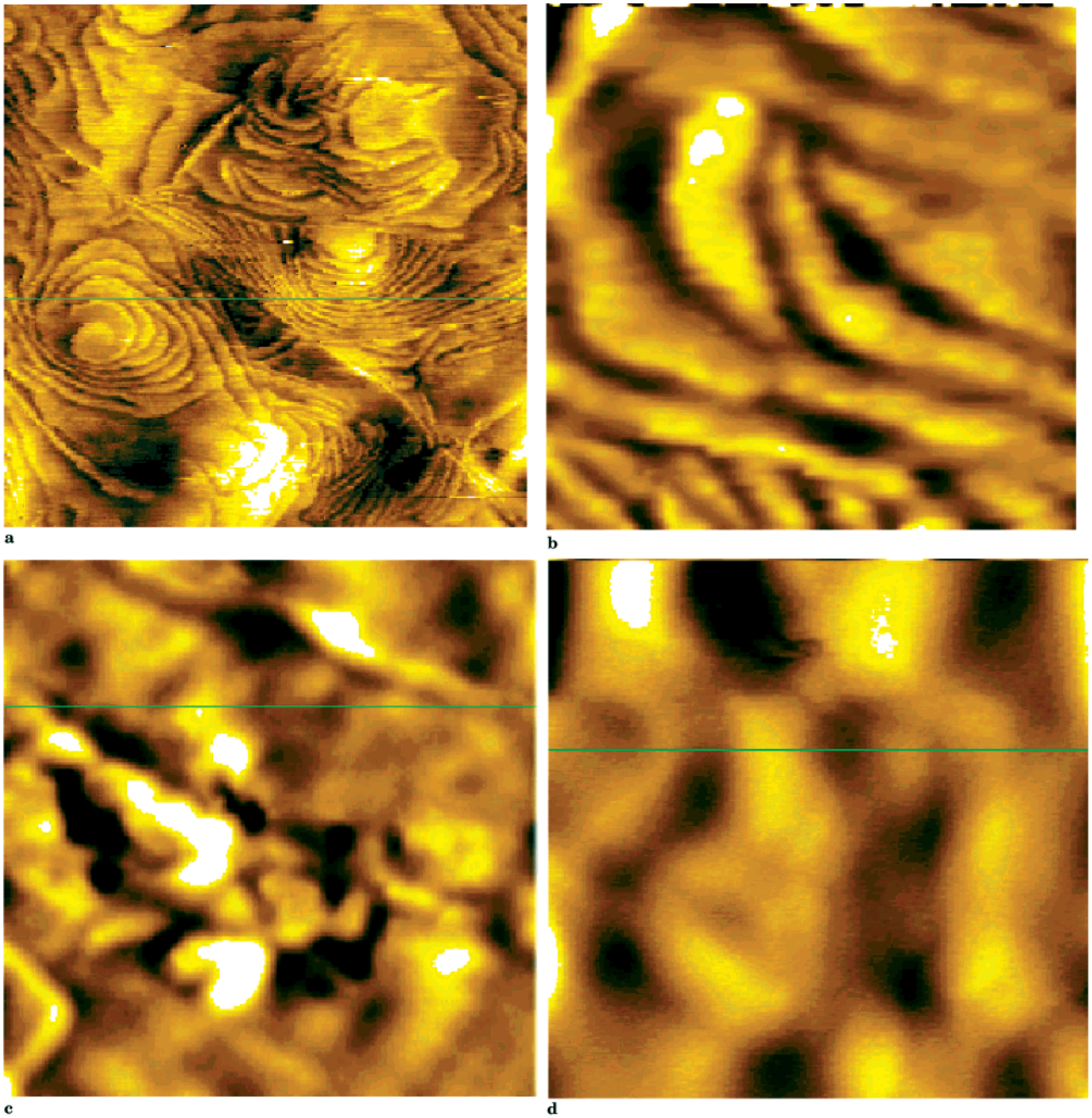

Figure 6. AFM images of PEG−AN hydrogel. (a) Scan size: 3 × 3 μm. Scan rate: 2.8 Hz. (b) Scan size: 190 × 190 nm. Scan rate: 3 Hz. 365 nm (10 min). (c) Scan size: 3 × 3 μm. Scan rate: 2.8 Hz. (d) Scan size: 190 × 190 nm. scan rate: 3 Hz. 365 nm (10 min) + 254 nm (5 min).

Atomic Force Microscopy (AFM). AFM was used to investigate surface structure of the PEG−AN hydrogel at a nanometric scale. Parts a and b of Figure 6 represent images of the surface of a PEG−AN gel prepared under 365-nm irradiation (10 min) at different scan sizes. Both images portray a heterogeneous orientation of microscopic structures aligned in two domains: flat layers and vertical edges. Polymer molecules aggregate into many stretching, bow-shaped islets separated by gaps with an average size of 15 nm.

Exposure of the PEG−AN gel to 254-nm light (5 min) caused a clear change on the topography of the gel surface as is shown in Figure 6, parts c and d. The structure of the gel surface now appears cracked and rough, the polymeric aggregates become smaller and more irregular, and the gaps between the irregular islets become wider (20 nm). Both photocleaved images, compared to the photo-cross-linked ones (Figure 6a,b), strongly indicate that 254-nm irradiation appreciably breaks the microscopic structure of the PEG−AN gel surface.

PEG−AN Hydrogel Reversibility. The reversibility of the hydrogel was illustrated by monitoring the UV−vis absorption spectrum of PEG−AN gels as a function of alternating wavelengths of irradiation (Figure 7). Following an initial absorbance decrease during the first photoreversible cycle (365/254 nm), photodimerization and photoscisision proceed for more than 10 cycles without additional losses in the photoreversibility efficiency, indicating that wavelength of irradiation can be used as a trigger to predictably alter the physicochemical properties of these gels. We have shown that 254-nm irradiation reverted the process only at a degree of 20%, instead of a complete sol−gel−sol process.

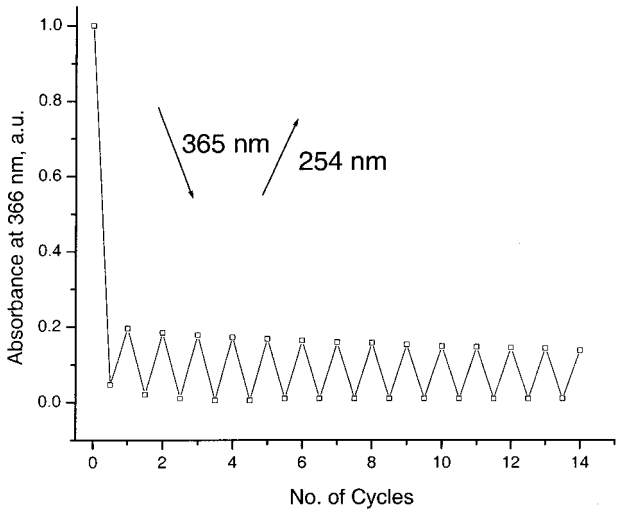

Figure 7. Number of reversible cycles of PEG−AN hydrogel monitored by UV−vis spectroscopy at 366 nm. An aqueous solution of PEG−AN (10% w/v) was exposed to alternating wavelengths of irradiation (365 nm for 10 min; 254 nm for 5 min.

Interestingly, studies by Coursan and Desvergne[14d] demonstrated that anthracene-modified polystyrene polymers underwent reversible transformations with minimum loss in photoreversibility efficiency. On their study, ω-hydroxy-telechelic polystyrene was derivatized with an anthracene moiety lacking a carbonyl functionality, namely 9-chloromethylanthracene. It was suggested that the presence of the carbonyl functionality may interfere with the photoreversible process. In subsequent experiments, we also synthesized highly modified PEG with anthracene groups through an ether linkage. However, the photoreversible efficiency did not change in comparison to the PEG−AN macromers. From a practical standpoint, the partial reversibility is still a valuable attribute; i.e., light can be used as a trigger to alter the physicochemical properties in a continuous and reversible manner, while not changing the gel nature of the system.

Conclusion

In this study, we have synthesized a highly modified PEG−AN macromer, which undergoes rapid photogelation in the absence of initiators or catalysts and demonstrates a photoreversible behavior. Physicochemical properties such as swellability, UV−vis absorption, and topography were all controlled by alternating the irradiation wavelength (365 and 254 nm). The reversible behavior of the PEG−AN gel provides a unique method of fine-tuning the gel's properties in a stimuli-responsive manner. We envision potential applications of such photoresponsive gels in photorecording as light switch materials and in biomedical engineering as controlled delivery vehicles.

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References and Notes

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