Electronic Supplementary Information

Coumarin Imparts Repeated Photochemical Remendability to Polyurethane

Jun Ling,[a] Min Zhi Rong,*[b] Ming Qiu Zhang*[b]
[a]Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou, 510275, P. R. China
[b]Materials Science Institute, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, P. R. China

Tab. S1 Glass transition temperatures of THHPEG400 before and after 350 nm UV irradiation determined by DSC

Irradiation time with 350 nm UV light (min)	T_g of the soft segments (°C)	T_g of the hard segments (°C)
0	-19.6	58.6*
15	-13.2	47.4*
30	-12.2	46.5*
45	-9.5	43.3
60	-12.2	35.6
75	-7.7	38.6
90	-7.1	41.2

*The values are the peak temperatures of the broad endotherms attributed to hard segments.

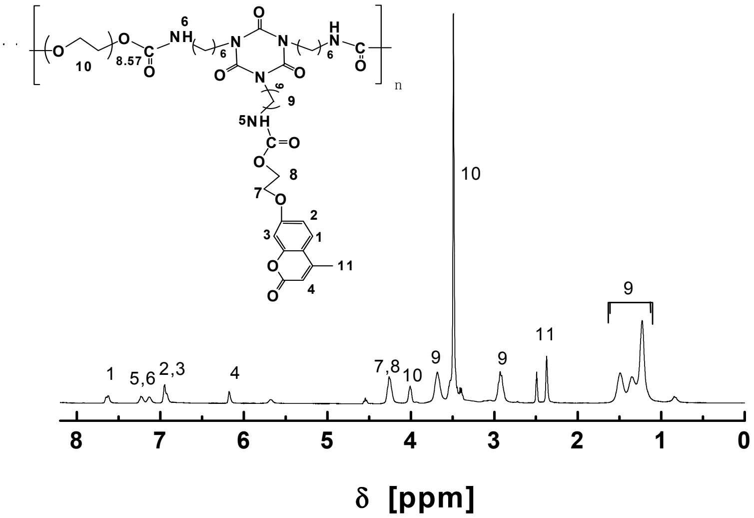


Fig. S1 ^{1}H NMR spectrum of THHPEG400 in DMSO-d_6.

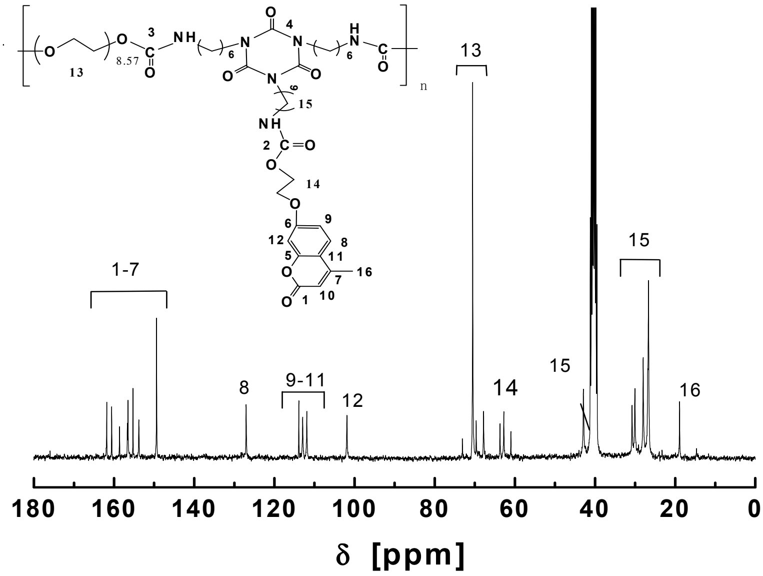


Fig. S2 ^{13}C NMR spectrum of THHPEG400 in DMSO-d_6.

After bromoethanol modification, reactivity of hydroxyl of HEOMC was greatly improved. It can easily react with NCO groups of tri-HDI. As show in ^{1}H NMR spectrum of THHPEG400 (**Fig. S1**), the aliphatic hydroxyl of HEOMC around 4.91 ppm is absent, whereas new peaks attributed to N-H proton of carbamate group (-O-(C=O)-NH-) are observed at 7.11-7.21 ppm (assigned as "5" and "6"). Moreover, the peaks of the main backbone of HEOMC are observed, such as that for methyl protons at 2.38 ppm and the overlapped signals of methylene protons at 4.26 ppm, as well as the peaks of protons of benzopyrone ring at 6.17, 6.95 and 7.62 ppm. The peaks at lower δ value regime (1.23-1.49 ppm) are attributed to methylene protons of tri-HDI, while some of them adjacent to carbamate group give peaks at higher δ regime (2.93 and 3.68 ppm). The methylenes of PEG400 are equivalent and show two peaks at 3.49 and 4.01 ppm. Accordingly, we can calculate the composition of THHPEG400. Using area integration of the peak at 2.93 ppm that represents 6H ("9") of tri-HDI, peak at 2.38 ppm of 3H ("11") of HEOMC, and peaks at 3.49 and 4.01 ppm for 34.28H ("10") of PEG400 per unit, it is known that the molar composition of THHPEG400 is tri-HDI : HEOMC : PEG = 1 : 1.1 : 0.84, which is very close to what we expect (i.e. 1 : 1.1 : 0.9).

In ^{13}C NMR spectrum of THHPEG400 (**Fig. S2**), the peaks at 149.39-161.83 ppm are attributed to carbonyl groups of carbamate, benzopyrone and isocyanurate rings, and carbon atoms of benzene connected to oxygen. The characteristic peaks of carbon atoms of PEG400 appear at 67.81-70.03 ppm, and those of tir-HDI peaks are perceived at 26.65-42.90 ppm.

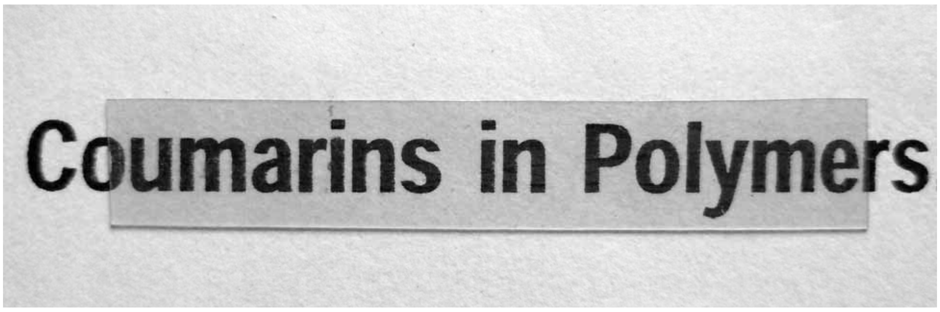


Fig. S3 Transparent appearance of crosslinked THHPEG400 film (200 μm thick), which was exposed to 350 nm UV light for 90 min. The film was made by solution casting (0.25 g THHPEG400 in 1 ml DMF), in which the solvent was removed at 80 ºC under vacuum.

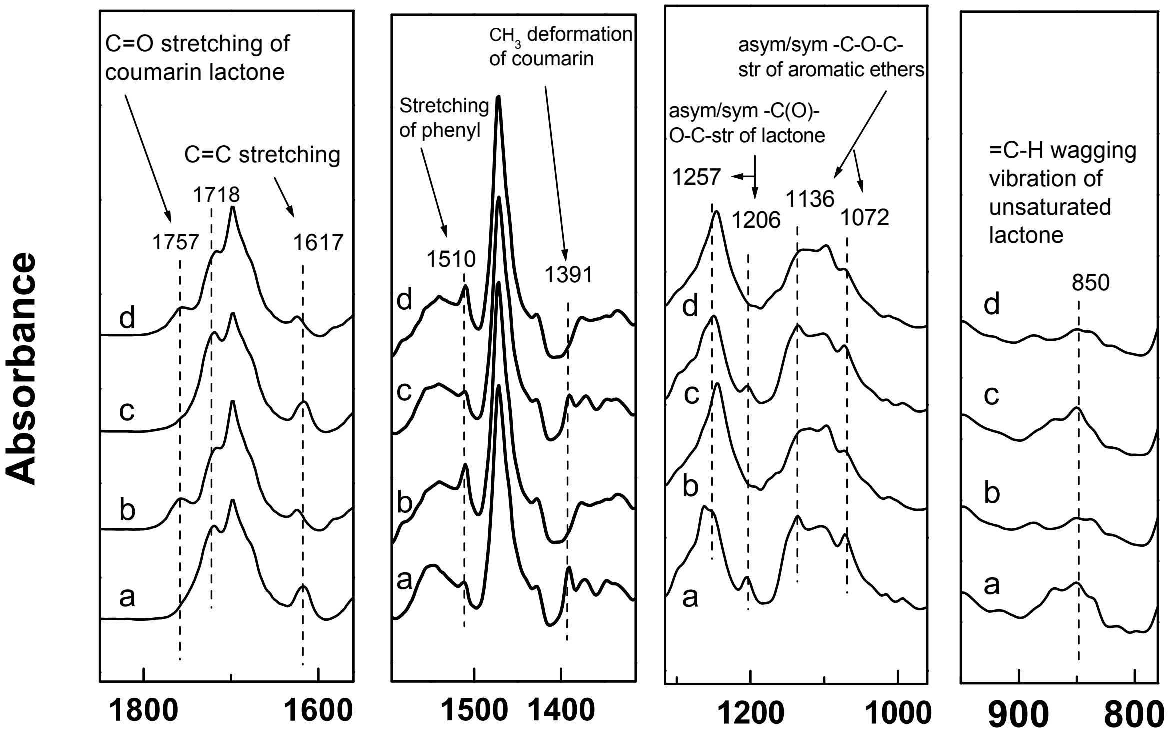


Fig. S4 FTIR spectra of THHPEG400 film (a) before photodimerization; (b) after photodimerization due to irradiation with 350 nm UV light for 90 min; (c) after photocleavage due to irradiation with 254 nm UV light for 1 min; and (d) after the second photodimerization due to irradiation with 350 nm UV light for 90 min. (*Prior to photodimerization, the bands of lactone C=O at 1718 cm^{-1} (overlapping the C=O absorption of PU main chain) and C=C at 1617 cm^{-1} (overlapping the absorption of phenyl backbone) are observed (**Fig. S4a**). Upon irradiation with 350 nm UV light for 90 min (**Fig. S4b**), the double bonds of coumarin lactone are crosslinked with each other, so that the carbonyl absorption shifts from 1718 to 1757 cm^{-1} due to the lack of* *conjugation of the double bonds. Meanwhile, the double bond absorption decreases and shifts from 1617 to 1624 cm^{-1}, which is mainly contributed by the stretching of phenyl backbone. Moreover, another stretching absorption of phenyl backbone at 1510 cm^{-1} also increases. As for the absorption of methyl that is connected to C=C of lactone, it shifts from 1391 to 1376 cm^{-1}, further evidencing coumarin dimerization. In addition, the asymmetric –C(O)-O-C- stretching vibration of coumarin at 1257 cm^{-1} shifts to 1245 cm^{-1}, and it's symmetric stretching at 1206 cm^{-1} disappears. The absorptions of asymmetric/symmetric ph-O-C- stretching vibration at 1136 and 1072 cm^{-1} and =C-H wagging vibration of unsaturated lactone at 850 cm^{-1} are reduced. All these changes are attributed to the loss of the conjugation of the double bond, and can be easily recovered by irradiation with 254 nm UV light (**Fig. S4c**). Further exposure to 350 nm UV light can result in dimerization again (**Fig. S4d**). The data reveal that photodimerization and photocleavage of coumarin moieties are reversible in the polymer.*)

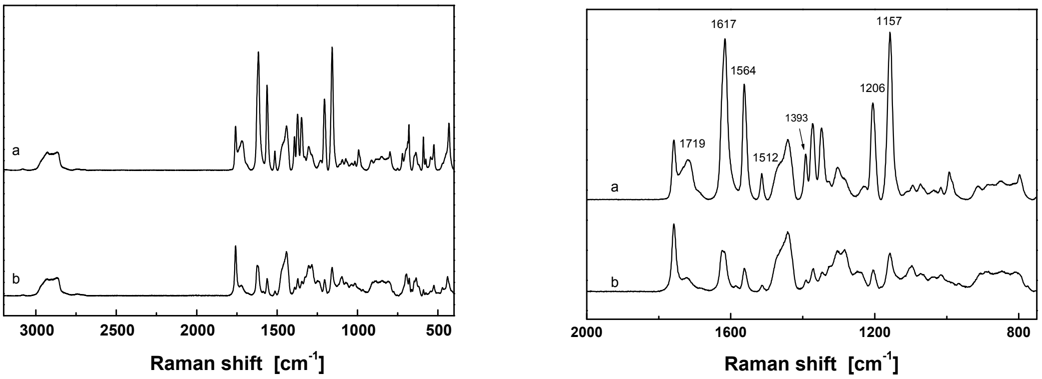
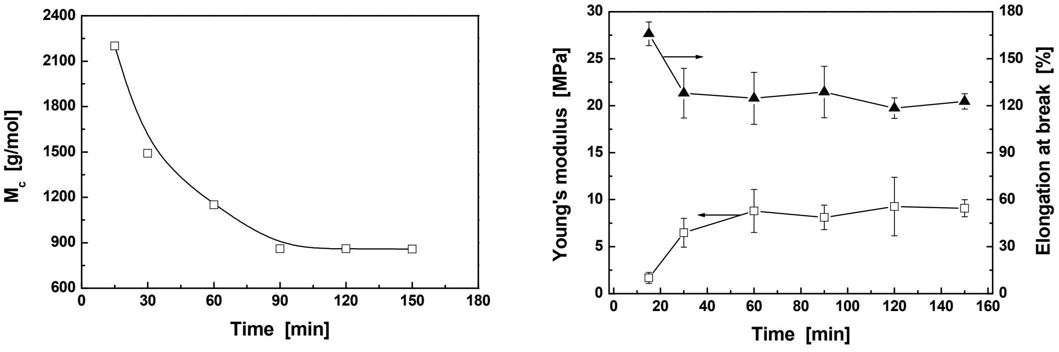


Fig. S5 Raman spectra of THHPEG400 (a) before photodimerization; and (b) after photodimerization due to irradiation with 350 nm UV light for 90 min. (*FTIR and Raman techniques are complementary. Some absorption bands that are weak at IR spectrum become strong at Raman spectrum, and vice versa. Like the C=O of lactone absorption band at 1719 cm^{-1}, it gives strong absorption at IR spectrum but turns weak at Raman spectrum. On the contrary, the weak C=C peak at 1617 cm^{-1} at IR spectrum becomes much stronger at Raman spectrum (cf. **Fig. S4** and **Fig. S5**). Additionally, the weak absorptions at IR spectrum (**Fig. S4**), including the peaks of phenyl backbone at 1564 and 1512 cm^{-1}, the asymmetric/symmetric deformation vibrations of -CH$_3$ at 1393 and 1378 cm^{-1}, symmetric –C(O)-O-C- stretching vibrations of coumarin at 1206 cm^{-1}, and symmetric ph-O-C- stretching vibrations at 1157 cm^{-1}, are easily detected at Raman spectrum (**Fig. S5**). Upon irradiation of 350 nm UV light, all the aforesaid absorption bands significantly decrease. The results also verify the effect of photodimerization.*)



(a) (b)

Fig. S6 (a) Average molecular weight between crosslinks, M_c, and (b) Young's modulus and elongation at break of THHPEG400 film (~200 μm thick) irradiated with 350 nm UV light for different times. *The data of M_c were determined by swelling method using 1,4-dioxane as the solvent (refer to: G. C. Zhu, G. Y. Wang, C. P. Hu, Effect of crosslink density on the structures and properties of aliphatic polyurethane elastomer, Acta Polymerica Sinica, 2011, (3), 274-280).*

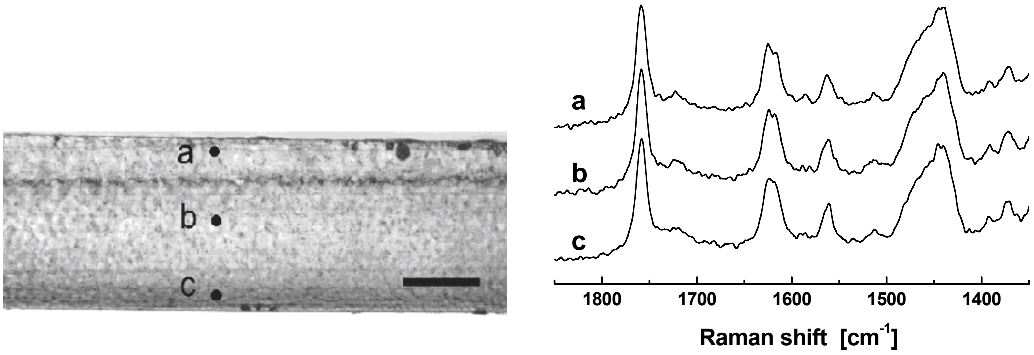


Fig. S7 Homogeneity analysis of coumarin moieties in THHPEG400 film (~200 μm thick) irradiated with 350 nm UV light for 90 min. Left: cross-sectional view of the film. The scale bar represents 100 μm in length. Right: Raman spectra collected from different sites on the film cross-section. The peak area ratios of ν(C=C) to ν(CH_2), which reflect the amount of residual coumarin moieties, are 0.363, 0.382 and 0.370 for sites a, b and c, respectively, indicating almost the same reaction degrees of coumarin moieties.

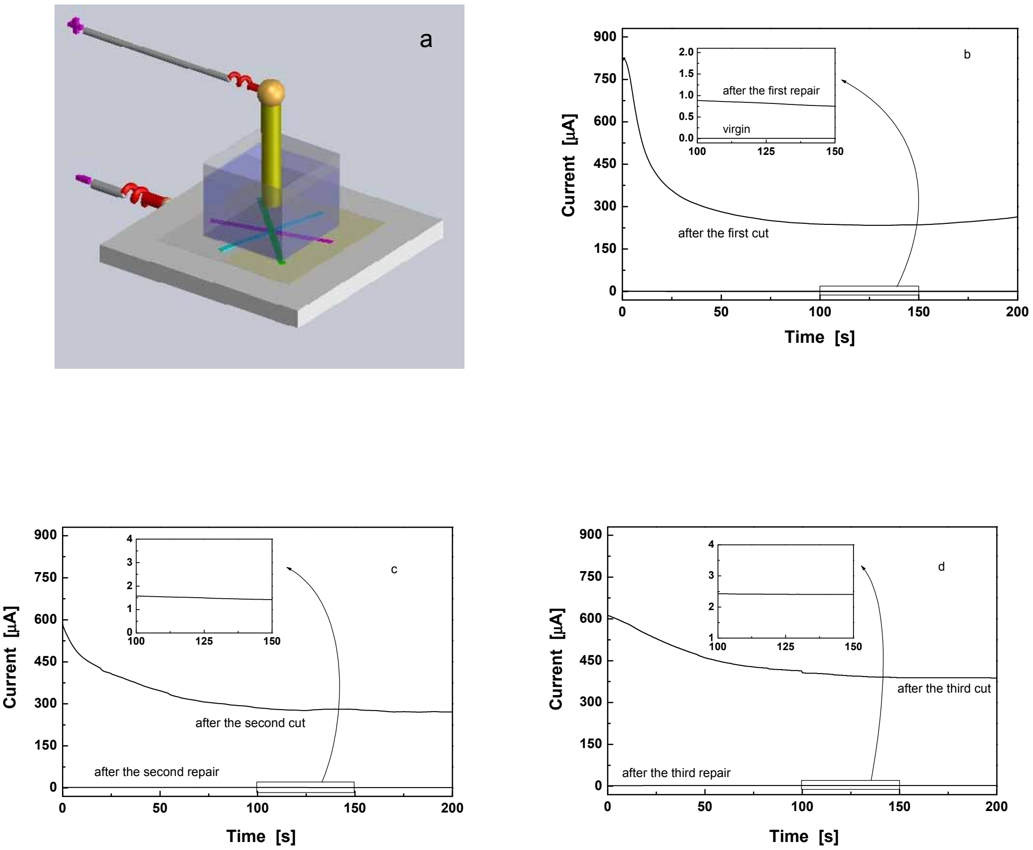


Fig. S8 Electrochemical testing of crosslinked THHPEG400 film subjected to three cycles of crack mending. (a) Schematic drawing of the testing set-up; (b) current versus time curves of virgin, the first cut and repaired specimen; (c) current versus time curves of the second cut and repaired specimen; (d) current versus time curves of the third cut and repaired specimen. (*Passing current versus time was measured in an electrochemical cell by using steel electrode coated with crosslinked THHPEG400 (**Fig. S8a**) (refer to the protocol proposed by Cho and co-workers in Adv. Mater. 21, 645-649 (2009)). The results can demonstrate effect of photochemical remendability of the material from another angle. Here the measurements were completed with a Shanghai Chenhua electrochemical workstation (model CHI660C) in a three-electrode cell with a Pt disk counter electrode, an Ag/AgCl reference electrode, and a glassy carbon working electrode. Prior to the test, THHPEG400 film (200 μm thick) was formed through solution (0.25 g THHPEG400 in 1 ml DMF) casting on the steel sheet, and crosslinked by irradiation of 350 nm UV light for 90 min. The initial voltage loading between the steel and platinum electrodes was held at 3 V through an aqueous electrolyte (1M NaCl). In the course of electrochemical testing, the crosslinked THHPEG400 film experienced three cycles of cut-repair (refer to the pattern of crossed wounds in **Fig. S8a**). Meantime, the current passing through the polymer film in each step of the circles was measured. It is seen from **Fig. S8b** that the passing current is 233.9 μA for the film after the first cutting, which is much higher than the virgin film value of 6.66×10^{-3} μA (refer to inset of **Fig. S8b**). Having* *been successively exposed to 254 nm UV light for 1 min and 350 nm for 90 min, the first razor wound was repaired and the passing current was reduced to 0.82 μA. The second cut crossed the first one and gave a passing current of 276.3 μA. After repair, the current was 1.49 μA (**Fig. S8c**). The third cut crossed the intersection of the first and the second cuts, showing a passing current of 389.5 μA. When the wound was repaired, the current was 2.41 μA (**Fig. S8d**).*)

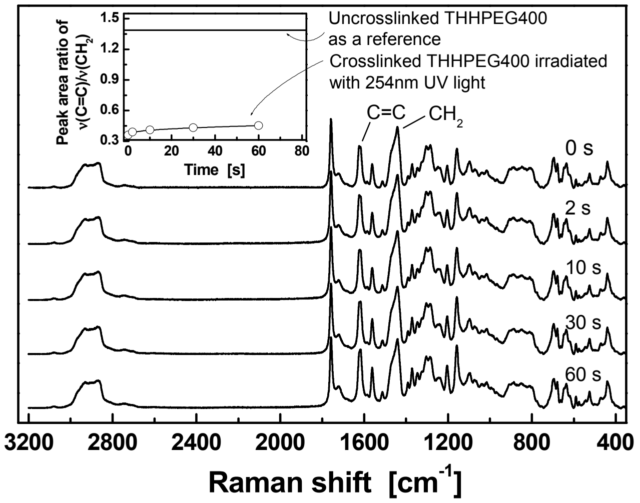


Fig. S9 Confocal Raman microscopy observation of THHPEG400 film (~200 μm thick) irradiated with 254 nm UV light for different times. The film had been crosslinked with 350 nm UV irradiation for 90 min in advance. The inset summarizes time dependence of the characteristic Raman peak area ratio (curve b), in comparison with the data of uncrosslinked version as a reference (curve a). Here two peaks are of interests: stretching mode of C=C (of lactone and phenyl ring) at 1617 cm^{-1} and that of methylene group at 1442 cm^{-1}. The intensification of the former with 254 nm UV irradiation time originates from appearance of coumarin moieties during photocleavage. Because the amount of methylene has nothing to do with coumarin dimerization, its peak area can be used as the reference for showing variation in the peak area of phenyl ring with time. *It is seen that the peak area ratio of v(C=C) to v(CH$_2$), which reflects the amount of cleft coumarin moieties, only increases from 0.36 to 0.45 after irradiation with 254 nm UV light for 1 min, much smaller than the value of uncrosslinked THHPEG400 (1.39, refer to the data in the inset of Fig. 2 at irradiation time of 0). In fact, almost all the dimerzied coumarin moieties in crosslinked thin specimen (3-5 μm thick) can be cleft within 1 min under irradiation of 254 nm UV light, as shown in Fig. 1b. The obvious difference implies that the peak area ratio of v(C=C) to v(CH$_2$) of 0.45(refer to curve b in the inset of **Fig. S9** at time of 1 min) must represent the average of cleft and dimerized coumarin moieties, and the dimerized coumarin moieties make greater contribution. The analysis is reasonable because Raman spectroscopy has considerable detection depth. For the current specimen (~200 μm thick), the Raman spectrometer can easily "see through"* *it. On the basis of the above discussion and the fact that short wave UV light has limited penetration depth, it is known that only the surface layer of the crosslinked THHPEG400 film (~200 μm thick) is de-crosslinked after exposure to 254 nm UV light, while the inner part, which takes the majority of the film, remains unchanged.*