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Photodimerization of Coumarin Functionalized Poly(alkyl Acrylate) and Poly(alkyl Methacrylate) Random Copolymers: Influence of Copolymer Composition on Photocrosslinking

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Coumarin-containing poly(alkyl (meth)acrylates) were prepared via 70–80% esterification of hydroxy-containing acrylic copolymers, then solution cast into thin films and photocrosslinked via the dimerization of coumarin derivatives with UVA light. The coumarin-modified polymers crosslinked upon exposure and exhibited gel fractions between 74 and 99%. Coumarin dimerization efficiency increased with higher polymer mobility at the irradiation temperature. The effects of light intensity and irradiation time in photo-dimerized systems followed the Bunsen-Roscoe reciprocity law indicating that coumarin photodimerization depended only on dose. Thus, low intensities are overcome with longer times. This is an important advantage over photoinitiated free radical crosslinking which depends on irradiation intensity to the $\frac{1}{2}$ power.

Keywords: photocrosslink; coumarin; UV-Vis spectroscopy; glass transition; reciprocity

1 Introduction

A recent review article highlighted the photochemistry of 7-hydroxycoumarin and various derivatives that are known to undergo photodimerization ($2\pi + 2\pi$ cycloaddition) reactions when irradiated with ultraviolet-A (UVA) sources (320–400 nm) (1). Some photodimerized coumarins have reversible cleavage potential at wavelengths below 290 nm, shifting the equilibrium toward the monomeric coumarin species. Assuming the absence of competing side reactions, UV adsorption at the irradiation wavelengths reflects the relative adsorption of the two species at a photostationary state. Since neither photodimerization nor subsequent cleavage is thermally induced, the photodimerized coumarins are thermally stable over a wide range of temperatures. Also, many photodimerized coumarins exhibit melting temperatures ranging between 170 and 200°C, reflecting the variation in regio-isomers formed upon addition (2).

A number of researchers have studied the use of coumarins in polymers, including the use of coumarins to

photoreversibly crosslink or chain extend various polymers and oligomers (3–8). Coumarin-bound polymers have also found use as liquid crystalline displays (9–12), as well as indicator and dye molecules for fluorescence measurements (13, 14). Recently, Jiang and coworkers (15) prepared amphiphilic diblock copolymers of a coumarin functionalized methacrylate and poly(ethylene oxide) for the formation of core crosslinkable micelles. In our labs, we have evaluated the photoreversible chain extension of coumarin-encapped poly(ethylene glycol) (PEG) monols and diols with exposure to UVA light (16, 17). The coumarin-encapped PEG diols doubled in molecular weight, and the polydispersity increased from 1.17 to 2.75 upon exposure to UVA light at $110 \text{ J} \cdot \text{cm}^{-2}$. The molecular weight of the chain extended PEG diols were subsequently reduced to the starting molecular weight by exposure to less than $2 \text{ J} \cdot \text{cm}^{-2}$ of irradiation at 254 nm.

Many factors influence successful polymer modification reactions including polymer concentration in solution, steric effects, and others. For example, bulkier alkyl ester side groups sterically hinder nucleophilic attack of adjacent pendant esters on a polymer chain (18). Other critical factors are polymer concentration in solution and solvent choice. In poor solvents, the concentration of reactive centers is higher in the collapsed polymer coils compared to

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solutions at the theta condition. The statistical distribution of chain composition in copolymers may also affect the presence of the desired reactive groups on each chain following functionalization. Both circumstances may lead to less functional chains which are typically inseparable from the bulk of the functionalized polymer.

In the early 1860s, Bunsen and Roscoe postulated that photochemical reactions may depend on the total dose absorbed and not on the rate of irradiation (Bunsen-Roscoe Reciprocity Law) (19). Adherence to the reciprocity law is plotted as an ideal horizontal line, where the degree of failure is determined as the deviation in the slope from the line. When applied to photoinitiated polymerization, the polymerization kinetics greatly influence adherence to the reciprocity law. Zumburum and Ward photopolymerized multifunctional acrylates and methacrylates while performing FTIR spectroscopy and reported deviations from the reciprocity law (20). The reciprocity plot for these systems produced a sigmoidal curve, and combinations of low intensity and long irradiation times led to lower conversions. Photodimerization, on the other hand, follows the reciprocity law as the dimerization rate and dose are linearly related (21).

Success of photodimerization reactions depends on a variety of factors and reaction conditions (18). Herein, we describe the effects of precursor polymer glass transition temperature, composition, and alkyl ester pendant group, on the ability to photocrosslink coumarin-functionalized polymeric acrylates. Coumarin groups were bound to (meth)acrylic precursors via esterification of 2-hydroxyethyl acrylate units and subsequently photocrosslinked by coumarin photodimerization. UV-Visible absorption spectroscopy, differential scanning calorimetry (DSC), and gel fraction measurements resolved the level of dimerization.

2 Experimental

2.1 Materials

7-Hydroxycoumarin, ethyl bromoacetate, 2,2'-azobisisobutyronitrile (AIBN) and thionyl chloride were purchased from Sigma Aldrich Chemical Company and used as received. Avery Dennison Chemical Company graciously provided *n*-butyl acrylate (*n*-BA), 2-hydroxyethyl acrylate (HEA), methyl acrylate (MA), and 2-ethylhexyl acrylate (EHA), which were passed through a neutral alumina column to remove radical inhibitors.

n-Butyl methacrylate (*n*-BMA), methyl methacrylate (MMA), 2-ethylhexyl methacrylate (EHMA), and *t*-butyl acrylate (*t*-BA) were purchased from Aldrich and passed through a neutral alumina column to remove radical inhibitors. THF was distilled from sodium/benzophenone under a nitrogen atmosphere prior to esterification. All other solvents and reagents were purchased commercially and were used as received.

2.2 Instrumentation

¹H-NMR spectra were recorded using either a Varian Unity 400 MHz or a Varian Inova 400 MHz spectrometer at 25°C in CDCl₃. UV-Vis spectroscopy was performed using an Analytical Instrument Systems Inc. spectrometer equipped with fiber optic light guides, a DT1000CE light source, and an Ocean Optics USB2000 UV-Vis detector. Molecular weights were determined at 40°C in chloroform or THF (HPLC grade) at 1 mL · min⁻¹ using polystyrene standards on a Waters 707 Autosampler equipped with 3 in-line PLgel 5 μm MIXED-C columns, a Waters 410 refractive index detector, and an in-line Wyatt Technology Corp. mini-DAWN[®] multiple angle laser light scattering (MALLS) detector. DSC was performed with a Perkin-Elmer Pyris 1 at a heating rate of 20°C · min⁻¹ under N₂. The T_g was measured during the second heat using the midpoint of the transition. Irradiation temperature was measured with a Raytek Thermalert TX optical pyrometer. Homogenous films of 1 to 2 μm thickness were solvent cast from chloroform onto quartz microscope slides and drawn using a doctor blade. All films were dried in air followed by drying in a vacuum oven. Film thickness was measured using microcalipers.

2.3 UV Irradiation

The UVA irradiation source was a F300s series microwave powered electrodeless lamp source coupled with a LC-6B bench top conveyer manufactured by Fusion UV Systems, Inc. A “D” bulb (linear power output of 80 W · cm⁻¹) was used with a glass filter, which efficiently blocked wavelengths below 300 nm. The belt speed was set at 3 m · min⁻¹ unless otherwise noted. A fused silica, Tech Spec[™] linear stepped neutral density filter (Edmund Optics) was used as an inline mask controlling light intensity during UVA irradiation of the polymers. The filter ranged from an optical density of 0 (100% transmission) to 2.0 (1% transmission) in 11 steps. UVA irradiance and effective energy density were measured before and after each sample set with an EIT UV Power Puck radiometer. Extent of photoreaction was monitored using UV-Vis spectroscopy. Gel fraction analysis by Soxhlet extraction in THF with subsequent weighing was also used to monitor the extent of photoreaction.

2.4 Synthesis of Coumarin Precursors

The synthesis of 7-hydroxycoumarin derivatives was published earlier (4, 22). Briefly, 7-hydroxycoumarin (10.0 g, 61.6 mmol) was combined with ethyl bromoacetate (12.4 g, 73.9 mmol), potassium carbonate (12.5 g, 90 mmol), and acetone (450 mL) and refluxed for 3 h. After salt filtration, the product was recrystallized from ethanol with an isolated yield of 90%. The product (7-ethoxycarbonylmethoxycoumarin) (7.05 g, 28.2 mmol) was subsequently hydrolyzed for 18 h in a mixture of 1,4-dioxane

(280 mL), water (400 mL) and sodium hydroxide (15.8 g, 395 mmol). The resulting product (7-carboxymethoxycoumarin) was extracted with a 3:1 chloroform/methanol mixture and recrystallized from ethanol with an isolated yield of 85%. The 7-carboxymethoxycoumarin (2.44 g, 11 mmol) was refluxed for 3 h in thionyl chloride (20.0 mL 277 mmol) providing 7-chlorocarbonylmethoxycoumarin at a yield greater than 98%. The removal of unreacted thionyl chloride was conducted under reduced pressure and confirmed with IR spectroscopy. ^1H NMR (CDCl_3): $\delta = 7.65$ (d, 1H, CH), 7.43 (d, 1H, ArH), 6.86 (d, 1H, ArH), 6.80 (s, 1H, ArH), 6.31 (d, 1H, CH), 5.02 (s, 2H, CH_2).

2.5 Synthesis of 10 mol% 2-Hydroxyethyl Acrylate Copolymers

The synthesis of a typical acrylate copolymer is described. The *n*-BA (10.0 g, 78.0 mmol) and 2-HEA (1.0 g, 8.61 mmol) monomers were added to a 100-mL round-bottomed flask with a magnetic stir bar. The reaction mixture was then diluted with ethyl acetate (49 mL, 80 vol.%). Finally, the initiator, AIBN (22.3 mg, 0.2 wt.%), was added to the reaction vessel. The reaction mixture was equipped with a water condenser, sparged with nitrogen for 10 min, and placed in a 70°C oil bath with a magnetic stirrer for 24 h. The polymer was precipitated into approximately a 600 mL 4:1 methanol:water solution. The isolated polymer product was dried in the vacuum oven at 65°C for 24 h. A similar method was utilized to synthesize a series of copolymers (Table 1).

2.6 Copolymer Modification with 7-Chlorocarbonyl Methoxycoumarin

A typical coumarin modification of acrylic copolymers is described (Sch. 1). Poly(*n*-BA-*co*-HEA) (3.60 g) was dissolved in 35 mL distilled THF then combined with triethylamine (0.625 g, 6.18 mmol) and stirred under nitrogen in a 100 mL round-bottomed flask. Triethylamine was added at a 25 mol% excess compared to the 7-chlorocarbonylmethoxycoumarin. 7-Chlorocarbonylmethoxycoumarin (1.19 g,

5.0 mmol) was dissolved in 12 mL distilled THF and added dropwise via an addition funnel to the poly(*n*-BA-*co*-HEA) and triethylamine mixture. The addition funnel was then rinsed with an additional 10 mL distilled THF. The reaction mixture was stirred at 0°C overnight under a nitrogen blanket with the reaction vessel covered in aluminum foil to avoid premature photoreactions. After filtration of the ammonium salt, the resulting polymer was precipitated into approximately 600 mL 4:1 methanol:water solution, stored in an aluminum foil covered 60 mL bottle, and dried in the vacuum oven at 65°C for 24 h. ^1H -NMR analysis confirms the removal of residual monomer and solvent impurities. The isolated yield was typically 70 to 80%.

3 Results and Discussion

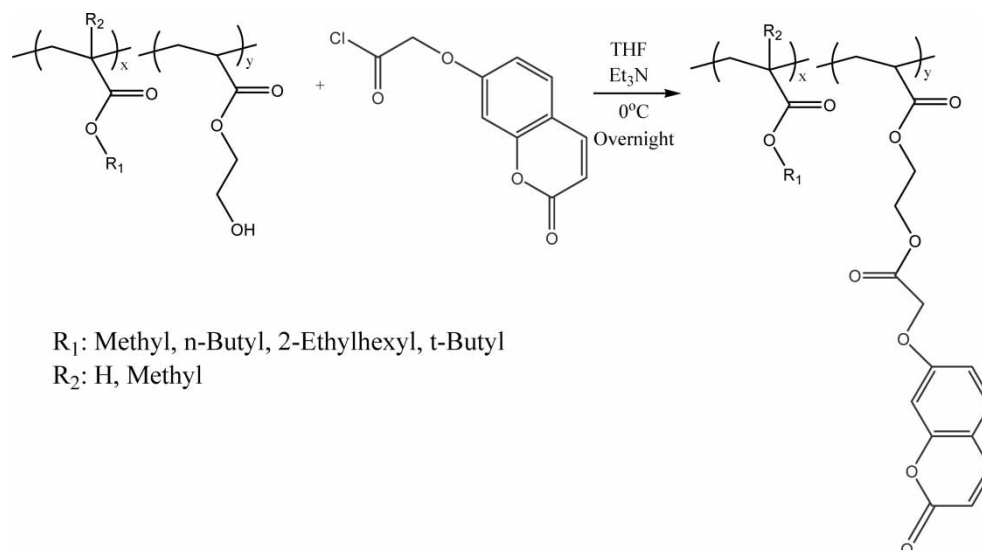
3.1 Synthesis and Functionalization of Poly(alkyl Acrylates) and Poly(alkyl Methacrylates)

Polymerization of all (meth)acrylic monomers afforded the desired high molecular weights and molecular weight distributions typical of free radical polymerization (Table 1). The molecular weight distribution did not significantly affect crosslinking or influence our conclusions regarding T_g effects relative to irradiation temperature or α -methyl and ester alkyl effects. Monomers were chosen to tailor T_g , with copolymer T_g values after coumarin functionalization ranging from -54 to 105°C . Each polymerization reaction was charged with 10 mol% HEA and ^1H -NMR spectroscopy was utilized to confirm the copolymer composition (Table 1). ^1H -NMR resonances for the methyl group at the end of the aliphatic side chain of the monomer (1.0 ppm for *n*-BA) and adjacent methylene protons to the hydroxyl group on HEA (3.8 ppm) were suitable for quantification.

Functionalization of the acrylic copolymers proceeded using the coumarin acid chloride derivative synthesized immediately prior to the functionalization step to ensure purity. The success of functionalization depended on the selection of the monomer side group due to steric hindrance (Table 2). For example, a greater molar excess of coumarin acid chloride was required at identical reaction conditions to functionalize 5 mol% of the HEA when using monomers

Table 1. Precursor alkyl acrylate and alkyl methacrylate copolymer compositions and SEC molecular weight characterization

Monomer	Charged mol% monomer:HEA	^1H -NMR mol% monomer:HEA	M_w ($\text{g} \cdot \text{mol}^{-1}$)	M_w/M_n
<i>n</i> -BA	90:10	89:11	273,000	3.65
<i>n</i> -BMA	90:10	89:11	163,000	1.82
<i>t</i> -BA	90:10	89:11	221,000	2.47
MA	90:10	90:10	390,000	2.50
MMA	90:10	90:10	138,000	1.63
EHA	90:10	88:12	248,000	3.73
EHMA	90:10	87:13	176,000	2.06



Sch. 1. Copolymer modification with 7-chlorocarbonylmethoxycoumarin.

with the bulkier side groups. The poly(EHA) and poly(EHMA) copolymers required more than a 10-fold molar excess of coumarin acid chloride whereas the copolymers with smaller side groups such as poly(MA) and poly(MMA) required only 3-fold molar excess.

The extent of copolymer coumarin modification was determined using $^1\text{H-NMR}$ spectroscopy and resulted in the incorporation of 5.0–7.0 mol% coumarin functionality (Table 2). The T_g of the functionalized polymers is shown in Table 2. The photodimerization of the coumarin-functionalized copolymers was expected to depend on the T_g ; the higher T_g polymers (i.e., poly(MMA) and poly(*t*-BA)) were expected to be more difficult to crosslink due to the restricted segmental mobility.

3.2 UV Irradiation of Coumarin-Modified Copolymers

Polymer films (1–2 μm) were solvent cast onto quartz slides for the irradiation experiments. Three samples for each coumarin-functionalized polymer were irradiated and averaged to confirm UV-Vis reproducibility. The λ_{Max}

absorbance near 325 nm in the UV-Vis absorbance spectrum of the coumarin-functionalized *n*-BA polymer is typical of 7-hydroxycoumarin containing polymers (Fig. 1) (1, 7, 16, 23). The reduction of the coumarin double bond absorbance at 325 nm was used to measure the extent of dimerization. As the unsaturated coumarin moieties were converted to cyclobutane dimers, the extent of coumarin side group conjugation decreased, which reduced absorbance at 325 nm and increased at 248 nm. The intensity of the decrease was proportional to the consumption of the 3,4-olefin in the coumarin derivative. Figure 1 shows the typical decrease in absorbance for the coumarin functionalized poly(EHMA) upon irradiation above 300 nm (UVA intensity $\sim 2.2 \text{ J} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$). This decrease in absorbance represents the extent of both inter- and intramolecular dimerization of coumarin groups, where intermolecular dimerization determines the extent of crosslinking.

The UV-Vis absorbance profiles for the coumarin-functionalized polymers are shown in Fig. 2. As samples were irradiated, the absorbance at λ_{Max} initially decreased and then reached a plateau as more coumarin was consumed. The

Table 2. HEA:Coumarin ratios utilized to functionalize the poly(alkyl acrylates) and poly(alkyl methacrylates) and the final compositions and T_g s of the coumarin-functionalized copolymers

Base polymer	HEA:coumarin molar ratio	Final conc. HEA (mol%)	Final coumarin functionality (mol%)	T_g ($^{\circ}\text{C}$)
EHA	1:10	8.0	4.0	–54
<i>n</i> -BA	1:3.5	7.0	4.0	–33
EHMA	1:12	6.0	7.0	3
MA	1:3	5.0	5.0	25
<i>n</i> -BMA	1:5	6.0	5.0	32
<i>t</i> -BA	1:5	6.0	4.0	51
MMA	1:3	5.0	5.0	105

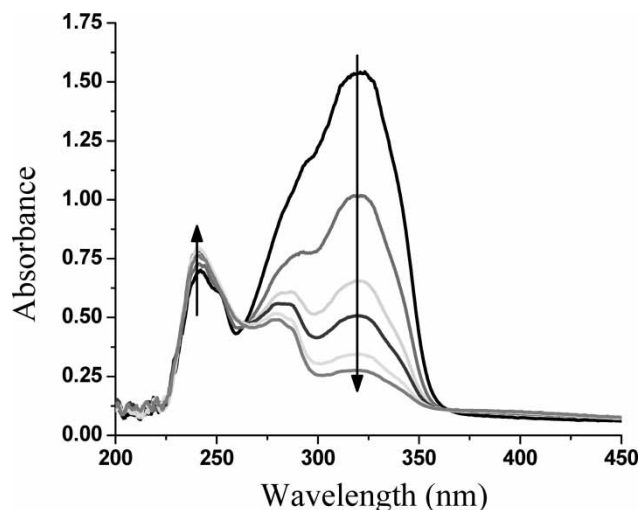


Fig. 1. Typical UV absorbance of a coumarin-containing polymer (in this case, poly(EHMA)). Arrows indicate the change in absorbance due to coumarin dimerization with UVA irradiation.

sample temperature reached 30–40°C due to infrared heating during sample irradiation, and the absorbance profiles showed two distinct groups of data, copolymers with a T_g below the irradiation temperature and copolymers with a T_g above the irradiation temperature. For the high T_g copolymers ($T_g = 51$ and 105°C) that were irradiated at a temperature below their T_g , significantly less coumarin ($\sim 17\%$) was consumed in the formation of the cyclobutane ring due to the limited mobility of each coumarin side group. The lower T_g functionalized copolymers ($T_g = -54$ to 32°C) were irradiated at a temperature above T_g , which allowed for increased chain mobility. Increased mobility allowed for increased coumarin photoreaction ranging from 47 to 59% after exposure to $\sim 22 \text{ J} \cdot \text{cm}^{-2}$ of UVA light. The greatest scatter in coumarin consumption data occurred for the coumarin-functionalized poly(*n*-BMA), since the T_g (32°C) was within the temperature range of the irradiation treatment (30–40°C). This increased scatter in percent coumarin

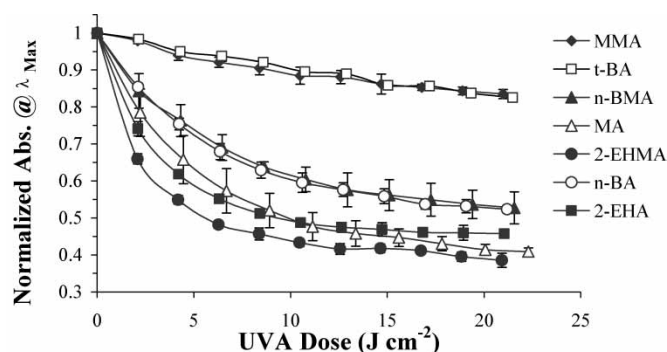


Fig. 2. Consumption of coumarin groups at $\lambda_{\text{max}} \sim 325 \text{ nm}$ as a function of irradiation dose and T_g for the coumarin-functionalized poly(alkyl acrylates) and poly(alkyl methacrylates).

consumption was attributed to reduced mobility when the sample temperature did not uniformly exceed T_g during irradiation. As expected for low levels of crosslinking, photocrosslinking of the coumarin-functionalized polymers had no effect on polymer T_g .

In addition to main chain mobility, the variation in alkyl ester side group was also hypothesized to restrict coumarin consumption during photoreaction (Fig. 2). The MA based polymer exhibited the highest coumarin consumption (59%). The poly(2-EHA) and poly(2-EHMA) consumed approximately 54%, followed by the poly(*n*-BA) and poly(*n*-BMA) at approximately 47%. The poly(MMA) and poly(*t*-BA) exhibited the lowest consumption at approximately 17%. The low coumarin consumption of the poly(MMA) and poly(*t*-BA) was attributed to low mobility as well as steric hindrance. The size of the pendant ester was expected to influence the coumarin consumption upon irradiation. Indeed, poly(MA) has the smallest side group and as anticipated, consumed the highest percentage of coumarin. The 2-ethylhexyl pendant group polymers (poly(EHA) and poly(EHMA)), however, showed greater consumption than the *n*-butyl side chain polymers (poly(*n*-BA) and poly(*n*-BMA)) although studies have shown that the 2-ethylhexyl side group has a larger molar volume than the *n*-butyl group (24, 25). It was also evident that the α -methyl on the backbone of the methacrylate copolymers had no effect on the efficiency of the photoreaction as the poly(2-EHA) and poly(2-EHMA) as well as the poly(*n*-BA) and poly(*n*-BMA) consumed comparable percentages of coumarin despite the significantly larger molar volumes of the poly(alkyl methacrylates) (24, 25). The exception to this trend was poly(MA) and poly(MMA). In this case, the α -methyl on poly(MMA) copolymer increased the T_g by 70°C to 105°C , making the difference in coumarin consumption between poly(MA) and poly(MMA) attributable to T_g effects rather than the steric effect of the α -methyl group. Another interesting point in Fig. 2 was the final coumarin consumption of poly(*t*-BA). The bulky *t*-butyl group was expected to have the greatest steric effect of all the side groups examined. While the data supported this hypothesis, the high T_g of the poly(*t*-BA) actually had more effect on the final coumarin consumption, in a similar manner as poly(MMA).

The effect of side group composition was also studied using gel fraction measurements (Fig. 3). A photocrosslinkable polymer becomes insoluble after irradiation, forming a mixture of an insoluble gel and any remaining uncrosslinked product (sol). Since only a few photoreactions per chain are necessary to crosslink, high gel fractions were expected (26, 27). Regardless of T_g , all coumarin-functionalized poly(alkyl acrylates) and poly(alkyl methacrylates) contained more than 75% gel after exposure to approximately $22 \text{ J} \cdot \text{cm}^{-2}$ of UVA irradiation. These high gel fractions indicated that the films were efficiently crosslinked, and therefore intermolecular dimerization was a dominant dimerization mechanism.

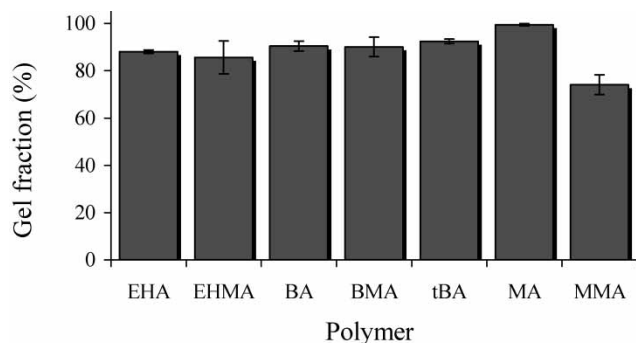


Fig. 3. Gel fraction after approximately $22 \text{ J} \cdot \text{cm}^{-2}$ of UVA irradiation based on copolymer side group composition.

3.3 Reciprocity of Coumarin-Functionalized EHMA Polymers

The coumarin-functionalized 2-EHMA copolymer was further evaluated to determine the effect of light intensity and irradiation time on the consumption of the coumarin groups. Figure 4 shows the effect of irradiation time and intensity on coumarin dimerization. The samples were placed on the conveyor and repeatedly passed under the UV lamp at approximately 3, 6, and 12 $\text{m} \cdot \text{s}^{-1}$, corresponding to doses of 2.2, 1.1, and 0.55 $\text{J} \cdot \text{cm}^{-2} \cdot \text{pass}^{-1}$, respectively. At a total dose of 2.2 $\text{J} \cdot \text{cm}^{-2}$ (1 pass at 3 $\text{m} \cdot \text{s}^{-1}$, 2 passes at 6 $\text{m} \cdot \text{s}^{-1}$, and 4 passes at 12 $\text{m} \cdot \text{s}^{-1}$) the film that received 1.1 $\text{J} \cdot \text{cm}^{-2} \cdot \text{pass}^{-1}$ displayed a slightly higher percent of coumarin consumption compared to the other two samples. However, at a total dose of 11 and 22 $\text{J} \cdot \text{cm}^{-2}$, approximately 52 and 55% of the coumarin, respectively, was consumed in all films. This indicated that the extent of coumarin dimerization was independent of the individual doses studied (2.2, 1.1, and 0.55 $\text{J} \cdot \text{cm}^{-2} \cdot \text{pass}^{-1}$) and suggested reciprocity law adherence.

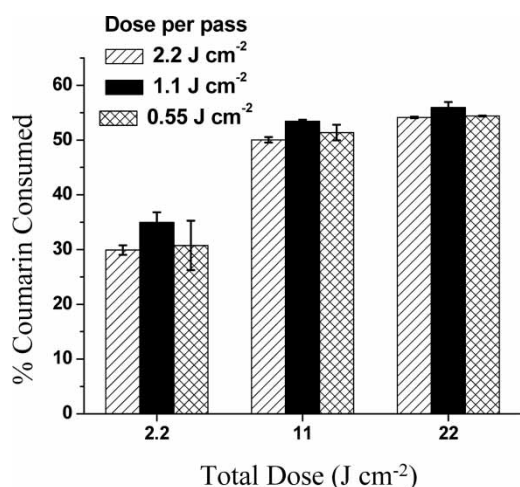


Fig. 4. Percentage of coumarin consumed in 2-EHMA copolymer films that received 2.2, 1.1, and 0.55 $\text{J} \cdot \text{cm}^{-2} \cdot \text{pass}^{-1}$ of UVA irradiation for a total dose of 2.2, 11 and 22 $\text{J} \cdot \text{cm}^{-2}$.

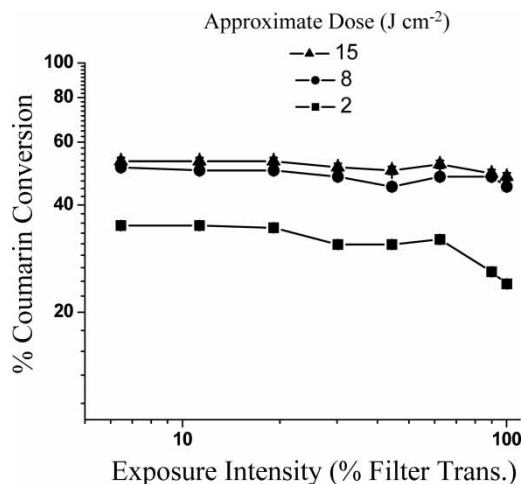


Fig. 5. Halm-type plot of conversion vs. exposure intensity showing reciprocity law agreement at doses of 15 and 8 $\text{J} \cdot \text{cm}^{-2}$.

A neutral density linear step filter was used to resolve the effect of light intensity on coumarin dimerization reaction of functionalized poly(EHMA). The first eight steps of the linear step filter were utilized, yielding seven steps of filter transmission ranging from 6 to 100% (optical density between 1.4 and 0). Each sample displayed a similar reaction profile and thus similar conversions at the same dose (equal doses were achieved with additional passes under the UV lamp). Figure 5 shows the reciprocity plot for the coumarin-functionalized poly(EHMA) utilizing Halm's method at three doses (2, 8, and 15 $\text{J} \cdot \text{cm}^{-2}$) (21, 28). The plot shows coumarin conversion (plotted on a log scale) vs. the log of the exposure intensity. Over the relatively narrow range studied, the polymer deviated with the reciprocity law only with the high intensity (100% transmission) 2 $\text{J} \cdot \text{cm}^{-2}$ sample.

4 Conclusions

Our work with coumarin-containing polymers found that photodimerization efficiency depends on a complex combination of factors, including T_g , composition, and steric hindrance of the alkyl ester pendant group. Regardless of polymer composition or T_g , all coumarin-functionalized polymers were efficiently crosslinked with >75% gel after UV exposure. However, T_g and pendant alkyl group choice significantly affected the amount of coumarin consumed during photodimerization. The limited mobility of coumarin groups in polymers with a T_g above the irradiation temperature restricted consumption to less than 20%, while 47–59% photoreaction was achieved for polymers with a T_g below the irradiation temperature (30–40°C). The α -methyl on the backbone of the poly(alkyl methacrylates) did not affect dimerization as there was no difference in coumarin consumption between poly(alkyl acrylates) and poly(alkyl methacrylates) with identical alkyl ester side groups (poly(*n*-BA) vs. poly(*n*-BMA), and

poly(EHA) vs. poly(EHMA)). The coumarin-functionalized acrylates obeyed the Bunsen-Roscoe reciprocity law indicating that the photodimerization of the coumarin groups depended only on the total irradiation dose and not on irradiation time or intensity. Therefore, low irradiation intensities are overcome with longer times in photodimerized systems, a significant advantage over photoinitiated free radical crosslinking systems.

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