



# Photo-stimulated self-healing polyurethane containing dihydroxyl coumarin derivatives

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## ABSTRACT

A novel polyurethane was synthesized, which consisted of isophorone diisocyanate, polyethylene glycol and photo-reversible moiety 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin. By taking advantage of reversible photodimerization and photocleavage habit of coumarin, the polyurethane can be repeatedly crosslinked and de-crosslinked under successive UV irradiations at 350 and 254 nm. More importantly, damages in crosslinked version of the polyurethane can be re-bonded through chain reconnection on fracture surfaces resulting from the photochemical reactions, as characterized by mechanical strength restoration tests. Compared to the previous proof-of-concept trial with monohydroxyl coumarin derivatives as the photosensitive groups, the application of dihydroxyl coumarin derivatives in the present work prevented the undesirable gelation during synthesis and enabled properties-oriented structure adjustment of polymerization products. Besides, structure–performance relationship study of the polyurethane revealed that rubbery domains resulting from microphase separation were necessary for the photo-remending with high efficiency.

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## 1. Introduction

Photo stimulated self-healing of polymers is a promising approach as it might be hopefully developed into the one simply making use of sunlight [1,2]. By that time, intrinsic self-healing would no longer needs manual intervention and can be conducted unconsciously.

Recently, several groups reported their achievements in this aspect. Chung et al. synthesized a photo-cross-linkable cinnamate monomer, 1,1,1-tris-(cinnamoyloxymethyl) ethane (TCE) bearing three optically active moieties [3]. It can crosslink to form a very hard solid via [2 + 2] photocycloaddition upon ultraviolet (UV) irradiation at  $\lambda > 280$  nm. When the sample of TCE suffers from impact, propagating microcracks result in cleavage of cyclobutane ring due to its low bond strength. Re-irradiation with UV light allows recovery of the crosslinked networks. Healing efficiencies in terms of flexural strength up to 14 and 26% were obtained in the case of UV stimulus or a combination of UV light and heating (100 °C). Urban and Ghosh developed a heterogeneous polyurethane network containing an oxetane-substituted derivative of chitosan (OXE-CHI) [4]. In case of mechanical damage of the

material, the four-membered oxetane rings open to create two reactive ends. When exposed to UV light, chitosan chain scission occurs, generating crosslinks with the reactive oxetane ends, so that the network acquires one way healability.

Amamoto et al. reported repeatable photoinduced self-healing of covalently crosslinked polymer through reshuffling of trithiocarbonate units. Healing of cracked parts (i.e. dynamic chain transfer), which was swollen in acetonitrile, was completed with UV light in nitrogen protection under catalysis of 2,2'-azobis(isobutyronitrile) [5]. Froimowicz et al. introduced anthracene into dendritic macromonomer to create a photo-reversible material, which was proven to build up networks possessing reversible self-healing property under successive UV irradiations at 254 and 366 nm [6]. Burnworth et al. proposed optically healable metallosupramolecular polymers based on macromolecules with pyridine derivative termini and  $Zn^{2+}$  ions complexes [7]. Liquefaction of the polymers due to photo-dissociation of  $Zn^{2+}$  motifs and the subsequent re-complex offer the self-healing function. In summary, the healing strategies reviewed in this section have one thing in common – they include fluidification in the course of bond rearrangement, which is different from the works mentioned in the last section.

Since our project aims to develop self-healing materials for structural application, macroscopic flow of the material during

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crack healing should be prohibited. Accordingly, polyurethane networks containing monohydroxyl coumarin side groups as crosslinkers were prepared in our proof-of-concept experiment [8]. Owing to reversible photodimerization and photocleavage characteristics of coumarin [9–12] (Scheme 1), the crosslinked polyurethane has acquired repeated self-healing ability under ultraviolet (UV) light. No detectable plastic deformation was observed in the course of photo-remending.

As viewed from synthesis control of the photo-remedable polyurethane, however, the system with monohydroxyl coumarin derivatives needs to be upgraded to prevent gelation and facilitate structural adjustment. According to the structural requirements for imparting photochemical reactivity to polyurethane, monohydroxyl coumarin derivatives should play dual-role as side groups and crosslinkers. It means that free isocyanate (NCO) groups have to be present on the main chains of the polymer for the reaction with monohydroxyl coumarin derivatives. As a result, tri-functional homopolymer of hexamethylene diisocyanate (tri-HDI) that contains three NCO groups per molecule is introduced. Ideally, monohydroxyl coumarin firstly reacts with one NCO group of tri-HDI, and then polyethylene glycol (PEG) is incorporated for chain extension, producing the desired polyurethane. Owing to the fact that reactivities of the three NCO groups of tri-HDI are almost identical, synthesis of the aforesaid intermediate from the reaction between monohydroxyl coumarin and tri-HDI is hard to be controlled. In many cases, all the three NCO groups of one tri-HDI molecule have reacted with monohydroxyl coumarin, so that excessive unreacted tri-HDI is left. When bifunctional PEG is added for the subsequent reaction, detrimental gelation of the system appears. On the other hand, monohydroxyl coumarin derivatives are attached to the hard segments of polyurethane (i.e. tri-HDI). Since both soft and hard segments should have the same equivalent as required by stoichiometry, the ratio of soft and hard segments in the polyurethane carrying monohydroxyl coumarin can be regulated only by changing molecular weight of PEG, but not by changing content of PEG with a given molecular weight.

To overcome the above shortcomings, dihydroxyl coumarin derivatives are employed as substitute for the monohydroxyl counterparts. Similar to the case of conventional polyether diols, polycondensation of dihydroxyl coumarin derivatives with bifunctional isocyanate only gives birth to linear polyurethane. Moreover, the ratio of soft and hard segments in the polyurethane can be regulated by changing the ratio of dihydroxyl coumarin derivatives and PEG, as well as by changing molecular weight of PEG. Comparatively, the synthesis becomes more flexible, favoring optimization of polyurethane structure and the integrated photoreversibility.

In this work, we synthesize a dihydroxyl coumarin derivative 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin (DHEOMC) by the reaction between 5,7-dihydroxy-4-methylcoumarin (DHMC) and 2-bromoethanol. Then, a novel optical stimuli-responsive polyurethane (IDHPEG, meaning a condensation polymer of IPDI, DHEOMC and PEG) is yielded (Scheme 2), which consists of isophorone diisocyanate (IPDI) and DHEOMC moieties as hard segments, while polyethylene glycol (PEG,  $M_w = 400$  or  $800$  g/mol) as the soft segments. Upon UV irradiation, the photo-reversible DHEOMC moieties are crosslinked forming cyclobutane

structures. When products made from crosslinked version of the polyurethane are scratched or cut, it is hoped that the cracked parts could be re-bound through UV induced reversible photoreaction of coumarin moieties (Scheme 3). The ether linkages offered by DHEOMC that connect coumarin moieties with the macromolecules is believed to increase localized mobility of the former, favoring photodimerization (i.e. healing reaction) of cleft coumarin dimers in bulk polyurethane. Hereinafter, structure and properties of IDHPEG with different molecular weights or contents of the PEG soft segment are discussed to find out the optimal recipe.

## 2. Experimental

### 2.1. Materials and reagents

Phloroglucinol, ethyl acetoacetate, ethyl acetate, 2-bromoethanol (BrEtOH), 1,4-dioxane, sulfuric acid (95.0–98.0%), and PEG ( $M_w = 400$  or  $800$  g/mol) were supplied by Alfa Aesar GmbH, Germany. Dibutyltin dilaurate (DBTDL, T-12) was purchased from Sigma Aldrich Co., whereas isophorone diisocyanate (IPDI) was obtained from Bayer Materials Science. All the above chemicals were used as received. N,N-dimethylformamide (DMF) was purified by vacuum distillation after being dried with anhydrous magnesium sulfate.

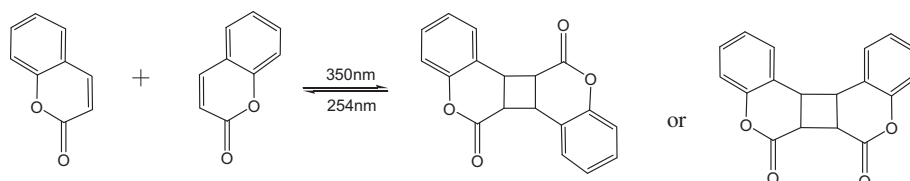
### 2.2. Synthesis of DHMC

DHMC was synthesized according to the route reported somewhere else [13]. Phloroglucinol (12.6 g, 0.1 mol) and ethyl acetoacetate (13.0 g, 0.1 mol) were completely dissolved in 1,4-dioxane (60 ml), and then concentrated sulfuric acid (3 ml) was dropped in the mixture. The system was warmed up to  $65^\circ\text{C}$  for 1 h, cooled down to room temperature, and poured into icy water (300 ml) to get a yellowish precipitate. The crude product was dried in vacuum and recrystallized twice in ethyl acetate to obtain white crystal DHMC with a yield of 83%.

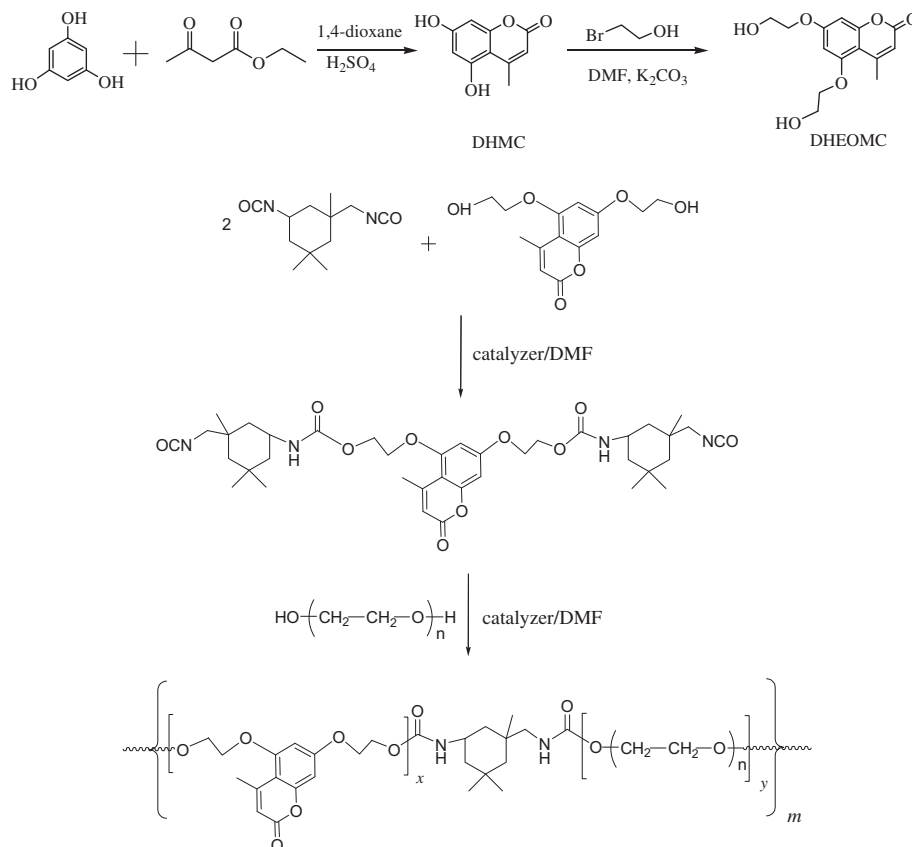
FTIR (KBr):  $\nu = 3444, 3155, 2932, 2842, 1670, 1622, 1588, 1554, 1389, 1303, 1238, 1161, 1099, 832, 761\text{ cm}^{-1}$   $^1\text{H NMR}$  (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 10.47 (s, 1H, -OH), 10.25 (s, 1H, -OH), 6.23 (d,  $J = 2.3$  Hz, 1H, Ar-H), 6.14 (d,  $J = 2.3$  Hz, 1H, Ar-H), 5.83 (d,  $J = 1.2$  Hz, 1H, C=C-H), 2.48 (d,  $J = 1.2$  Hz, 3H, -CH $_3$ ).  $^{13}\text{C NMR}$  (75 MHz, DMSO- $d_6$ ,  $\delta$ ): 161.62, 160.64, 158.50, 157.07, 155.53, 109.49, 102.76, 99.75, 95.20, 24.27. EI-MS: 192 ( $M^+$ ). Anal. Calcd. for  $\text{C}_{10}\text{H}_8\text{O}_4$ : C, 62.04; H, 4.14. Found: C, 62.50; H, 4.17.

### 2.3. Synthesis of DHEOMC

DHMC (0.86 g, 4.47 mmol) was dissolved in DMF (10 ml) under continuous stirring. Potassium carbonate (6.3 g, 0.0456 mol) was added to the mixture, and BrEtOH (1.67 g, 13.4 mmol) diluted in DMF (5 ml) was added dropwise within 15 min. The reaction proceeded at  $85^\circ\text{C}$  for 18 h under Ar atmosphere and then cooled down to room temperature. Anhydrous ethanol (20 ml) was added to dissolve the organic layer and the inorganic salt was filtrated. By removing the solvents, brown oily liquid was obtained. The crude product was further purified by chromatography on a silica gel



Scheme 1. Reversible photodimerization and photocleavage reactions of coumarin upon irradiation with 350 and 254 nm UV light.



Scheme 2. Synthesis of IDHPEG.

column with mixed solvents of ethyl acetate/petroleum ether (3/1, v/v). The solvents were removed by a rotary evaporator to give white crystal DHEOMC [14] (30% yield).

FTIR (KBr):  $\nu = 3391, 3089, 2952, 2879, 1726, 1685, 1612, 1494, 1390, 1238, 1176, 1120, 1084, 898, 854, 545 \text{ cm}^{-1}$ .  $^1\text{H NMR}$  (300 MHz,  $\text{DMSO-d}_6, \delta$ ): 6.54 (d,  $J = 2.3 \text{ Hz}$ , 1H, Ar-H), 6.46 (d,  $J = 2.4 \text{ Hz}$ , 1H, Ar-H), 5.97 (d,  $J = 1.2 \text{ Hz}$ , 1H, C=C-H), 4.90 (m, 2H, -OH), 4.07 (m, 4H, -CH<sub>2</sub>), 3.74 (m, 4H, -CH<sub>2</sub>), 2.54 (d,  $J = 1.0 \text{ Hz}$ , 3H, -CH<sub>3</sub>).  $^{13}\text{C NMR}$  (75 MHz,  $\text{DMSO-d}_6, \delta$ ): 162.60, 160.29, 158.90, 156.84, 155.11, 111.15, 104.65, 97.03, 94.70, 71.69, 70.94, 60.09, 24.54. EI-MS: 280 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_6$ : C, 59.82; H, 5.62. Found: C, 60.00; H, 5.71.

#### 2.4. Synthesis of IDHPEG

IPDI (5 g, NCO content: 43.75 mmol) was poured into a 50 ml three-neck round-bottom flask, degassed at 80 °C for 1 h, cooled to 50 °C, and diluted with DMF (15 ml) under continuous stirring and Ar protection. The solution of DHEOMC (2.90 g, 10.36 mmol) and two drops of DBTDL in DMF (15 ml) were added dropwise into the system within 1 h. After 3 h, PEG with  $M_w = 800 \text{ g/mol}$  (PEG800, 8.18 g, 10.25 mmol) was slowly incorporated within 30 min to reach stoichiometric ratio of total NCO and OH groups ( $\text{NCO}/\text{OH} = 1.05:1$ ). Then, the system temperature was raised to 70 °C, allowing reaction for 12 h to get the desired solution of polyurethane of IPDI-DHEOMC-PEG800 (IDHPEG800-0.5). The molar feed ratio of the polyurethane is  $n_{\text{IPDI}}:n_{\text{DHEOMC}}:n_{\text{PEG800}} = 1.05:0.5:0.5$ .

Following the same procedures, other two types of polyurethane, IDHPEG400-0.5 and IDHPEG800-0.25, were produced. Here PEG400 refers to PEG with  $M_w = 400 \text{ g/mol}$ . The corresponding molar feed ratios are  $n_{\text{IPDI}}:n_{\text{DHEOMC}}:n_{\text{PEG400}} = 1.05:0.5:0.5$ , and  $n_{\text{IPDI}}:n_{\text{DHEOMC}}:n_{\text{PEG800}} = 1.05:0.25:0.75$ , respectively.

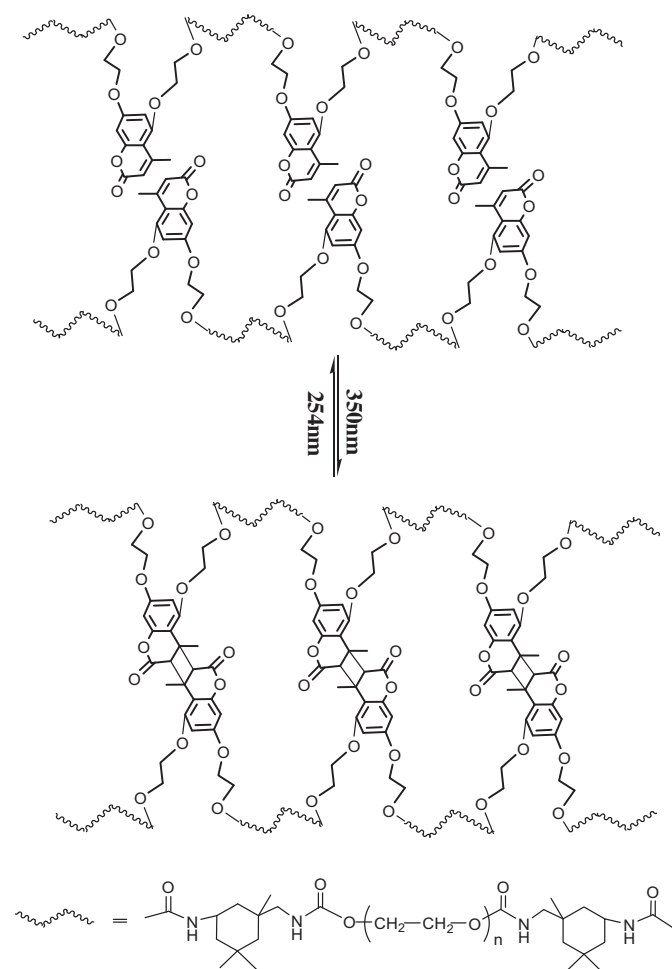
Integration of characteristic peaks on  $^1\text{H NMR}$  spectra of the resultants indicates that molar proportions of IDHPEG800-0.5, IDHPEG400-0.5 and IDHPEG800-0.25 are  $n_{\text{IPDI}}:n_{\text{DHEOMC}}:n_{\text{PEG800}} = 1.05:0.45:0.49$ ,  $1.05:0.45:0.47$ , and  $1.05:0.23:0.74$ , respectively, which are very close to the above molar feed ratios.

#### 2.5. Characterization

To understand the habit of reversible photoreaction of the resultant polyurethanes, Hitachi 3900 UV-vis spectrophotometer was used to record UV-vis spectra. The filmy samples (3–5  $\mu\text{m}$  thick) were prepared by casting the above solution of the polymer (IDHPEG800-0.5 or IDHPEG400-0.5 or IDHPEG800-0.25) on outside wall of a quartz cell. When the solvent was evaporated, the cell was put into a photochemical reactor (model RPR-100 from Rayonet, equipped with 16 UV lamps). Firstly, the polyurethane was exposed to 350 nm light ( $14.4 \text{ mW}/\text{cm}^2$ ), allowing to react for a preset period of time producing crosslinked version via photodimerization. Afterwards, all the lamps were changed to give out 254 nm light ( $15.6 \text{ mW}/\text{cm}^2$ ), and photocleavage of the crosslinked polyurethane occurred. The two photoreactions were successively carried out, and traced by means of the aforesaid UV-vis spectrophotometer.

Fourier transform infrared (FTIR) spectra were collected with a Bruker EQUINOX55 Fourier transformation infrared spectrometer coupled with an infrared microscope spectrometer. Powder samples of DHMC and DHEOMC were prepared as KBr discs, while filmy samples of polyurethane (3–5  $\mu\text{m}$  thick) were produced by casting the solution of the polymer (IDHPEG800-0.5 or IDHPEG400-0.5 or IDHPEG800-0.25) on aluminum foil.

$^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra were measured on a VARIAN Mercury-Plus 300 (300 MHz) with dimethyl sulfoxide ( $\text{DMSO-d}_6$



**Scheme 3.** Reversible photodimerization and photocleavage reactions of coumarin moieties in IDHPEG upon irradiation with 350 and 254 nm UV light.

as solvent. Electron-ionization mass spectrometry spectra (EI-MS) were obtained from a Thermo DSQ-EI-Mass spectrometer. Elemental analysis was performed with a Vario EL elemental analyzer.

Differential scanning calorimetry analysis (DSC) was conducted on a TA Instruments DSC Q10 under a heating rate of 5 °C/min using nitrogen purge and an empty aluminium pan as reference. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments DMA 2980 under 1 Hz at a heating rate of 5 °C/min in nitrogen.

Average molecular weight between crosslinks of the photocrosslinked polyurethane,  $M_c$ , was determined by swelling method using 1,4-dioxane as the solvent. Details of the measurement refer to Ref. [15].

To quantify self-healing efficiency of the materials, tensile tests were carried out as follows. The solution of the polymer (IDHPEG800-0.5 or IDHPEG400-0.5 or IDHPEG800-0.25) was poured into a polytetrafluoroethylene (PTFE) mould, which was then put in a vacuum oven at 80 °C for 48 h to remove the solvent forming a thin film of  $200 \pm 25 \mu\text{m}$  thickness. The film was crosslinked with 350 nm irradiation for 90 min on two sides in advance, and cut to get a standard dumbbell-shaped specimen according to ISO 527-3 (115 mm in length and 6 mm in width). The specimens were stretched to failure at  $23 \pm 2$  °C under a crosshead speed of 10 mm/min on a SANS-CMT6103 universal tester. The fractured surfaces of the broken specimen were exposed to 254 nm UV light, placed in contact immediately, and followed by irradiation with 350 nm light for a preset period of time. The healed specimen was tested to

failure again. Healing efficiency is defined as the ratio of tensile strength of healed specimen to that of virgin specimen. Five specimens were tested for each case and average response was used for analysis.

Fracture surface of the specimens was observed by scanning electron microscopy (SEM, Hitachi S-4800).

### 3. Result and discussion

#### 3.1. Reversible photodimerization and photocleavage reactions of the polyurethanes carrying dihydroxyl coumarin derivatives

As mentioned in the Introduction, coumarin possesses inherent reversible photoreactivity. To check whether and to what extent the habit is inherited by the IDHPEG polyurethane in solid state, UV–vis spectroscopic analysis was performed. The issue is closely related to photo-remendability of the polymer.

By taking IDHPEG800-0.5 as an example, Fig. 1 shows the results of photochemical reactions (DHPEG400-0.5 and IDHPEG800-0.25 have similar behaviors and their data are omitted accordingly). It is seen from Fig. 1a that absorption peaks appear at  $\sim 319$  nm for the specimen irradiated by 350 nm UV light for different times. With a rise in time, the peak height decreases. In fact, the peaks reflect contribution of  $\pi$ - $\pi^*$  transitions of the conjugated benzene nucleus and pyrone nucleus in 4-methylcoumarin chromophores. Because the double bonds of 4-methylcoumarin gradually dimerize to form cyclobutane rings under 350 nm UV illumination, the conjugation between double bonds and phenyl groups has to be destructed (Scheme 3). As a result, the absorbance becomes more and more weaker.

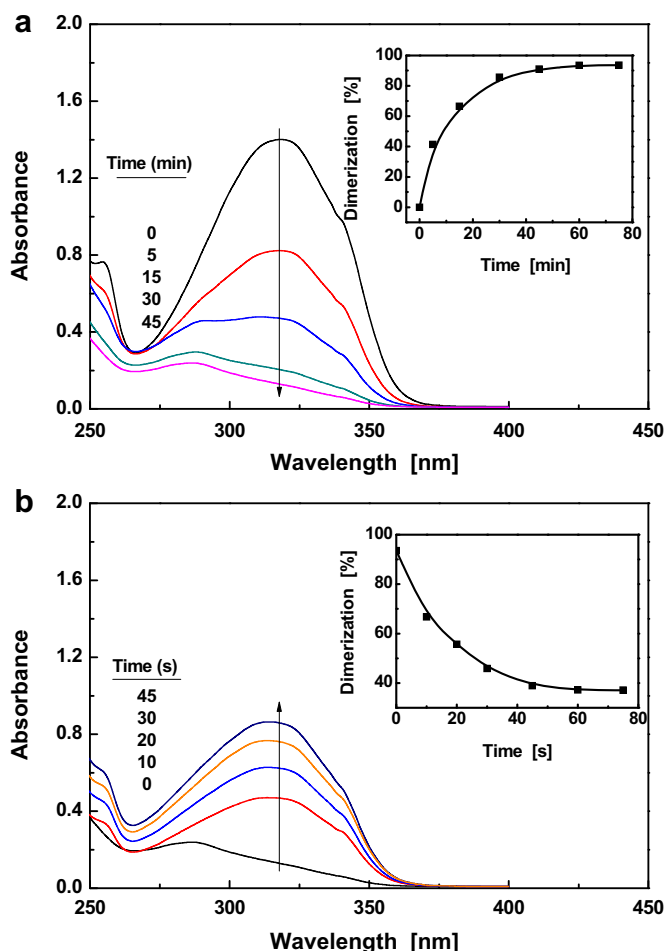
The phenomenon suggests that photodimerization process of the polymer can be quantitatively described by the time dependence of the peak height at 319 nm on the spectra. That is, the dimerization degree of 4-methylcoumarin moieties in the polyurethane can be estimated from:

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

where  $A_t$  denotes the absorbance at 319 nm at time  $t$ , and  $A_0$  the original absorbance at 319 nm prior to 350 nm exposure. The inset in Fig. 1a plots dimerization degree as a function of UV irradiation time, which approaches to the equilibrium value of 93.6% at 60 min. It means that a maximum of 93.6% of coumarin moieties in the polymer can be dimerized under the circumstances.

When the specimen was exposed to 254 nm light, the absorbance at 319 nm of the polyurethane is strengthened with increasing time (Fig. 1b). Clearly, the cyclobutane derivatives are rapidly recovered to 4-methylcoumarin monomers, so that dimerization degree decreases to the minimum within 1 min (inset of Fig. 1b). It is worth noting that the minimum value is not zero because both photocleavage and photocrosslinking of 4-methylcoumarin groups simultaneously take place upon 254 nm irradiation [16]. Nevertheless, the results shown in Fig. 1 prove that the polyurethane has acquired the desired reversible photoreactivity.

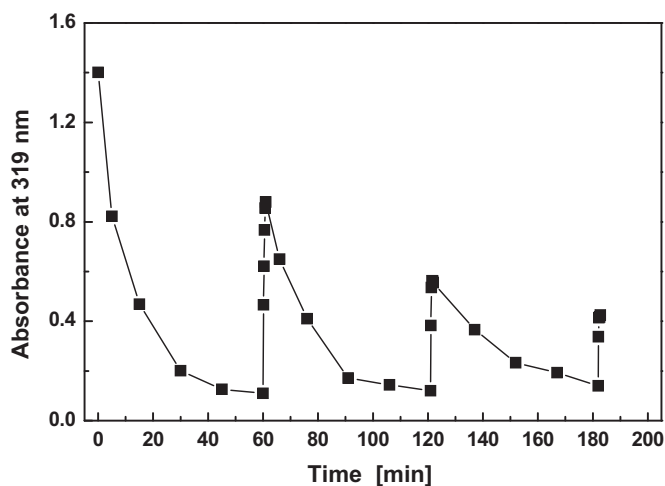
To further understand reversibility of photoreaction in the polyurethane, the specimens were alternatively exposed to 350 and 254 nm UV lights. Then, the absorbance values at 319 nm on their UV–vis spectra are plotted against irradiation time. A typical curve of IDHPEG800-0.5 is shown in Fig. 2. The data reveal that after each cycle of photodimerization and photocleavage, the maximum absorbance at 319 nm declines, implying decay of the photo-reversibility. It should be attributed to asymmetric fission of coumarin dimer during photocleavage under 254 nm light, which results in cleft products different from original coumarin moieties [17].



**Fig. 1.** Typical UV–vis spectra of IDHPEG800-0.5 film irradiated by UV light at wavelength of (a) 350 nm and (b) 254 nm. For (b), the specimen had been exposed to 350 nm UV light for 60 min in advance allowing maximization of photodimerization.

Supposing the peak absorbance at 319 nm, of the specimen exposed to 254 nm UV light is represented by  $A'_{\infty}$ , its reversibility can be characterized by the percentage recovery as follows:

$$\text{Recovery} = (A'_{\infty} - A_{\infty}) / (A_0 - A_{\infty}) \times 100\% \quad (2)$$



**Fig. 2.** Typical time dependence of absorbance at 319 nm of IDHPEG800-0.5 film exposed to alternative UV illuminations at 350 nm (for 60 min) and 254 nm (for 1 min).

where  $A_{\infty}$  denotes the minimum absorbance at 319 nm after exposure to 350 nm UV light, and  $A_0$  has the same meaning as that in Equation (1). Table 1 lists the values of dimerization degree and percentage recovery of all the three polyurethanes during the first photodimerization and photocleavage cycle. Comparatively, IDHPEG400-0.5 exhibits the poorest reversibility. Although the percentage recovery of IDHPEG800-0.5 is the highest, it is only 59.1%.

According to the results of  $^1\text{H}$  NMR measurement, the initial concentrations of coumarin moieties in the polyurethanes are calculated (Table 1). It can be concluded that the amount of available coumarin moieties is not the controlling factor for photo-reversibility. Otherwise, IDHPEG400-0.5 should have percentage recovery superior to the other two polymers. When looking at glass transition temperatures of the polymers, we can see different phase structures and viscoelastic states are involved for the room temperature photoreactions in the present work. In the case of IDHPEG400-0.5, only one glass transition temperature is perceived before and after exposure to 350 nm UV light owing to the good miscibility between soft and hard segments. Moreover, glass transition temperature of the photocrosslinked version is raised from 34.6 to 53.2 °C, following the general law of crosslinking. It means that either photodimerization or photocleavage of the crosslinkages has to occur in the glass state. Molecular mobility that is related to kinetics of photoreaction is thus reduced. With respect to IDHPEG800-0.25 and IDHPEG800-0.5, however, their glass transition temperatures are lower than room temperature before being exposed to 350 nm UV light. Photocrosslinking leads to appearance of two glass transition temperatures as a result of microphase separation of soft and hard domains. Although the glass transition temperatures of soft segments are slightly increased, they are still far lower than room temperature. Clearly, the longer molecular chain of PEG800 than PEG400 should account for the results. Since the soft segments in IDHPEG800-0.25 and IDHPEG800-0.5 exhibit rubbery feature at room temperature, the neighboring coumarin dimers or moieties must be much more mobile as compared to the case of IDHPEG400-0.5. The analysis is supported by the rate constants of dimerization (Table 1), and explains higher dimerization degrees and percentage recovery of the former two polymers.

On the other hand, Table 1 reveals that the molecular weight between crosslinks of crosslinked IDHPEG800-0.5 resembles that of crosslinked IDHPEG400-0.5, which is obviously smaller than that of crosslinked IDHPEG800-0.25. If viewed merely from the restriction effect exerted by crosslinked networks, coumarin dimers or moieties in the latter polymer have the highest mobility and hence we should observe the highest dimerization degree and percentage recovery, but this is not the case. By taking all factors into consideration, it is known that appearance of rubbery domains resulting from microphase separation is the most important condition for the reversible photoreactions. Once this prerequisite is satisfied, initial concentration of coumarin moieties attached to the polymer plays the leading role, so that IDHPEG800-0.25 exhibits poorer reversibility than IDHPEG800-0.5.

In short, reversibility of photodimerization and photocleavage reactions in the polyurethanes turns out to be a function of photo-reactivity of coumarin itself, fraction of coumarin group, phase separation structure, molecular mobility, glass transition temperature, etc. This finding might help to further improve photo-reversibility of the polymers.

### 3.2. Evaluation of photo-remendability in terms of tension test

The polyurethanes have been shown to possess reversible photochemical reactivity in the last section. Therefore, it should be known whether they are capable of self-healing under UV stimulus.

**Table 1**  
Characterization of the first cycle of photodimerization and photocleavage of the polyurethanes in relation to their structural information.

Polymer	Dimerization (%)	Recovery (%)	Initial coumarin content ( $\times 10^{-1}$ mol/dm <sup>3</sup> )	Rate constant ( $\times 10^{-3}$ dm <sup>3</sup> /mol min)	$M_c$ (g/mol)	$T_g^1$ (°C)	$T_g^2$ (°C)
IDHPEG400-0.5	50.5	16.2	9.91	8.052	1754	34.6	53.2
IDHPEG800-0.5	93.6	59.1	6.92	328.0	1539	−26.8	−24.8 (43.7)
IDHPEG800-0.25	86.3	35.2	2.94	412.5	15,413	−37.1	−35.1 (47.1)

Rate constant: parameter quantifying the speed of photocrosslinking (refer to the Electronic Supplementary Data for more details of the calculation based on the UV–vis spectroscopic data).  $M_c$ : average molecular weight between crosslinks of the photocrosslinked polyurethanes.  $T_g^1$ : glass transition temperatures of the polyurethanes prior to photocrosslinking, measured by DSC.  $T_g^2$ : glass transition temperatures of the polyurethanes that had been exposed to 350 nm UV irradiation for 60 min, measured by DSC. The data outside and inside the parentheses are glass transition temperatures of soft and hard segments, respectively. For more information about microphase separation of the polyurethanes, refer to the DMA spectra of the Electronic Supplementary Data.

For this purpose, tensile tests were conducted on dumbbell-shaped specimens 200  $\mu$ m thick, which were crosslinked by 350 nm UV irradiation in advance. For a typical cycle of test, as mentioned in the Experimental part, the specimen was firstly tested to failure, and 254 nm UV light was shone on the fractured surfaces, which were then brought into contact and followed by irradiation with 350 nm light. The healed specimen was tested to failure again, so that efficiency of healing can be estimated from the strength recovery.

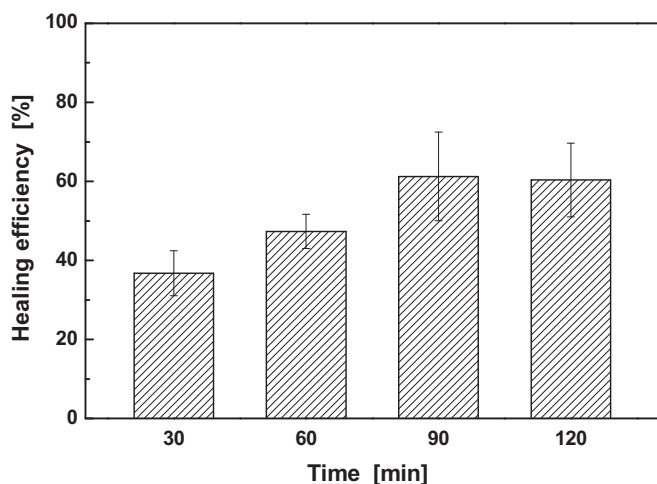
Considering that the specimens have to be respectively exposed to UV lights at 350 and 254 nm, influence of the irradiation times should be studied. At the first step, the time of 254 nm illumination is kept at 5 min, while that of 350 nm illumination varies from 30 to 120 min. When the specimens of IDHPEG400-0.5 were tested, however, no healing effect was detected because coumarin dimers in the polymer are difficult to be recovered to original coumarin moieties under 254 nm light (Table 1). Besides, its higher  $T_g$  should be detrimental to the molecular motion and contacts at the fractured surfaces. The situation is changed in the case of IDHPEG800-0.5. As shown in Fig. 3, the ruptured specimens can indeed be reconnected due to UV stimulus. With a rise in the time of 350 nm irradiation, healing efficiency rapidly increases, and approaches to the equilibrium of 61.3% at 90–120 min. It implies that 90 min of photodimerization is sufficient for maximizing the amount of coumarin dimers (crosslinkages) in the healed specimens. In addition, when the time of 254 nm illumination changes from 0.5 to 5 min and that of 350 nm illumination is fixed at 90 min according to the result in Fig. 3, similar healing effect is observed, except that the healing efficiency peaks at 64.4% after 1 min of 254 nm irradiation (Fig. 4). The relatively lower healing efficiencies

due to 2.5 and 5 min of 254 nm irradiations should originate from the above-mentioned effect of simultaneous photodimerization and photocleavage, which reduces the amount of available coumarin moieties for the subsequent photodimerization induced by 350 nm UV light. In summary, the optimal healing conditions lie in that 1 min of 254 nm UV irradiation and then 90 min of 350 nm illumination.

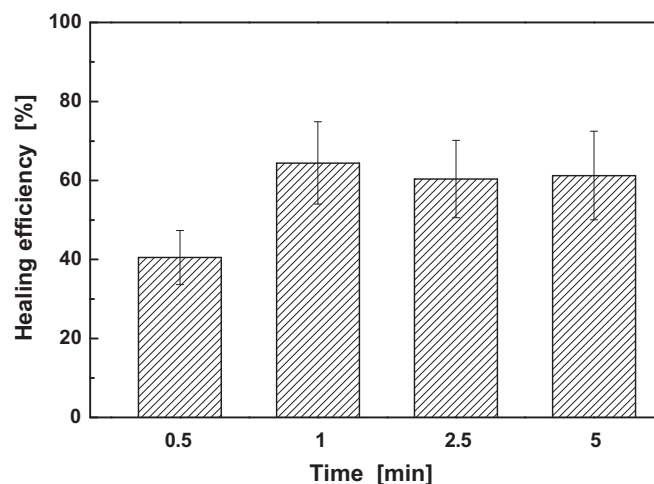
On the basis of the above discussion, repeated failure–repair tests were conducted to examine the multiple remendability of IDHPEG800-0.5. The representative load–displacement curves are plotted in Fig. 5, which show that the polymer can be self-repaired under UV irradiation as expected. Due to the declined coumarin reversibility revealed by the above UV–vis spectroscopy study and misalignment of fractured surfaces, however, healing efficiency has to be successively reduced.

In contrast, when the same optimal healing conditions were applied to the repeated failure–repair tests of IDHPEG800-0.25 (Fig. 6), full restoration of tensile strength is achieved. A close view of the re-fractured surface of a healed specimen indicates that some parts of the failure path generated during the first tensile test were so well re-bonded that crack propagation during the second failure has to deviate from the original fracture plane (Fig. 7). Moreover, the rate of decline of healing efficiency becomes not that obvious in comparison with that of IDHPEG800-0.5 (Fig. 5).

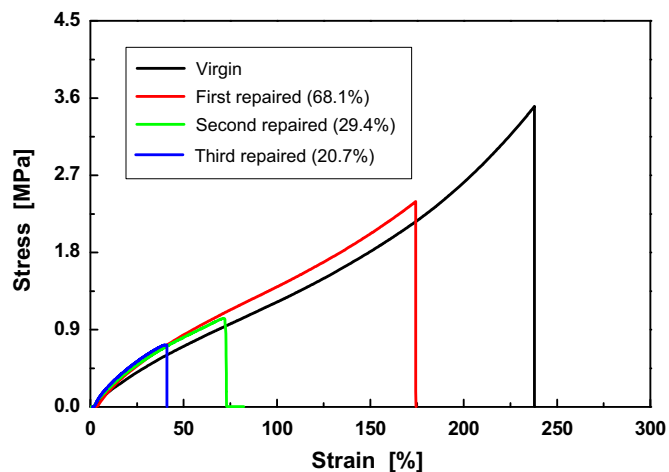
Although the result is encouraging, it seems to be contradictory to the partial data in Table 1, where dimerization degree and percentage recovery of IDHPEG800-0.25 are lower than those of IDHPEG800-0.5. To understand the discrepancy, (i) difference between constrained state of the coumarin moieties inside bulk polyurethane and that on fractured surface of the polymer, and (ii)



**Fig. 3.** Effect of irradiation time of 350 nm UV light on healing efficiency of crosslinked IDHPEG800-0.5 specimens. Irradiation time of 254 nm light = 5 min.



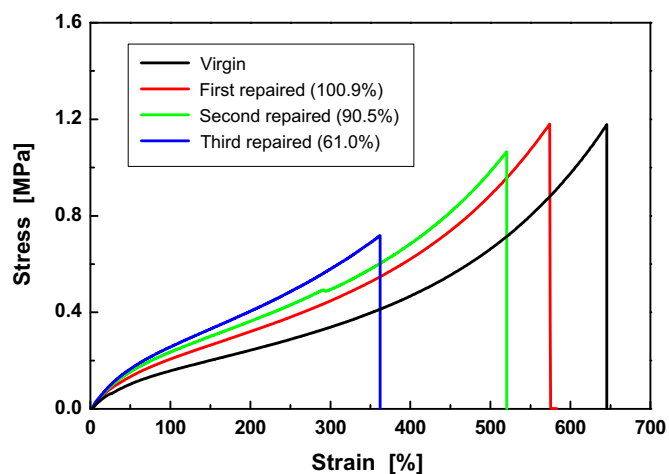
**Fig. 4.** Effect of irradiation time of 254 nm UV light on healing efficiency of crosslinked IDHPEG800-0.5 specimens. Irradiation time of 350 nm light = 90 min.



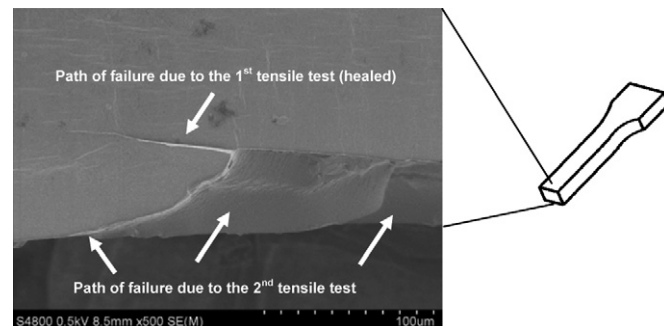
**Fig. 5.** Representative stress-strain curves of virgin and repeatedly repaired IDHPEG800-0.5 specimen. Healing conditions: irradiation with 254 nm UV light for 1 min followed by irradiation with 350 nm for 90 min. The data inside the parentheses in the legend are healing efficiencies.

wetting and diffusion between cracked surfaces to be re-bound [18,19], which are prerequisites for the mechanical property recovery due to interfacial photoreaction, should be considered. The UV-vis spectroscopic data in Table 1 only deal with densely packed molecules in the as-cast specimens, rather than contact problem of molecules from broken materials. Because IDHPEG800-0.25 has lower  $T_g$  and greater  $M_c$  than IDHPEG800-0.5, mobility of the dangling chains [20,21] carrying cleft coumarin moieties on the fracture surface of the former is higher. This is proved by the higher photoreaction rate constant of IDHPEG800-0.25 than IDHPEG800-0.5 (see Table 1). The interdiffusion induced chains entanglements and hydrogen bonding furnish basis for the subsequent development of strong links across the interface via photodimerization. The higher healing efficiency of IDHPEG800-0.25 than IDHPEG800-0.5 (or IDHPEG400-0.5) demonstrates that this is a critical factor.

For verification of the analysis, control experiments were done. The tensile failed specimens were no longer exposed to UV light, but directly reconnected and heated in an oven at 40 °C for 90 min.



**Fig. 6.** Typical stress-strain curves of virgin and repeatedly repaired IDHPEG800-0.25 specimen. Healing conditions: irradiation with 254 nm UV light for 1 min followed by irradiation with 350 nm for 90 min. The data inside the parentheses in the legend are healing efficiencies.



**Fig. 7.** Re-fractured surface of a healed IDHPEG800-0.25 specimen.

The thermal treatment temperature simulated the environment temperature inside the UV chamber, and the healing process excludes the contribution of photochemistry. In the case of IDHPEG800-0.25, healing efficiencies for the successive three cycles of such control failure-repair tests are: 30.3, 28.4 and 24.3%; while for IDHPEG800-0.5, the values become: 15.4, 12.6 and 11.2%. It means that the mechanism of entanglements between the opposite sides of the damaged specimen did take effect, and molecular mobility on the fractured surfaces of IDHPEG800-0.25 is superior to that of IDHPEG800-0.5. The attached coumarin moieties in IDHPEG800-0.25 have more opportunities to encounter with each other for the photodimerization, despite the low initial coumarin content.

On the other hand, by comparing the results of the control tests with those of authentic tests in Figs. 5 and 6, it is known that both photochemical reactions and localized viscoelastic flow are responsible for tensile strength restoration, but the latter makes less contribution. After all, the polyurethanes are photocrosslinked in advance, and photocleavage of coumarin dimers (i.e. de-crosslinking of the polyurethane networks) only takes place on superficial layer due to the limited penetration depth of short wave (254 nm) UV light.

#### 4. Conclusions

Dihydroxyl coumarin derivatives are successively introduced into polyurethane to construct photo-remendable polymer networks. The reversible photodimerization and photocleavage reactivity of coumarin has been imparted to the polymer. Accordingly, mechanical strength of broken specimens can be repeatedly restored at room temperature by successive exposure to 254 and 350 nm UV lights without the aid of additional catalysts. Dependence of healing efficiency on structure of the macromolecules reveals that chain mobility on fracture surfaces plays an important role for crack healing, which is in agreement with previous work on self-healing [8,20–25]. In this context, crosslinked polyurethane is ideal for making UV stimulated self-healing products. On one hand, the soft segments provide the photochemical groups with possibility of moving about at ambient condition (i.e. microscopic flow localized at fracture surfaces is allowed); on the other hand, majority of the crosslinked structure in the bulk material is not affected by short wave UV irradiation so that the material would not flow and still have load bearing ability even during crack repair.

The molecular design philosophy proposed in this work enables photoinduced reversible self-healing in solid polymer. Structure and performance of the material can be conveniently regulated by changing the ratio of soft and hard segments as well as the content of dihydroxyl coumarin derivatives.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found online at [doi:10.1016/j.polymer.2012.04.016](https://doi.org/10.1016/j.polymer.2012.04.016).

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