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Coumarins in Polymers: From Light Harvesting to Photo-Cross-Linkable Tissue Scaffolds

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1. Introduction

The use of polymer photoreactions dates back some 4000 years to when ancient Egyptians and Babylonians used sunlight to photo-cross-link linens during mummification and to waterproof papyrus boats via the photopolymerization of an asphalt oil.[1−3] The first synthetic photoreactive polymers resulted from work done by Minsk and co-workers on the photodimerization of poly(vinyl cinnamate).[4−8] Soon afterward, Plambeck developed and patented the photoinitiated free-radical polymerization of acrylates.[9]

The uses for coumarins are as diverse as the structures of the 800 different derivatives in the coumarin family. Coumarins are used in the fields of biology, medicine, and polymer science. They are also present or used in perfumes and cosmetics,[10−16] cigarettes,[11−15] alcoholic beverages,[17] and laser dyes[18−30] and were linked to a number of cases of homicide and suicide in Korea.[31]

This review will focus on the use of coumarin and coumarin derivatives in polymers. First, an overview of coumarin and coumarin derivatives is presented, followed by a discussion of the use of coumarin-containing polymers in electro-optical studies, the development of photoreversible polymer systems, the use of coumarin in biopolymer studies, and the use of coumarins in other systems.

2. Coumarin, Coumarin Derivatives, and Properties

Coumarin (Figure 1a) was first reported and isolated in the 1820's, recognized as the hay-like sweet aroma of the tonka bean.[10,15] Since then, more than 1000 derivatives have been investigated with naturally occurring coumarin derivatives isolated from over 800 species of plant life. Most of the coumarin derivatives have at least one additional oxygen atom at one or more of the six other available positions (i.e., positions 3−8 in Figure 1a), with all but approximately 35 derivatives being oxygenated at the seventh position.[12,15] For this reason, 7-hydroxycoumarin, shown in Figure 1b, also known as umbelliferone, is often considered the "parent" of the more complex coumarins. For earlier reviews on individual coumarin derivatives, their biological action, and occurrences, the reader is referred to reviews by Murray et al., Nielsen, and O'Kennedy et al.[11,12,14,15]

The uses for coumarins are as diverse as the structures of the over 1000 different derivatives in the coumarin family. In addition to the previously mentioned uses, coumarins are well documented as therapeutic agents and have been used as medicines in ancient Egypt and in aboriginal cultures.[11−13,32−39] One example, warfarin, is the most prescribed anticoagulant on the market.[40−42] Recent medicinal research has focused on the use of coumarin derivatives as anti-HIV agents. A recent review by Yu and co-workers described the study of over 150 coumarin derivatives and their efficacy in fighting HIV. Some of the derivatives have effective concentrations (EC_{50}) 180 000 times less than that of azido-thymidine (AZT), though poor water solubilities have hampered further testing and development.[43]

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Dr. Allan R. Shultz was born January 8, 1926, in Huntington, IN. He earned his B.A. degree in chemistry from Manchester College in 1948. In 1953, he received his Ph.D. degree in physical chemistry at Cornell University under Professor Paul J. Flory followed by postdoctoral work at MIT with W. H. Stockmayer. Dr. Shultz was employed by 3M Company at Central Research in St. Paul, MN, for 9 years before going to GE Research and Development in Schenectady, NY, from where he retired in 1991. Since coming to Blacksburg, he has served as Adjunct Professor in the Chemistry Department at Virginia Tech, mentoring graduate chemistry students. During his career, he authored over 100 articles in professional journals in his field of polymer research.

Brian J. Love has been at Virginia Tech in materials science and engineering since 1993. He received his B.S. (chemistry) and M.S. (metallurgy and mining engineering) degrees from the University of Illinois, Urbana-Champaign, and his Ph.D. (applied science) degree from Southern Methodist University in Dallas in 1990. Dr. Love spent time in industry at Texas Instruments at their corporate headquarters and was appointed a NIH Postdoctoral Training Fellow at Georgia Tech in 1991 prior to his appointment at Virginia Tech. Dr. Love's main areas of research relate to structure/property relationships of polymeric materials, photopolymerization, biomaterials, and pre-polymer fluid dispersion transport.

The ability of coumarin to reversibly photodimerize and subsequently photocleave (to be described in section 2.3) was studied as a possible controlled drug release mechanism.[44,45] Tanaka and co-workers synthesized mesoporous silica substrates with coumarin groups attached to the pores. A model drug, cholestane, was impregnated into the coumarin-functionalized silica substrates and released when the silica substrates were washed without irradiation. If the impregnated substrates were irradiated above 300 nm and then washed, the substrate failed to release the cholestane since the photodimerized coumarin now blocked the pores. With subsequent re-irradiation at 250 nm, the coumarin dimers were photocleaved and the cholestane was released with washing. This model system worked well, but other systems may fail if the drug, pore, and coumarin dimer size are not matched.

Timothy E. Long received his Ph.D. degree in chemistry from Virginia Tech in 1987 under the direction of Professor James E. McGrath and subsequently joined the Corporate Research Laboratories at Eastman Kodak Company in Rochester, NY. In 1993 he moved to the Polymers Research Division at Eastman Chemical Company in Kingsport, TN. He joined the Virginia Tech Department of Chemistry as an Assistant Professor in January 1999 and was recently promoted to full Professor of Chemistry. Dr. Long's research goal is to integrate fundamental research in novel macromolecular structure and polymerization processes with the development of high-performance macromolecules for advanced technologies. His research interests include living polymerization, well-defined macromolecular architecture, liquid crystalline polymers, ion- and hydrogen-bond-containing polymers, in-situ FTIR spectroscopy, blend compatibilization, and novel pressure-sensitive adhesives. Dr. Long has published over 100 journal and conference articles and is currently serving as Vice-Chair of the American Chemical Society Division of Polymer Chemistry. Dr. Long has served as the General Secretary of the Macromolecular Secretariat for the American Chemical Society and as the National Program Co-Chairperson for the American Chemical Society Division of Polymer Chemistry.

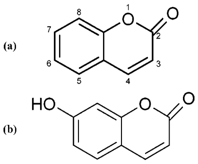


Figure 1. Structure and numbering scheme of (a) coumarin and (b) 7-hydroxycoumarin.

2.1. Synthesis of Coumarin and Coumarin Derivatives

Simple coumarin derivatives are naturally derived as a derivative of cinnamic acid via the shikimate–chorismate biosynthetic pathway.[12] Briefly, *trans*-cinnamic acid is hydroxylated, glucosylated, and isomerized to the *cis*-2′-glucosyloxycinnamic acid, resulting in the bound form of coumarin (coumarinyl glucoside). Coumarin derivatives were first synthesized via the Perkin reaction in 1868, and many simple coumarins are still derived from this method. In the early 1900s, the Knoevenagel reaction emerged as an important synthetic method to synthesize coumarin derivatives with carboxylic acids at the 3 position.[46,47] Later, researchers condensed ethyl cyanoacetate and various *o*-hydroxyacetophenones to synthesize 4-methylcoumarin derivatives.[48,49]

Recently, the Pechmann reaction was utilized in conjunction with Nafion/silica nanocomposites as catalysts to synthesize 7-hydroxycoumarin derivatives.[50] Via a reaction of resorcinol and ethyl acetoacetate, 7-hydroxy-4-methylcoumarin was synthesized at yields of 81−96% with high recyclability of the Nafion/silica nanocomposite catalysts. A more recent scheme that was utilized to synthesize coumarin derivatives is ring-closing metathesis using Grubb's catalyst.[51] De Kimpe and co-workers synthesized six coumarin derivatives starting with phenolic compounds which then underwent *O*-allylation followed by an *o*-Claisen rearrangement, base-induced isomerization, acylation with acryloyl chloride, and finally ring-closing metathesis. The yields of the five-step reaction ranged from 70% to 90%.

While coumarin derivatives are readily synthesized by the aforementioned reactions, most require harsh reaction conditions and non-environmentally friendly solvents. Sartori et al. reported "greener" reaction schemes utilizing recyclable catalysts and water as the solvent.[52−54] Sartori modified the Knoevenagel reaction, using montmorillonite clays as catalysts, to synthesize coumarin-3-carboxylic acids with yields ranging from 50% to over 90%. Their research indicated that the clays serve as a ditopic catalyst with both acidic and basic sites. They proposed that the basic sites activated the Knoevenagel reaction, while the acidic sites promoted α-pyrone ring formation via transesterification. Sartori's group also studied the use of water as a solvent to synthesize 3-carboxy coumarins via a reaction between Meldrum's acid and salicylaldehydes. The reactants were refluxed in water for 10 h with yields above 78%. Their proposed mechanism included nucleophilic attack of the active methylene (on Meldrum's acid) to the carbonyl group of the salicylaldehyde followed with dehydration leading to the coumarin derivative.

2.2. Photophysics and Fluorescence

Coumarin and its derivatives show sufficient fluorescence in the visible light range to be used in laser dyes and organic light-emitting diodes (LEDs).[20−25,27,55] Figure 2a shows the fluorescence, phosphorescence, and polarized phosphorescence spectra of coumarin in ethanol when irradiated at 320 nm. Researchers have studied the photophysics of coumarin compounds since the 1940s due in part to the tunability of their absorbance and fluorescence.[21−23,26−30,56−64]

In the late 1950s, Wheelock showed substitutions on the coumarin structure shifted the fluorescence band.[57] For instance, adding a methyl group to the 4-position of 7-hydroxy- or 7-methoxycoumarin red shifts (i.e., shifts to longer wavelengths) the fluorescence spectra. Wheelock's results showed that the addition of electron-repelling groups in the 4, 6, or 7 position or electron-attracting groups in the 3 position all shift the fluorescence band to longer wavelengths. When the carbonyl is substituted with a thione, the absorbance was red shifted and the fluorescence was quenched.[26,28]

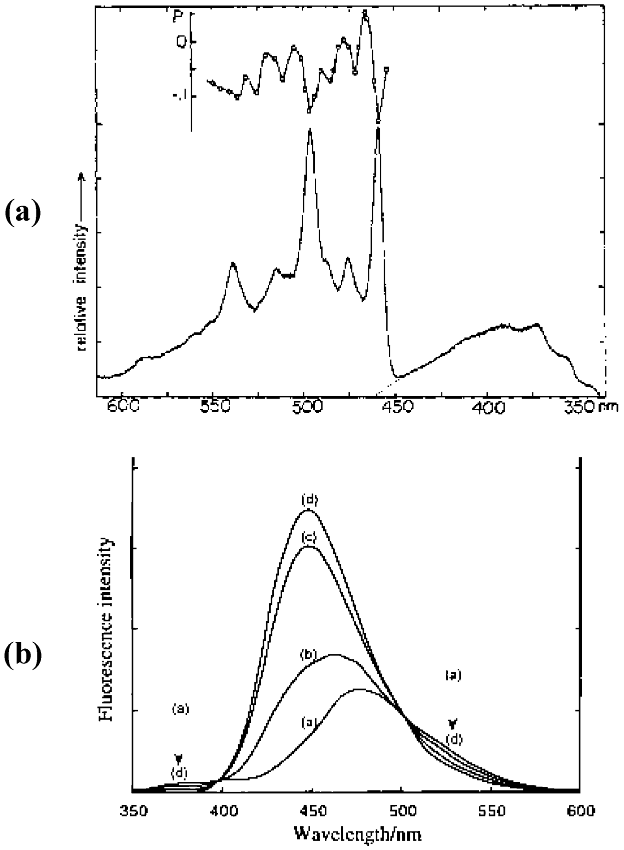


Figure 2. (a) Phosphorescence (left of 450 nm), fluorescence (right of 450 nm), and polarized phosphorescence (inset) of coumarin in ethanol when excited with irradiation at 320 nm.[58] (b) Effect of pH on the fluorescence spectra of 7-hydroxy-4-methylcoumarin in MeOH−H_2O solution with KCl and HCl as pH increases from 1 (curve a) to 10.5 (curve d). (Reprinted with permission from ref 29. Copyright 2001 Elsevier.)

Changing the solvent or the solution pH also affected the fluorescence spectra. The effect of solution pH on 7-hydroxy-4-methylcoumarin is shown in Figure 2b, illustrating that increasing the solution pH raised the fluorescence intensity.[29] As for the solvent, Jones and co-workers studied the effect of changing the solvent polarity on 13 coumarin derivatives. They found that increasing solvent polarity red-shifted the absorbance as well as red-shifted and broadened the emission of the coumarins due to increased hydrogen bonding.[22] In a similar study, Sharma et al. studied the excited-state properties of 4- and 7-substituted coumarin derivatives. They also observed that solvent polarity shifts both the emission and absorption peaks, with a greater shift observed in the emission spectra. This indicated that the excited-state dipole moment of the solute molecule was greater than the ground-state dipole moment.[65]

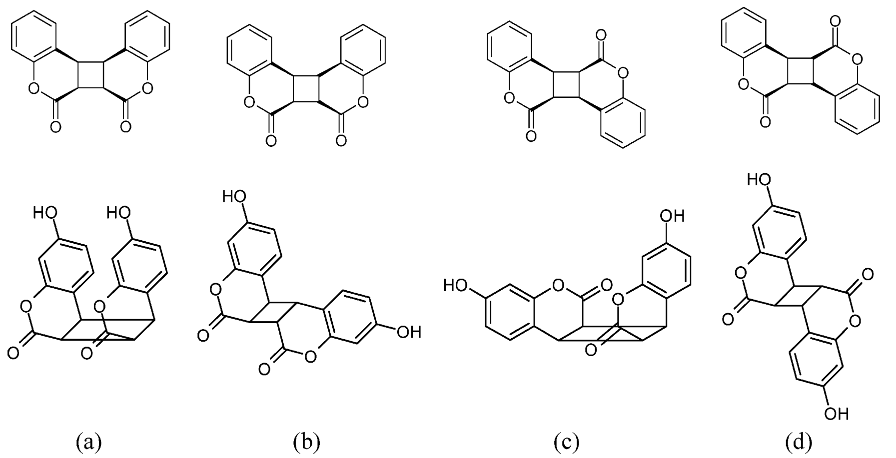


Figure 3. Four isomers resulting from the photodimerization of coumarins (coumarin top and 7-hydroxycoumarin below) using different conditions: (a) syn head-to-head dimer, (b) anti head-to-head dimer, (c) syn head-to-tail dimer, and (d) anti head-to-tail dimer.[67,71−75]

2.3. Photodimerization and Photocleavage

The photodimerization of coumarin was discovered by Ciamician and Silber in 1902, when they used sunlight to irradiate coumarin dissolved in alcohol for over 2 years.[66] The dimerized product exhibited a melting point of 262 °C, much higher than the original coumarin's melting temperature of 68−70 °C.[66,67] In 1904, Ström reported a dimer with a melting point above 320 °C.[67,68] In the early 1960s, Anet synthesized the head-to-head cis and the head-to-tail trans coumarin dimers via sunlight exposure.[69,70] Since the first studies reported two different melting points, it was not resolved until Schenck and co-workers observed that both structures were in fact dimers of coumarin.[67] Schenck used ^{1}H NMR spectroscopy to determine the structure of the four possible dimers that were produced from the irradiation of coumarin at different reaction conditions. Figure 3 shows the structure of the four possible dimers formed from the UV irradiation of coumarin.

The actual coumarin dimer formed on irradiation depends on the combination of dose, solvent, and coumarin concentration. The structure of the dimer resulting from irradiation was contested in the late 1960s and early 1970s by the research groups of Schenck, Morrison, Anet, and Hammond.[67,69−73] They concluded that the dimer formed via the $[2\pi s + 2\pi s]$ cycloaddition formation of a cyclobutane ring. The combined results of their studies indicated that coumarin irradiation yielded mainly three products: the syn head-to-head dimer (Figure 3a), the anti head-to-head dimer (Figure 3b), and the syn head-to-tail dimer (Figure 3c). At high concentrations, the coumarin singlet reacts with a ground-state coumarin and forms the syn head-to-head dimer, while at low concentrations, inefficient intersystem crossing produces the triplet coumarin and the anti head-to-head dimer is formed.[74]

The reaction scheme in Figure 4 summarizes the UV radiation-induced formation of the coumarin photodimers. In polar solvents, the singlet state is favored, resulting in the formation of mostly syn photodimers, while nonpolar solvents or the addition of photosensitizers such as benzophenone lead to mostly anti photodimers.[71−78] The heavy-atom effect becomes important with chlorinated solvents. It reduces the concentration of the excited singlet state coumarins by reducing the lifetime of the excited singlet. The shorter lifetime is due to a shift in the equilibrium of molecular spin and orbital motions, making the spin change more desirable and thus reducing the lifetime of the singlet excited states. The smaller singlet concentration increases the relative concentration of excited triplet state coumarins, thus pushing the dimer equilibrium toward the anti products.[72,73,77] Belfield and co-workers recently studied the two-photon dimerization of 5,7-dimethoxycoumarin as a model for psoralen enone photochemistry.[79] They found that ratios of the dimer formed, via two-photon excitation at 650 nm, were similar to the ratios achieved with the traditional single-photon UV exposure.

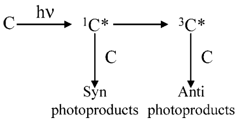


Figure 4. Reaction scheme leading to the dimerization of coumarin.[71−74,77]

Researchers have also studied the solid-state dimerization of coumarin compounds both in the bulk and in inclusion complexes.[75,80−82] In one such study, Brett and co-workers studied the photodimerization of 7-hydroxy-4-methylcoumarin in a β-cyclodextrin complex. The host β-cyclodextrin materials allowed for the positioning of the reactive double bonds on the coumarin to be 3.5−3.7 Å apart and aligned parallel to adjacent coumarin groups. Upon UV irradiation for 7 days, the coumarins dimerized, forming the anti head-to-tail dimer as observed using X-ray crystallography.[75]

Ramamurthy et al. studied the solid-state dimerization of 28 coumarin derivatives.[81] Figure 5 shows their results in the form of dimer yield as a function of irradiation time. Of the 28 coumarin derivatives studied, 12 formed dimers in the solid state. From their measurement using ^{1}H NMR spectroscopy, thin-layer chromatography, and X-ray analysis, they resolved several conditions for promoting solid-state dimerization, such as close proximity of the double

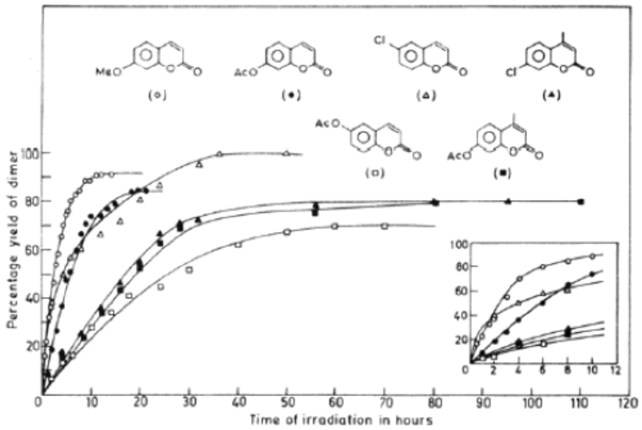


Figure 5. Dimer yield for various coumarins as a function of irradiation time using a 450 W medium-pressure Hg arc lamp, as measured using ^{1}H NMR.[81]

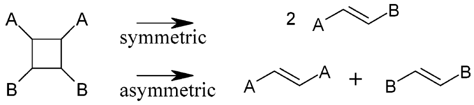


Figure 6. Symmetric and asymmetric cleavage of cyclobutane compounds formed via photodimerization.[86-88]

bonds. Ramamurthy found that a double-bond separation of less than 4.2 Å was necessary for most coumarin derivatives. The exception proved to be 7-chlorocoumarin, which dimerized with separations up to 4.5 Å. Chloro and acetoxy groups also enhanced dimer formation by "steering" the double bonds into the correct position, but no explanation on how this is accomplished was provided.[81]

Delzenne and Laridon first studied the photodimerization of coumarin groups attached to polymers in the mid 1960s.[2] This group studied copolymers of ethyl acrylate and 7-acryloxycoumarin, poly(hydroxyethers) with coumarin derivatives, and partially hydrolyzed poly(vinylbutyral) modified with 6-coumarin sulfonyl. They were able to photo-cross-link the polymers through the coumarin moiety to form insoluble networks where the light sensitivity of the polymer was directly proportional to the degree of coumarin substitution.

Schenck and co-workers first discovered the photocleavage of a coumarin dimer during their research on the dimerization of coumarin.[67,83,84] However, the photoscission reaction has not been studied as extensively as the dimerization reaction. Most of the references in the literature on the photocleavage of cyclobutane dimers points toward work by Lamola on the photocleavage of thymine dimers.[85,86]

Cyclobutane photocleavage has been studied to some extent by Hasegawa and co-workers.[86-88] The generic photocleavage reaction scheme is shown in Figure 6. Cyclobutane rings that are formed from coumarin dimerization undergo symmetric cleavage. Several interesting trends emerged from their studies. All of the compounds that have stable five- or six-membered rings attached to the cyclobutane ring cleaved, preserving the more stable ring. For the dimers without stable rings, the symmetric or asymmetric cleavage that resulted was due to either steric repulsions or other repulsions between neighboring groups.[86] Coumarin photodimers have also been cleaved via a two-photon excitation to circumvent difficulties encountered when attempting to irradiate at 254 nm, i.e., composite layers with high UV absorptions. Kim and co-workers utilized a Nd:YAG (yttrium aluminum garnet) laser at 532 nm to cleave the coumarin dimers. While they were able to quantitatively cleave the dimers, the dose necessary for the reaction was approximately 9.0 kJ at 532 nm, whereas for the same unit area less than 500 mJ was necessary to cleave the dimer at 266 nm.[89]

3. Coumarins in Electro-optical Studies

3.1. Liquid Crystalline Polymers

A number of researchers have reviewed polymeric liquid crystals, and liquid crystals have recently attracted considerable attention due to the combination of polymer-specific properties and the unique anisotropic behavior of liquid crystalline (LC) molecules.[90-98] The introduction of polymers into LC systems can increase the mechanical strength and may considerably change the LC phase behavior. Photoinduced alignment control has also been the focus of recent research activity due to the ability to induce structural and orientational alterations of the macromolecules that are localized at the surface of the construct.[99]

Most of the polyimide films currently used as LC substrates necessitate mechanical rubbing/buffing to induce the desired orientation and thus LC alignment. The use of photoalignment techniques eliminates the need for the mechanical buffing of the films used as LC substrates, which can damage the construct.[100] Photo-cross-linkable liquid crystalline polymers (LCP) have the added advantage of containing both photoactive groups and mesogens in their structures.[98] In particular, photo-cross-linkable side chain liquid crystalline polymers (SCLCP) are useful in manufacturing information storage devices, nonlinear optical devices, aligned membranes for permeation of drugs and gases, and flat television and computer displays.[98,101]

Work on coumarin SCLCPs began with the work of Schadt and co-workers, who studied LC alignment patterns with bias tilt angles.[101] Using the polymer and photoalignment reaction shown in Figure 7, they bypassed the abrasion process and produced a film which was optically and thermally stable to 200 °C. When coumarin side chains were used, the tilt angle changed from perpendicular to the electric field vector ($\hat{\mathbf{E}}$), as with the use of cinnamate side groups, to **n** (shown in Figure 7) which is a function of $\hat{\mathbf{E}}$ and **k**, the angle of the incident UV radiation.[101-103] The tilt angle of the coumarin SCLCP was adjustable from 0° to 90° by changing the polarization of the light. Coumarin SCLCPs performed better than cinnamate SCLCPs as the cinnamate SCLCPs undergo a competing cis/trans isomerization in addition to the [2+2] photodimerization, which leads to added complications.[99,104,105]

Schadt's publication spawned a number of other coumarin SCLCPs studies.[99,100,104-107] Obi and co-workers studied the factors that affected the align-

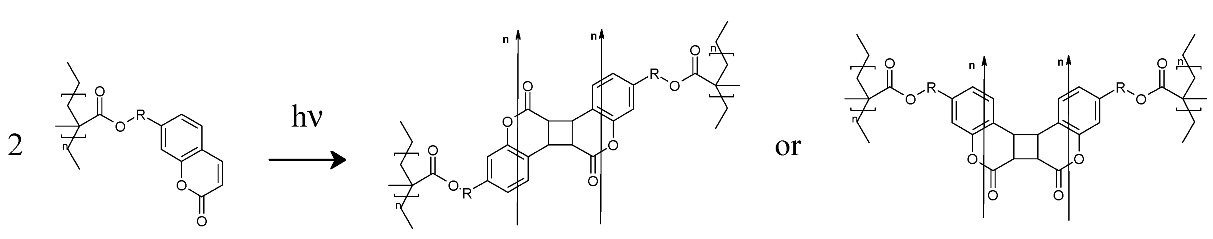


Figure 7. Side chain LCP used by Schadt and co-workers, where *n* = director direction and R = unspecified side chain spacer.[101]

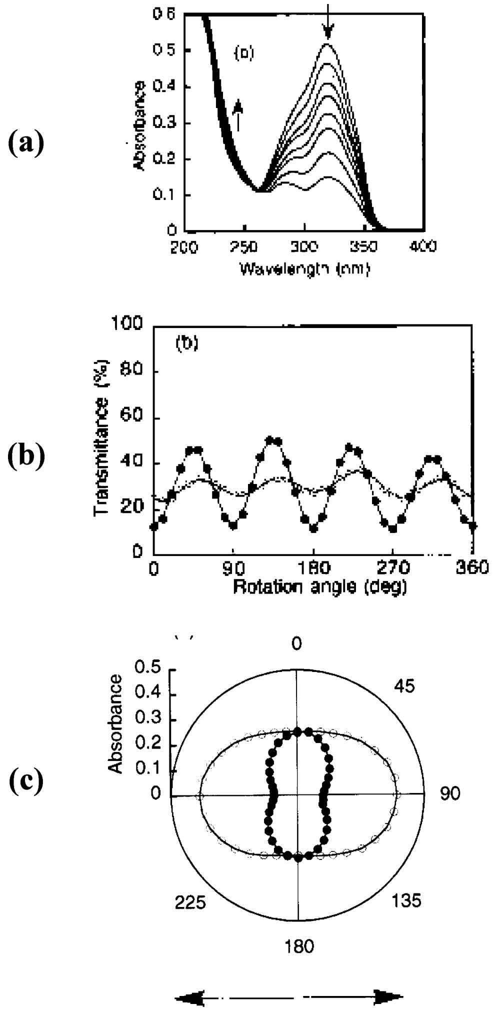


Figure 8. Coumarin SCLCP ($n = 2$). (a) UV absorbance change with irradiation at 313 nm (arrows indicate trends with increasing irradiation time). (b) Percent transmittance of linearly polarized light as a function of LC cell rotation angle after exposure doses of (○) 5 and (●) 10 mJ/cm^2. (c) Circular diagram absorbance of a dichroic dye in an LC cell (coumarin SCLCP with $n = 0$) after exposure doses of (○) 1 and (●) 10 J/cm^2.[99]

ment of coumarin SCLCPs using a polymer similar to the one used by Schadt.[99] Obi's study defined the R group in the side chain as $(CH_2)_n$ with $n = 0$, 2, or 6. The results of their study on the polymer with $n = 2$ is shown in Figure 8.

Figure 8a is a plot of UV absorption versus wavelength and shows the decrease in absorbance at 320 nm resulting from the dimerization of the coumarin group. As the coumarin dimerizes, the level of unsaturation decreased due to the formation of cross-links between cyclobutane rings. Figure 8b illustrates the influence of irradiation on the azimuthal orientation of a LC cell. With an irradiation of 10 mJ/cm^2, the LC cell shows homogeneous alignment. The results from this study indicated that the coumarins photodimerized without any side reaction (such as the isomerization observed with the use of cinnamates). Additionally, an increase in dimerization speed was observed with increasing spacer length, a result attributed to increased molecular mobility.

Obi's study revealed that the alignment direction of the coumarin SCLCP without a methylene spacer ($n = 0$) changed on prolonged polarized irradiation. With short irradiation times, the film's orientational alignment was parallel to the polarization direction (**P**). With further irradiation, the alignment degraded prior to adopting an alignment perpendicular to **P**. Figure 8c shows the circular diagram of absorbances of a dichroic dye in a LC cell fabricated from the SCLCP polymer with $n = 0$ and the direction of the electric vector of the incident light. The change in the shape of the plot indicated a reorientation of the LC from one that was parallel to the vector to one that was perpendicular. The polymers which were synthesized with two and six methylene spacers displayed no change in orientation and remained aligned parallel to **P**.[99,100]

Jackson and co-workers further studied orientation changes using the coumarin SCLCP shown in Figure 9a.[100,106,108,109] These researchers found that the alignment direction of the polymer was aligned parallel to **P** at small exposure doses (<0.72 J/cm^2), while the alignment switched to one perpendicular to **P** at a higher dose of 0.72 J/cm^2. This jump from parallel to perpendicular is plotted in Figure 9b as the change in Φ, the angle between the LC alignment direction at the photoaligned surface and the polarization direction of the incident beam. On the basis of birefringence, FTIR spectra, and anchoring data as a function of UV exposure, Jackson hypothesized that the parallel alignment was due to the initial photo-cross-linking of the dimers. Changes in the FTIR spectra coupled with the low birefringence of the system led to the conclusion that photo-cross-linking saturated after approximately 40% of the side chains had dimerized. As the polymer was exposed to more energy, the birefringence and anchoring energy increased. In addition, the alignment switched to one perpendicular to **P**, due to possible photodegradation of the nondimerized and photodimerized side chains. The photodegradation of the dimerized side chains entails the breaking of the cyclobutane rings, which lead to a decrease in the LC dispersive interaction parallel to **P**.

Degradation of the polymers was further studied using grazing angle X-ray reflectivity.[106] X-ray data

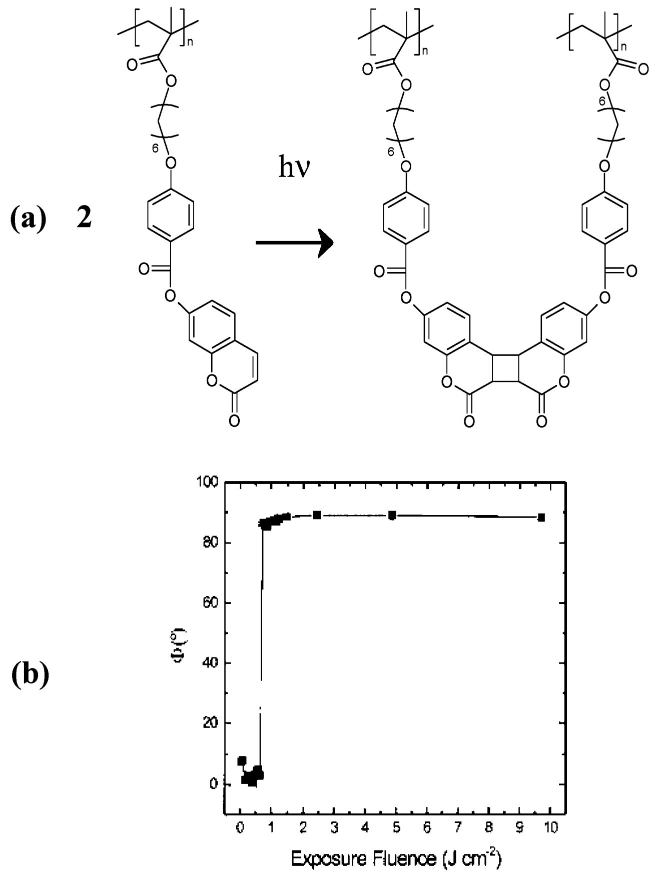


Figure 9. (a) Polymer and reaction studied by Jackson and co-workers, and (b) LC alignment direction measured with respect to P as a function of UV irradiation at $\lambda = 300.5$ nm.[100,106,108,109]

showed an increase in the surface roughness of irradiated coumarin SCLCPs spun-cast on silicon wafers, confirming polymer degradation. While degradation is usually undesirable in LC systems, Jackson and co-workers noticed no deterioration in the performance of their coumarin SCLCP after 2 years, once the alignment switched to perpendicular alignment to **P**.[100]

Using the same acrylate backbone, Tian and co-workers also studied the liquid crystalline properties of two series of coumarin side-chain polymers and coumarin-containing block copolymers.[107,110] Figure 10 shows examples of each polymer series studied and optical micrographs of the smectic A phase of the polymers at 190 °C. This group found that the chemical composition of the side groups at the 3 and 4 positions of the coumarin ring (see Figure 1a for the numbering scheme) greatly affected the LC phase. For example, when a polymer had a substituent in the third position such as the polymer shown in Figure 10a, the polymer exhibited a mesophase. When the fourth position had a substituent, the polymer had no mesophase. As for crystallinity, polymers in series 1 (Figure 10a) were amorphous while the polymers in series 2 (Figure 10c) exhibited a crystalline state.

Tian's group also synthesized di- and triblock copolymers of both the polymer in Figure 10a and polystyrene by atom transfer radical polymerization from a polystyrene macroinitiator.[110] GPC traces showed a distinct shift in the peak, which indicated quantitative initiation from the polystyrene macroinitiator. Irradiation of the homopolymers and copolymers led to coumarin dimerization and insolubility of the polymers. One difficulty with the study was encountered when the DSC curves were compared to the TEM micrographs of the diblock copolymers. The DSC thermograms showed only a single T_g (between 20 and 24 °C), which indicated phase mixing, and a high-temperature isotropic transition. The TEM micrographs indicated microphase separation, which should lead to two T_gs; one for the

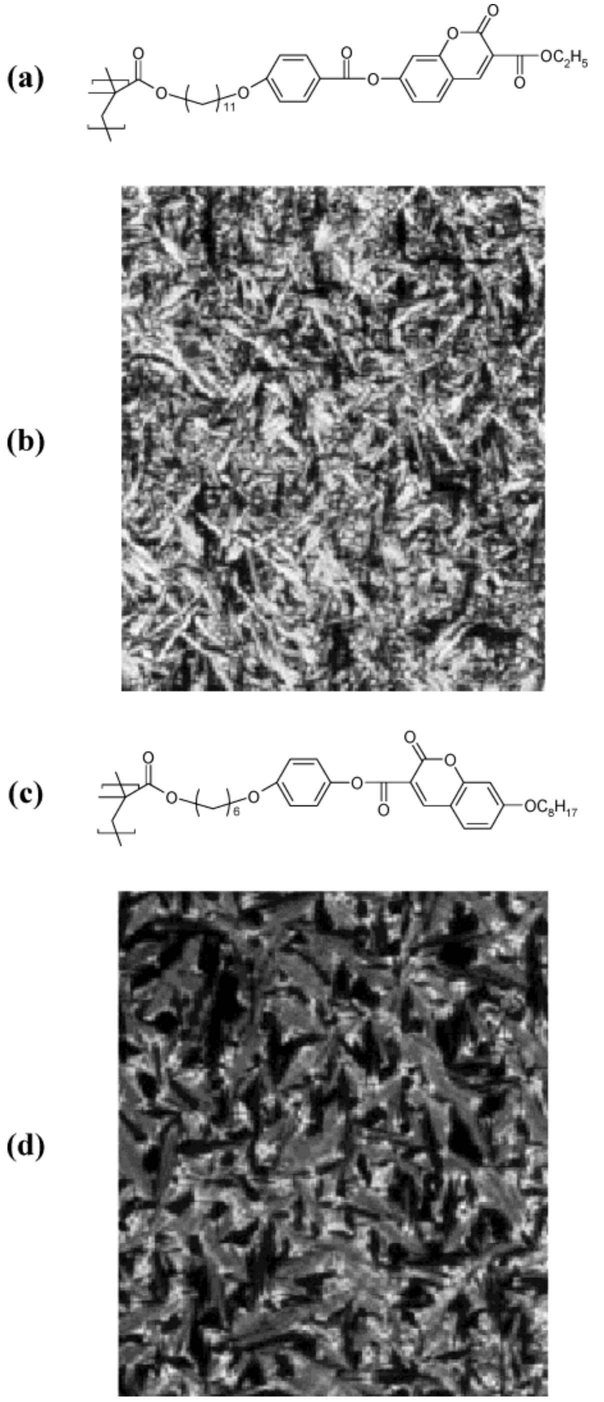


Figure 10. (a) structure of a series 1 polymer, (b) optical polarizing micrograph of smectic A phase of a, (c) structure of a series 2 polymer, (d) optical polarizing micrograph of smectic A phase of c. (Reprinted with permission from ref 107. Copyright 2000 John Wiley & Sons, Inc.)

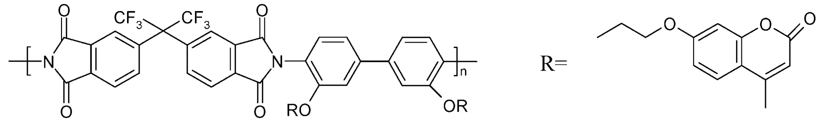


Figure 11. Structure of the coumarin SCLCP polymer studied by Ree and co-workers.[111]

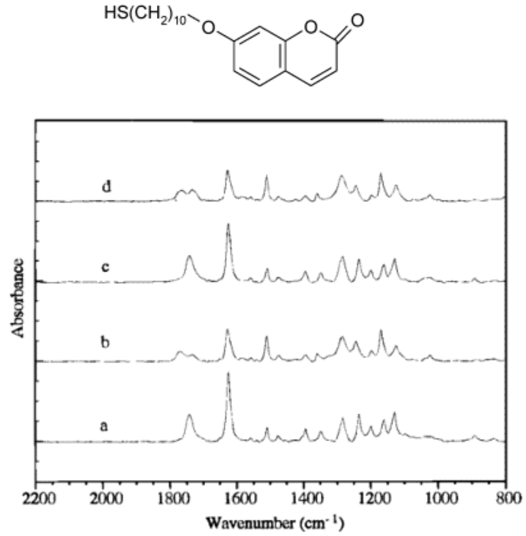


Figure 12. Structure of 7-(10-mercaptodecyloxy)coumarin and grazing angle FTIR spectra of a monolayer of 7-(10-mercaptodecyloxy)coumarin: (a) before dimerization, (b) after photodimerization, (c) after photocleavage, and (d) after a second dimerization.[114]

coumarin-containing block (between 10 and 20 °C) and one for the polystyrene block (near 100 °C). This contradiction was not described in their report. One interesting finding was the disappearance of the isotropic transition upon photo-cross-linking of the coumarin blocks.

Ree and co-workers recently studied the alignment behavior of photosensitive polyimides with coumarin and cinnamoyl side groups.[111] The polymer, shown in Figure 11, has an absorption maximum at 306 nm. An exposure dose of 7.5 J/cm^2 was sufficient to complete the coumarin groups in the polymer. As with the other coumarin SCLCPs, the photosensitive groups that aligned with the electric vector of the incident polarized light dimerized sooner that those with other alignments.[99−101,106,108,109,111] Dimerization of the coumarin groups reoriented the polymers with the new preferred alignment at the polymer surface.[111]

3.2. Photoactive Surfaces

Coumarins, in oligomeric as well as polymeric form, have been the focus of recent research. Oligomeric coumarins have been studied for possible photomemory and photoactive surface applications.[112−114] Fox's group studied the photodimerization of 7-(10-mercaptodecyloxy)coumarin) monolayers on gold using grazing angle FTIR, contact angle measurements, and surface fluorescence measurements. The structure of the coumarin molecule and the FTIR data are shown in Figure 12.

The FTIR spectra tracked the dimerization reaction through changes in the peaks at 1745 and 1626 cm^{-1} due to the C═O stretch and the C═C ring stretch, respectively. As the dimerization reaction proceeded, the carbonyl stretch splits into two peaks due to the emergence of the new nonconjugated carbonyl. Simultaneously, the peak at 1626 cm^{-1} decreased in size and the peaks due to the C═C bond (1200, 1161, and 1129 cm^{-1}) decreased in size and shifted as the double bond was broken to form the cyclobutane ring. With photocleavage, the two C═O peaks merge and the double-bond peaks increase in size and shift back to their original positions. The authors found quantitative recovery of the monomer upon photocleavage of the dimer. The water contact angle on the monomer was also reversibly changed from 58° to 63° for the monomer and dimer, respectively.[114] In a similar study, Fang examined the photodimerization of self-assembled monolayers of 7-(8-trimethoxysilyoctyloxy-)coumarin on silicon and quartz. Their research also demonstrated that the coumarin dimerization induced homogeneous alignment of the liquid crystal coumarin monomers.[112]

Tian and co-workers also studied oligomeric coumarin derivatives by attaching coumarins to cyclic tetramethyltetrasiloxanes.[113] The attachment was accomplished via the hydrosilylation of vinyl-terminated coumarin derivatives with 2,4,6,8-tetramethylcyclotetrasiloxane. Each of the cyclic coumarin-containing molecules with substitution at the 3 position of the coumarin group displayed mesomorphic properties. The length of the tail group (substituted at the 3 position) influenced the crystallizability of the molecules, i.e., longer tail groups displayed no melting transition while those with shorter tails melted. Ultraviolet-A (UVA) irradiation of the films cross-linked the molecules, although high-temperature irradiations were not performed to determine if the liquid crystalline phases could be locked in.

3.3. Electroluminescence Studies

Polymeric electroluminescent materials have distinct advantages over their inorganic counterparts, including ease of film preparation and color tunability throughout the visible spectrum.[115] Polymers garnering their electroluminescent properties from coumarin moieties have received some interest in both published and patent literature.[115−123] Uchida and co-workers patented a series of acrylate-based polymers consisting of a coumarin derivative and *N*-vinylcarbazole used in the production of an electroluminescent device.[118] They fabricated electroluminescent devices with colors ranging from red to violet by changing the coumarin derivative and the ratio of the number of coumarin groups to the number of *N*-vinylcarbazole groups in the polymer.

Fomine and co-workers studied the use of coumarin-containing polymers for electroluminescent devices and synthesized a wide range of polymers. By employing techniques such as ring-opening metathesis polymerization, free-radical polymerization,

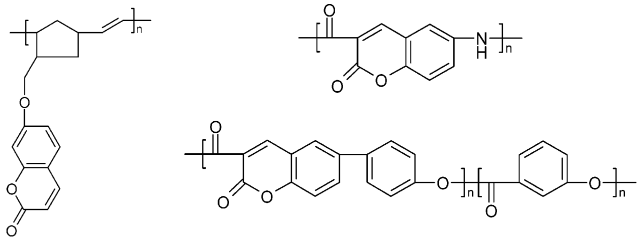


Figure 13. Examples of electroluminescent polymers synthesized by Fomine and co-workers.[115,116,120]

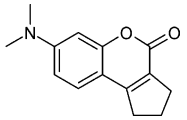


Figure 14. Structure of coumarin 138.

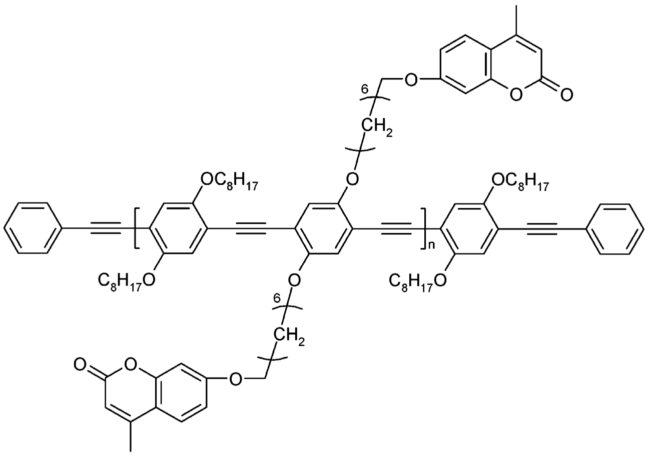


Figure 15. Coumarin-modified poly(*p*-phenyleneethynylene) studied for energy harvesting and transfer.[125]

and step-growth polymerization, they synthesized polyamides, polyesters, hyperbranched, comblike, and fully aromatic polymers containing coumarin groups.[115,116,119,120,122] Examples of some of the polymers synthesized are shown in Figure 13. All of their formulations displayed electroluminescence in the blue-green range. These polymers exhibited turn-on voltages of 3−6 V, which depended on the specific polymer structure.

3.4. Light and Energy Harvesting

The harvesting of solar energy has been a topic of interest for quite some time. Recently, coumarins have been incorporated into polymers in an attempt to harvest and transfer solar radiation energy.[124−128] These studies began in the early 1990s with the work of Lang and Drickamer on the energy transfer between 7-dimethylaminocyclopenta[c]coumarin (coumarin 138, Figure 14) and rhodamine B in a poly(acrylic acid) matrix.[124] The work on energy harvesting using coumarin groups was continued by Palmans and co-workers when they attached coumarin side groups to a poly(*p*-phenylene ethynylene) backbone resulting in the polymer shown in Figure 15.[125] The existence of energy transfer in the polymer was evidenced by the absence of donor emission (i.e., the emission of the coumarin group) and a large increase in the emission of the polymer when the polymer was irradiated at the excitation wavelength of the coumarin (λ_{ex} = 320 nm). Palmans and co-workers measured energy-transfer efficiencies of approximately 80%.

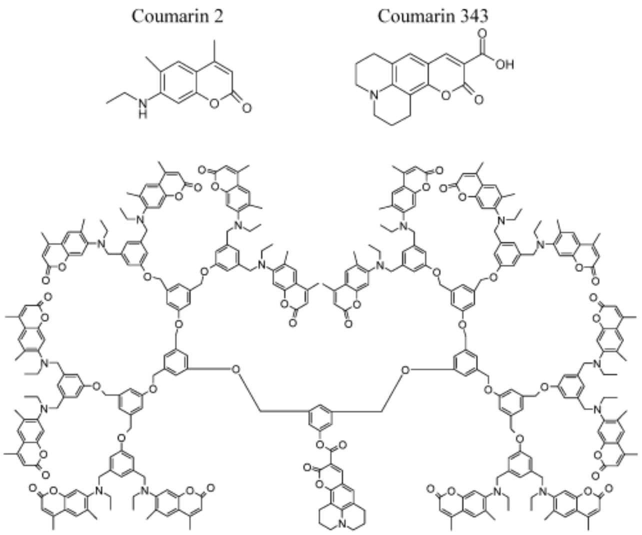


Figure 16. Structure of coumarin 2, coumarin 343, and the coumarin-labeled G-4 poly(aryl ether dendrimer).[127,130,131]

Fréchet and co-workers also studied energy transfer in coumarin-containing polymers.[126−131] Their first effort was the synthesis of coumarin-labeled poly(aryl ether) dendrimers. The dendrimers were envisioned as antennae with coumarin 2 (*H*-1-benzopyran-2-one, 7-(ethylamino)-4,6-dimethyl- (9CI)) groups at the periphery and a coumarin 343 (1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid, 2,3,6,7-tetrahydro-11-oxo- (9CI)) moiety as the core. The structure of the coumarins used and the fourth-generation (G-4) dendrimer are shown in Figure 16.[127,130]

The dendrimers were synthesized using a typical convergent strategy with the exception that the terminal and focal functionalities were reversed. Coumarin 2 (donor molecule) has an absorption in the range of 310−380 nm and emits between 400 and 480 nm in the range of absorption for coumarin 343 (acceptor molecule). Thus, coumarin 343 absorbs the emission from the coumarin 2 antennas and emits light with a maximum near 480 nm. As the dendrimer increases in generation, the number of coumarin 2 groups present in the dendrimer doubles and the dendrimer is able to absorb more light. The intensity of the emission of the dendrimer's core (the coumarin 343 molecule) also nearly doubles with each increase in generation, which indicated that the energy transfer from the antenna to the core was extremely efficient.

Also notable was a significant blue-shifting of the photoluminescence spectra as the generation increased from G1 (generation 1) to G4. The blue shift indicated film inhomogeneities in the lower generation polymers, which were later detected utilizing photoluminescence near-field scanning optical microscopy.[131] Utilizing steady-state and time-resolved fluorescence spectroscopy, Fréchet measured the energy-transfer efficiency of each generation of the dendrimers, which ranged from a low of 92.0% to a high of 98.9%.[127,130]

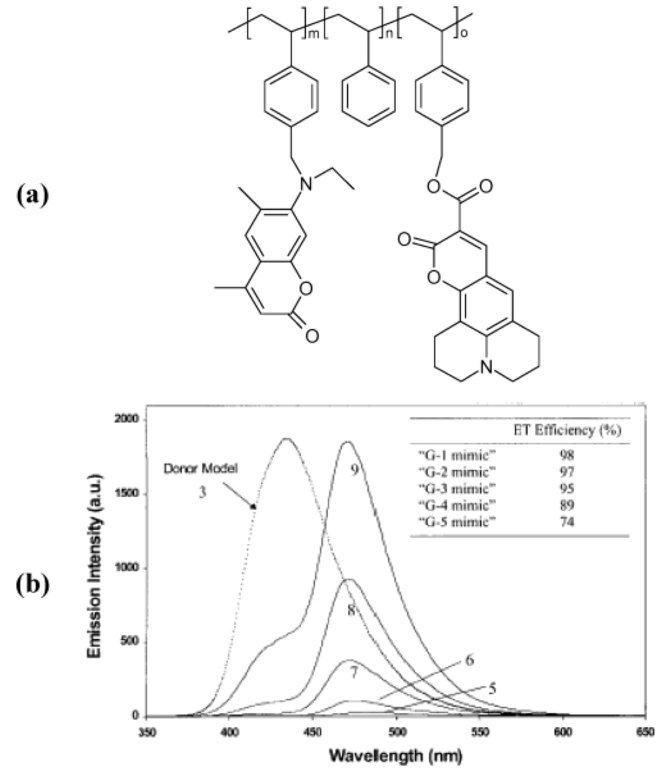


Figure 17. (a) Structure of the coumarin-labeled polymers, and (b) emission spectra and energy-transfer efficiencies of the polymers with 3 = no acceptor moieties, 5 = G-1 mimic, 6 = G-2 mimic, 7 = G-3 mimic, 8 = G-4 mimic, and 9 = G-5 mimic. (Reprinted with permission from ref 126. Copyright 2001 John Wiley & Sons, Inc.)

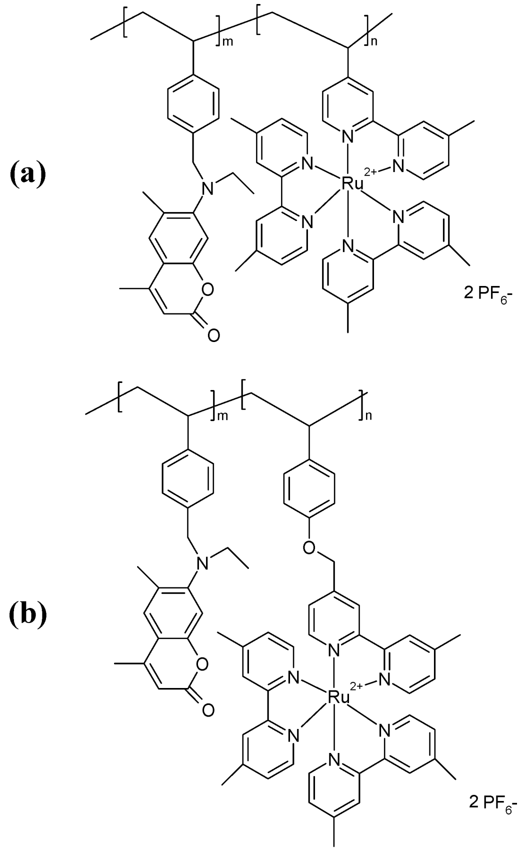


Figure 18. Coumarin-labeled ruthenium-containing metallopolymers.[128]

Although Fréchet's dendrimers harvested and transferred energy, they proved to be difficult to synthesize.[128] To circumvent the difficult synthetic methods, linear polymers with chemical compositions mimicking the first five generations of the dendrimers were synthesized.[126,128] Coumarin 2- and coumarin 343-functionalized monomers were synthesized by reacting the respective coumarin with vinyl benzyl chloride. Coumarin 2- and coumarin 343-functionalized polymers were synthesized by polymerizing the vinyl benzyl-functionalized coumarins with styrene. The general structure and emission spectra of the resulting polymers are shown in Figure 17. The coumarin-labeled polymers had comparable energy-transfer efficiencies to the model dendrimers. Unfortunately, the coumarin-labeled polymers also had some undesirable properties not present in the dendrimers such as low fluorescent quantum yields and low solubilities in nonchlorinated and nonpolar solvents.

Fréchet and co-workers also studied the vinyl benzyl coumarin 2 and ruthenium complexes shown in Figure 18.[128] The metallopolymer shown in Figure 18a exhibited an energy-transfer efficiency of 70%. It also exhibited a 5-fold increase in the fluorescence of the ruthenium complex when irradiated at wavelengths that excite the coumarin groups, versus irradiation at the wavelength, which excites the ruthenium complex. Similarly, the polymer shown in Figure 18b had an energy-transfer efficiency of 95% and a 3.6-fold increase in the fluorescence of the ruthenium complex. When a second coumarin chromophore was added (coumarin 343), a terpolymer was formed and the absorption and luminescence properties of the metallopolymers were improved compared to the single-coumarin-containing polymer. The metallopolymers are under continuing research for use in photonic and photovoltaic devices.

4. Polymer Photoreversibility

The ultraviolet light-triggered photodimerization of cinnamates,[4−8,104,132−152] chalcones,[153,154] anthracenes,[143,155,156] acridiziniums,[143,157] stilbazolium salts,[158,159] and coumarins[2,26,66,67,71−74,77,78,80−84,86,99,100,104,106,107,111,112,117,135,143,160−183] has been well studied since it was first utilized in the photo-cross-linking of poly(vinyl cinnamate) by Minsk and co-workers in the 1950s. With the exception of the anthracene groups that dimerize via a [4+4] cycloaddition, the photodimerization proceeds by the [2+2] cycloaddition of the ethylenic groups above 300 nm.[143,155] In addition to the cycloaddition reaction, photocleavage allows some dimers to revert to their original structure.[77,83,84,161−164,168,183,184] For example, cyclobutane rings that are derived from α-truxxilate, *β*- or *δ*- truxinates, and the coumarin and thymine dimers reverse upon irradiation near 250 nm.[132] When the cyclobutane rings formed by coumarin dimers are used as cross-links or branch points in polymers, the cross-link is breakable, thus reducing the cross-link density of the light-modified polymer.

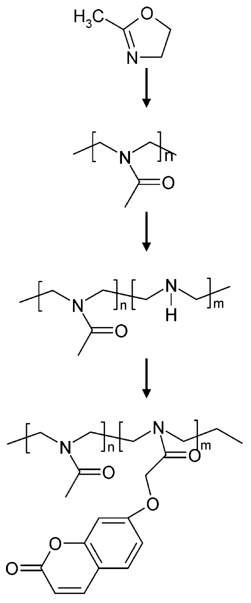


Figure 19. Synthesis of Saegusa's coumarin-modified polyoxazoline.[183]

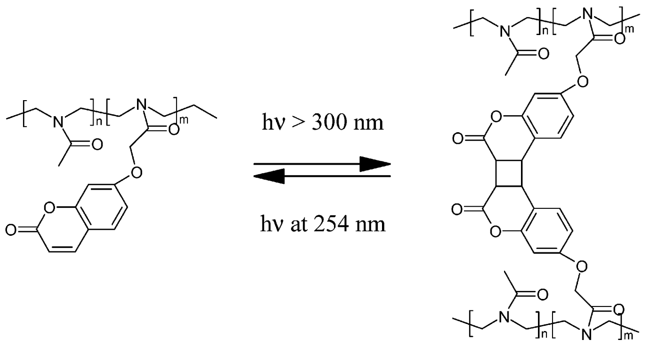
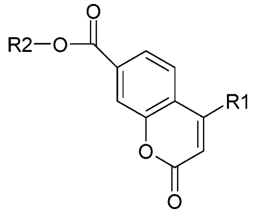


Figure 20. Reversible photo-cross-linking of the coumarin-modified polyoxazoline.[183]

4.1. Reversible Photo-Cross-Linking and Photocleavage

While coumarin groups were first incorporated into polymers in the mid 1960s, they were not utilized for their reversibility until the late 1980s.[2,183,184] Saegusa and co-workers studied the gelation and reversible gelation of polyoxazolines. Saegusa synthesized polyoxazolines via the ring-opening polymerization of 2-methyl-2-oxazoline, and then modified the polymer by hydrolyzing the pendent methyl group and reacting it with 7-coumaryloxy acetic acid (shown in Figure 19).

The resulting polymer had degrees of coumarin substitution between 1.2% and 30.4%. The photodimerization of the polymer was performed with a 450 W high-pressure Hg lamp for up to 3 h, while the photocleavage reaction was accomplished with 253 nm irradiation for 2 h (reaction shown schematically in Figure 20). After 30 min of irradiation, an insoluble gel with a swelling ratio of 14:1 (w/w H_2O/gel) formed. Further irradiation increased both the gel yield (to 69%) and the cross-link density. UV–vis spectroscopy indicated that 95% of the coumarin groups had dimerized with 350 min of irradiation. UV–vis spectroscopy and swelling experiments verified the photocleavage of the coumarin polymer, showing that 55–60% of the dimer reverted back to the starting material. Cross-linked polymer films irradiated for long times were not soluble after irradiation at 253 nm. Films that were photo-cross-linked for shorter times and rendered insoluble in methanol, however, dissolved after irradiation at 253 nm. This study was the first to demonstrate the photoreversibility of cross-links using coumarin groups.



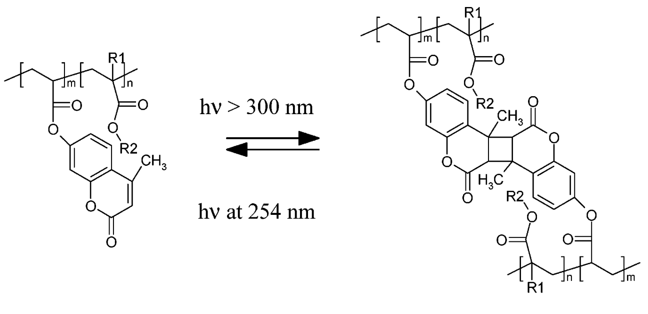
R1	R2
CH_3	CH_3-CH_2
CH_3	CH_3-$(CH_2)_{13}$-CH_2-
H	CH_3-CH_2
H	CH_3-$(CH_2)_{13}CH_2$

Figure 21. Structure of the coumarin derivatives synthesized by Chen and co-workers for dispersion in PVAc.[162]

Little work utilizing the reversible dimerization of coumarin in polymers was published until Chen and co-workers studied the reversible photodimerization of coumarin derivatives in poly(vinyl acetate) (PVAc).[162] Previous studies from Chen's group dealing with optically active polymers containing coumarin moieties will be described in section 5.2.2. In their photoreversible polymer studies, Chen attached alkyl chains to 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin resulting in the structures shown in Figure 21. The photodimerization (at 300 and 350 nm) and photoscission reactions of the coumarin derivatives were followed using UV–vis spectroscopy. They demonstrated that their coumarin derivatives underwent dimerization at 300 and 350 nm, with the dimerization occurring more rapidly for the derivatives with the longer alkyl chains. Chen's work also found that the coumarin derivatives with the methyl group at the 4 position dimerized at a rate 200 times quicker at 350 nm and 2 times faster at 300 nm than those without the methyl group.

Building on their work with coumarin derivatives in PVAc, Chen and co-workers synthesized a number of polymers containing coumarin derivatives. They studied the photo-cross-linking and photoscission of polyacrylates and polyamides as well as the chain extension of polyethers, polyurethanes, and polyesters.[77,83,84,161,163,164,168] Chen copolymerized various acrylates with 7-acryloyloxy-4-methylcoumarin, resulting in the polymers shown in Figure 22 and corresponding to the cross-linked polymer structure.

Photo-cross-linking was performed in chloroform with irradiation at 300 nm, and the photoscission of the acrylate was conducted at 254 nm. The photoreactions were monitored using UV–vis spectroscopy (shown in Figure 23). Figure 23a shows the reduction



(a) (b)

Figure 22. (a) General structure and (b) dimerized (cross-linked) structure of coumarin-functionalized acrylic polymers. R1 and R2 are various alkyl groups.[83,163]

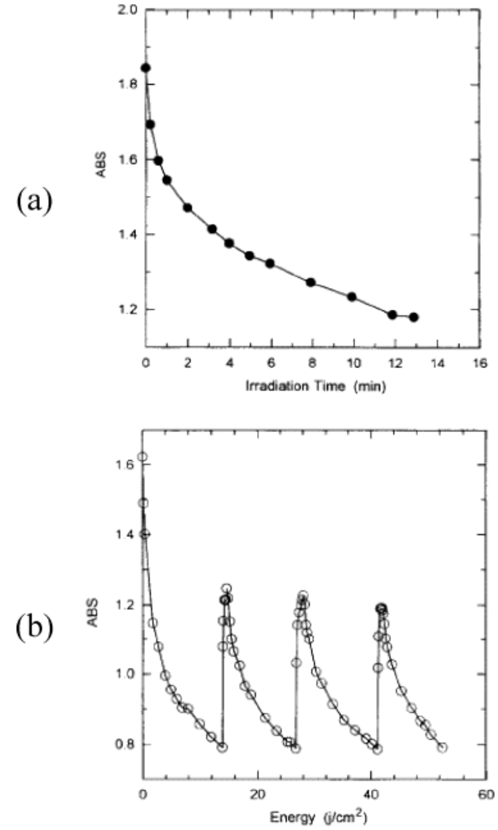


Figure 23. (a) Absorbance of polymer shown in Figure 22a at 310 nm as a function of irradiation time, and (b) change in absorbance due to irradiation at 300 (decrease in absorbance) and 254 nm (increase in absorbance). (Reprinted with permission from ref 163. Copyright 1996 Elsevier.)

in the absorbance of the acrylate polymer at 310 nm on cross-linking. As the cyclobutane cross-links form, the coumarin double bond, which absorbs at 310 nm, disappears. The change in absorbance due to the photo-cross-linking and photoscission reactions is shown in Figure 23b. The increase in the absorbance at 310 nm is indicative of scission of the cyclobutane ring and reversion to the starting material. The amount of photoscission at 254 nm was found to be the result of a dynamic equilibrium, with both cross-linking and scission occurring at 254 nm. These researchers performed a similar study with copolymers synthesized from *n*-(1-phenylethyl)acrylamide and 7-acryloyloxy-4-methylcoumarin.[168] Similar to the acrylate study, polymers that were reversibly cross-linkable in solution were also obtained.

4.2. Reversible Photoextension and Photocleavage

In our labs, we studied the reversible chain extension of coumarin-functionalized poly(ethylene glycol) methyl ether and telechelic PEG oligomers.[185] PEG monols were quantitatively functionalized with 7-hydroxycoumarin acid chlorides (Figure 24) then solvent cast from chloroform onto glass microscope slides. UVA irradiation of the films dimerized and chain-extended the PEG molecules as observed with UV−vis spectroscopy (Figure 25a). Subsequent irradiation at 254 nm cleaved and reverted the dimers to their initial state (Figure 25b).

Chen and co-workers also studied the reversible chain extension of a series of polymers in solution, including polyesters (Figure 26a), polyethers (Figure 26b), and polyurethanes (Figure 26c) endcapped with coumarin groups.[77,84,161,164] The reversible photoextension and photocleavage reactions of the polyurethanes and polyethers were monitored using UV−vis spectroscopy. The results of the absorbance measurements as a function of irradiation time and wavelength resemble those shown in Figure 23a and 23b, which indicated the dimerization and cleavage of the coumarin group. They also studied the effect of the presence of a methyl group at the coumarin 4 position. While the major photoproduct of the chain-extended polymers without the methyl group was the head-to-head form of the dimer, the presence of the methyl groups produced the head-to-tail form of the dimer (see section 2.3 for description of head-to-head versus head-to-tail).

Chen and co-workers also discovered differences in the photocleavage reaction between the methyl-substituted coumarin and the non-methyl-substituted coumarin; the methyl-substituted polymer was more reversible than the other polymer. In both studies, the photodimerization reaction proceeded more rapidly when irradiated at 300 versus 350 nm, due to a better match of the coumarin absorbance using the 300 nm light. Photocleavage at 254 nm proceeded more rapidly than the photodimerization at both 350 and 300 nm. In addition to the effect of wavelength on photodimerization rate, the addition of benzophenone (which is a triplet photosensitizer, see section 2.3) also increased the dimerization rate without changing the photocleavage rate.[84,161,164]

Chen's group utilized fluorescence spectroscopy, solution viscosity, and absorbance measurements to characterize the photoreactions of coumarin-end-capped polyesters (Figure 26a).[77] The results indicated similar trends to those established in their studies on polyethers and polyurethanes with regard to 4-methyl substitution, polarity of the solvent, and addition of benzophenone. Fluorescence spectroscopy results of the unsubstituted polyester dissolved in DMSO after 2 h of irradiation at 350 nm revealed a second broad peak centered at 510 nm. This peak was indicative of the emission of the singlet excimer. The second peak was not present when either the polyester was dissolved in dichloromethane or the 4-m-

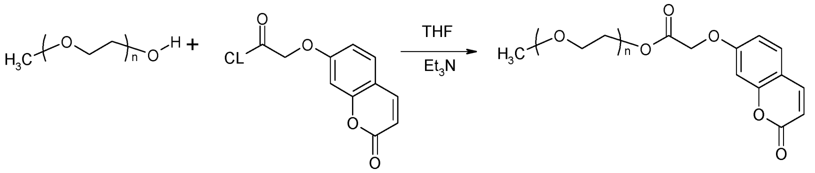
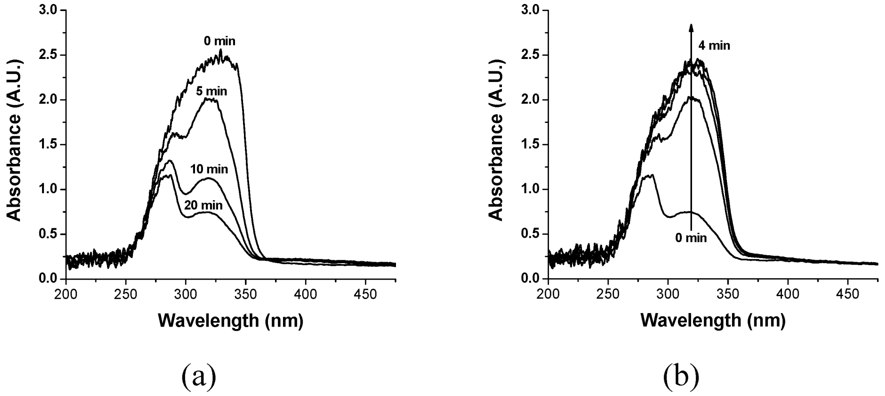


Figure 24. PEG methyl ether modification reaction scheme.



(a) (b)

Figure 25. (a) Decrease in UV absorbance of coumarin-modified PEG with UVA irradiation, and (b) the increase in UV absorbance of chain-extended, coumarin-modified PEG with 254 nm irradiation.

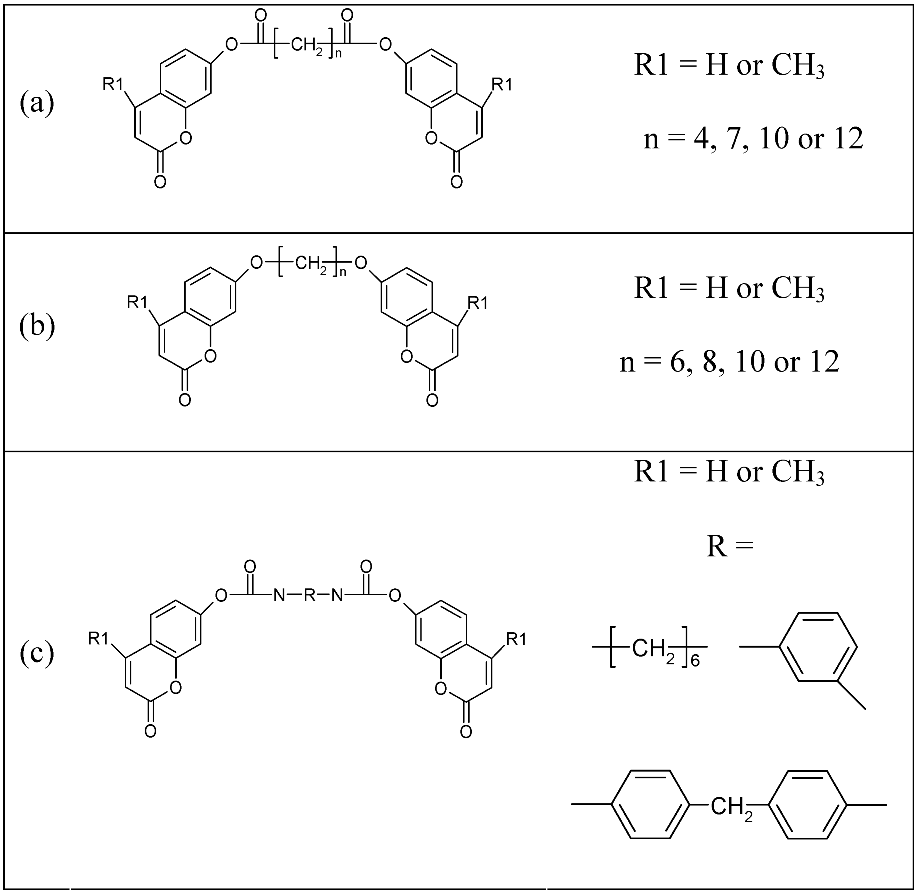


Figure 26. Coumarin-endcapped (a) polyesters, (b) polyethers, and (c) polyurethanes studied by Chen and coworkers.[77,84,161,164]

ethyl-substituted polyester was studied. The lack of the second emission band in dichloromethane was due to the heavy-atom effect described in section 2.3.

Chen and co-workers concluded that the polymers (when dissolved in DMSO) undergo the same singlet reaction scheme as monomeric coumarin (shown in Figure 2). In dichloromethane, alternatively, dimerization proceeded through the triplet state (also shown in Figure 2). The reversibility of the photodimerization was observed with absorbance and viscosity measurements shown in Figure 27. The measured absorbance increased at 312 nm which was due to the formation of the double bonds (Figure 27a). The intrinsic viscosity decreased from 0.42 to 0.008

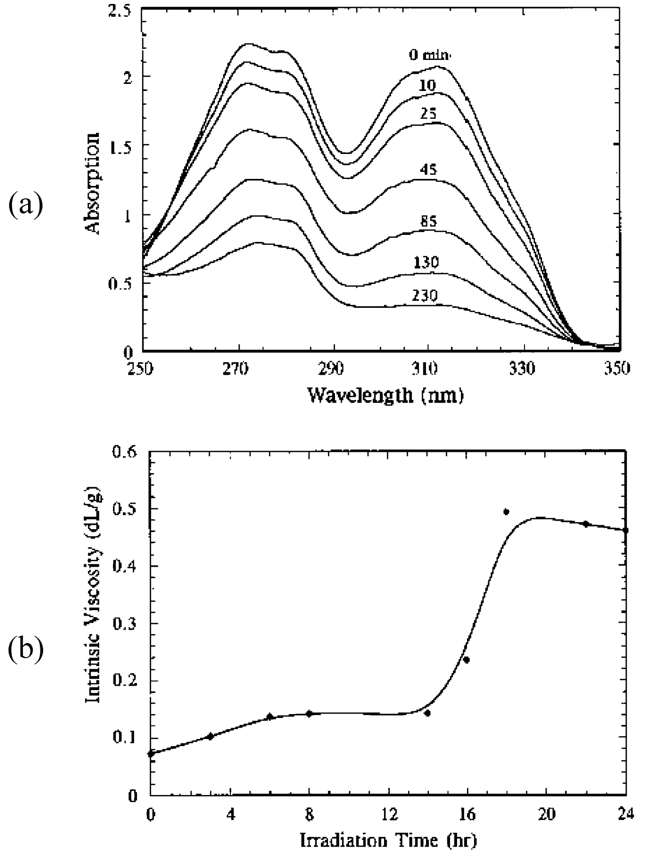


Figure 27. Change in (a) absorbance and (b) intrinsic viscosity of the polymer shown in Figure 33a ($n = 10$) as a function of irradiation time. (Reprinted with permission from ref 77. Copyright 1997 John Wiley & Sons, Inc.)

dL/g with 4 h of irradiation, which is also indicative of a decrease in molecular weight (Figure 27b).

5. Coumarins in Biomaterials and Other Studies

5.1. Biomaterials

Photoreactive biopolymers have recently received increased attention in biological materials and processes.[176,182] Since the early 1980s, Yamamoto and co-workers have studied photoresponsive peptides and polypeptides, initially focusing on the optical activities of phenylazobenzyl-modified poly(L-lysine).[176,182,186−196] Recent work has shifted to the photo-cross-linking of polypeptides containing coumarins for the preparation of biodegradable cross-linked materials. The two polypeptides studied were based on L-ornithine (Orn, $C_5H_{12}N_2O_2$) and L-lysine (lys, $C_6H_{14}N_2O_2$) and coumarinated versions of the peptides as shown in Figure 28. Both polymers were synthesized containing 0−100 mol % of the coumarinated peptide. Both studies found that the rate of biodegradation of both polymers by enzymes (trypsin or protease type XXIII) or by soil fungi was controlled by the ratio of coumarinated to native protein and by the cross-link density of the polypeptides.[176,182]

Matsuda and co-workers synthesized 4-arm stars based on random copolymers of ϵ-caprolactone (CL) and trimethylene carbonate (TMC) and subsequently endcapped the arms at the hydroxyl terminus with coumarin groups (poly(CL/TMC)).[172−175,197] The chemical structure of the stars is shown in Figure 29. The goal of these studies was to design liquid photocurable precursors that were amenable to photo-cross-linking into desired geometries for the microfabrication of medical devices and drug encapsulation. The authors utilized stereolithography to photo-cross-link the stars, build three-dimensional structures, and study the degradation of the cross-linked stars both in vitro and in vivo (subcutaneously).

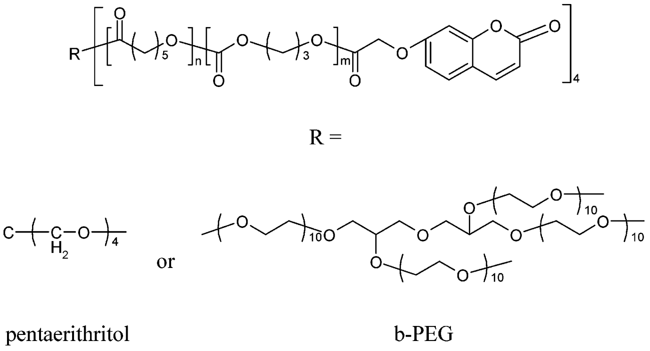


Figure 29. Structure of poly(CL/TMC).[172,174,175]

Scanning electron photomicrographs of the three-dimensional photo-cross-linked (60 min at 10 mW/cm^2) constructs are shown in Figure 30. The labels on the images refer to the chemical composition of the construct. Sample "e" was prepared from b-PEG with a ratio of 0.49 CL:0.51 TMC. Samples "b" and "d" were prepared from the pentaerithritol with ratios

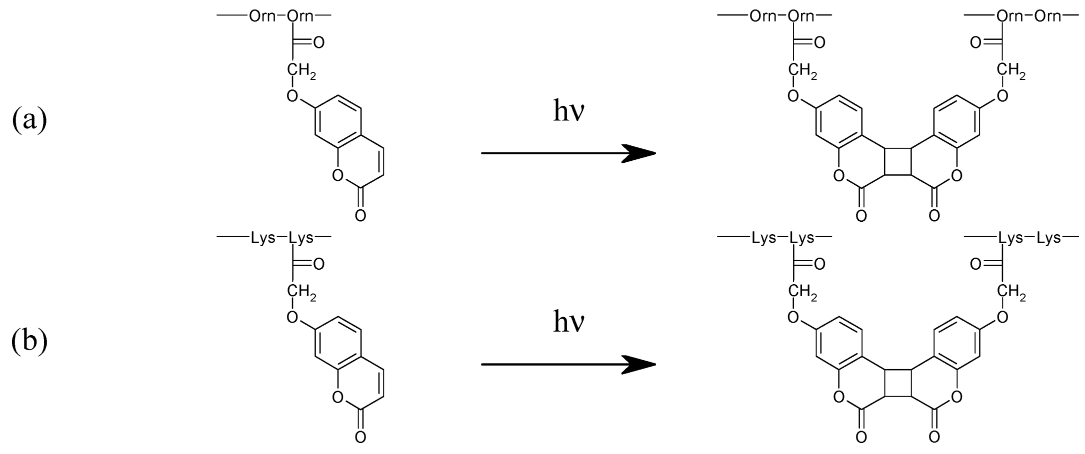


Figure 28. General structure and photo-cross-linked structure of (a) ornithine and (b) lysine polymers.[176,182]

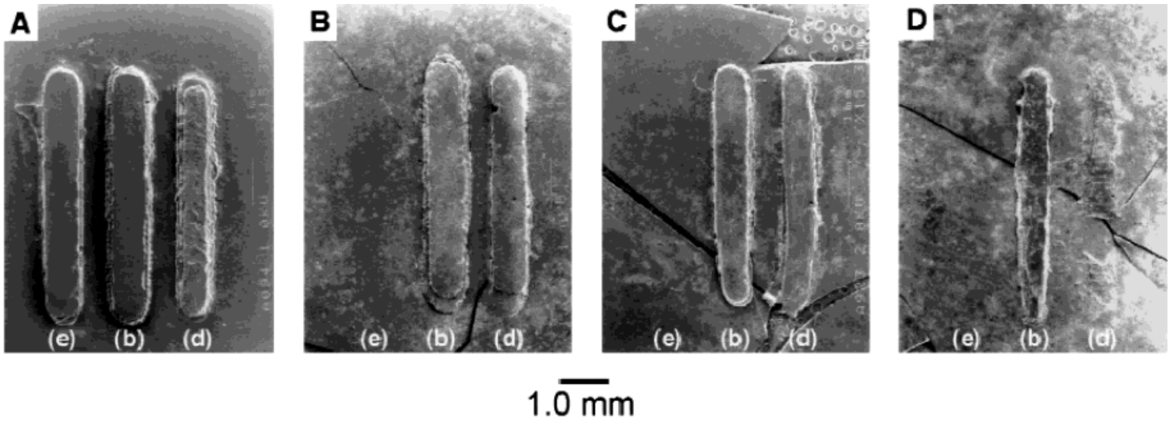


Figure 30. Scanning electron photomicrographs of films (A) before implantation, (B) after 1 month of implantation, (C) after 3 months of implantation, (D) after 5 months of implantation. (Reprinted with permission from ref 172. Copyright 2002 John Wiley & Sons, Inc.)

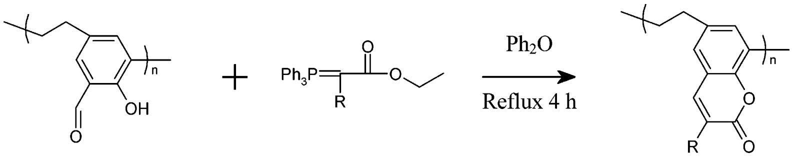


Figure 31. Synthesis of poly(3-substituted coumarin ethylene) under Witting reaction conditions.[160]

of 0.49 CL:0.51 TMC and 0.00 CL:1.00 TMC, respectively. As implantation time increased, the disappearance of the materials due to surface erosion was evident (with sample "b" degrading at the slowest rate). They were able to manufacture tailor-made and precision-shaped templates, in vitro degradation tests of the films were good indicators for the in vivo degradation, and surface erosion proceeded without causing any significant tissue damage.[172]

The biological activity of poly(coumarin ethylene)s has been recently studied by Patel and co-workers. The authors synthesized poly(3-substituted coumarin ethylene) by reacting salicylaldehyde-1,2-dichloroethane resin ($M_n = 1530$ g/mol) with various carbethoxytriphenyl alkylidine phosphoranes under Wittig, Knoevenagel, and Perkin reaction conditions, as shown in Figure 31.[160] They also reacted a polymer synthesized from salicylaldehyde and 1,2-dichloroethane with carbethoxytriphenyl alkylidine phosphoranes under Perkin and Knoevenagel reaction conditions with *N*-acetyl glycine and ethyl acetoacetate, respectively. The polymers were tested for their toxicity using fungal growth measurements. All of the polymers exhibited less than 50% inhibition on the growth of *Aspergillus niger* and insignificant inhibition on the growth of *Antrodiella* leading to the conclusion that the polymers display no considerable toxic effect on fungal growth.

5.2. Other Studies

5.2.1. Fluorescent Tags and Fluoroprobes

As previously mentioned in section 2.2, coumarins exhibit fluorescence, and this feature was exploited to monitor the kinetics of activation/deactivation in the living free-radical polymerization of a TEMPO (2,2,6,6-tetramethylpiperidyl-1-oxyl)-capped polystyrene.[156,198] The nitroxide switch, shown in Figure 32, fluoresces when it traps macroradicals. When the coumarin-modified nitroxide is added in excess to a TEMPO-mediated reaction, the trapping of the macroradical by the modified nitroxide is favored over trapping by TEMPO. The propensity of the modified nitroxide to trap the radical allowed the authors to determine the rates of radical formation by measuring fluorescence and, in turn, to determine bond dissociation energy (30.2 kcal/mol) for the C−O bond cleavage in the polystyrene−TEMPO system.

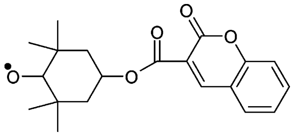


Figure 32. Coumarin-modified nitroxide switch.[198]

Coumarin fluoroprobes have also been studied for use in fluorescent ligand displacement assays for herbicide detection, in domain-forming polymers, and as an aid in measuring diffusion.[199−201] By binding 7-carboxymethoxy-4-methylcoumarin to a molecularly imprinted cross-linked polymer of 4-vinylpyridine and ethylene glycol dimethacrylate, researchers have manufactured a competitive assay. As the herbicide enters the polymer and the imprinted regions, the coumarin probe is displaced and the fluorescence of the imprinted polymer decreases. The sensitivity of the system was determined to be approximately 100 nM.[200,202] A review of the utility of imprinted polymers for immunoassays is provided by Bruggemann et al.[203]

Similarly, coupling coumarin 343 to poly(organosiloxane) microgels (radius ≈ 10 nm), the particles can be used as tracers in diffusion studies using fluorescence correlation spectroscopy.[201] Schmidt and coworkers attached the coumarin to the core of the particle, which prevented it from interfering with the diffusion behavior of the particle under investigation. Although there have been further studies on the

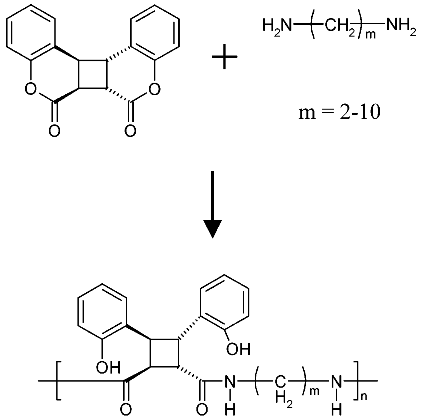


Figure 33. General reaction scheme used to synthesize optically active polymers.[179]

formation of poly(organosiloxane) microgels for use as cocatalysts, no further work has been published on the coumarin-derivatized microgels.[203−207]

The fluorescent properties of the 7-aminocoumarins (coumarin 7, coumarin 30, and coumarin 6) have also been utilized as probes to study domain-forming polymers and polysaccharides.[21,199,208] As a result of solubilizing the dyes in the polyelectrolyte poly(methacrylic acid), researchers correlated changes in the fluorescence wavelength, quantum yields, lifetimes, and polarization of the coumarins in water to changes in the identity of the bound dye due to pH and the conformational details of the macromolecule. These changes led to the production of a monitoring system for macromolecular properties in solution by fluorescence measurements. Similarly, initial research by Carré and co-workers indicated that coumarin-functionalized dextrans were suitable for use as fluoroprobes to characterize the cell−carbohydrate interactions.[208]

5.2.2. Chiral Stationary Phases for HPLC

Because many drug and pharmaceutical compounds show different activities between their optical isomers, optical resolution of enantiomers has become an important research topic.[167] To design a chiral stationary-phase packing material for HPLC columns, Hasegawa and co-workers synthesized optically active polymers containing coumarin dimer components.[86,165−167,170,178−180] The reaction scheme used for the synthesis of the optically active polymers is based on ring-opening step-growth polymerization and is shown in Figure 33.

From this scheme, the authors synthesized a number of chiral stationary phases by varying the methylene spacer ($m = 2-10$) and tested the effectiveness on over 20 different racemates with varying degrees of success. The polymer in Figure 33 displayed an even−odd discrimination: polyamides with an even methylene number (m is even) showed chiral recognition ability, whereas those with an odd methylene number showed no chiral recognition.[177,179] Chen, who was Hasegawa's co-worker, continued the work on optically active polymers with the synthesis of optically active polyurethanes by a polyaddition reaction of the ring-opened dicoumarin and 4,4′-diphenylmethane isocyanate.[165,167] The polyurethanes displayed satisfactory resolution ability to some of the aromatic racemates tested.

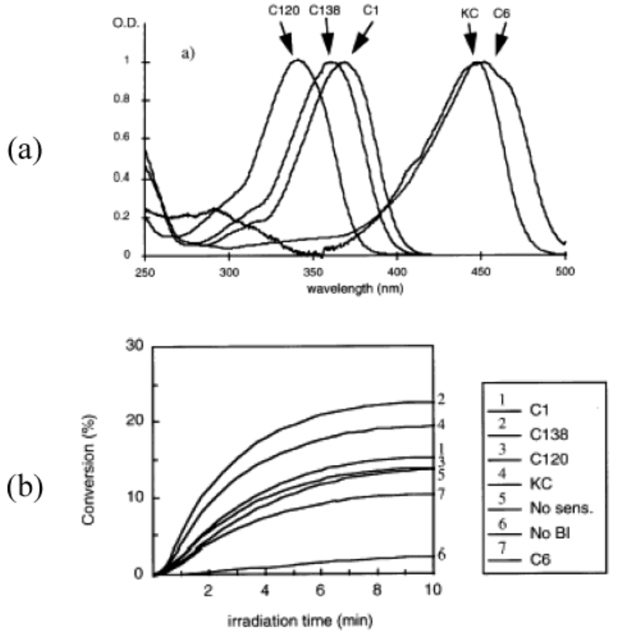


Figure 34. (a) Absorbance of the coumarin derivatives used as photosensitizers in the photopolymerization of styrene, and (b) conversion as a function of irradiation time at 405 nm. No sens. = no sensitizer, No BI = no chlorohexaaryl-bisimidazole radical initiator. (Reprinted with permission from ref 209. Copyright 2001 Elsevier.)

5.2.3. Polymerizations

Coumarin derivatives have recently been utilized as initiators in free-radical and two-photon polymerizations.[209−213] Mixtures of various coumarin derivatives were used as sensitizers in photoinitiating systems for acrylic monomers.[209] The coumarins were chosen due partially to their absorbance in the UV and visible regions, as shown in Figure 34a, which allows for the initiation of polymerization using visible light. Figure 34b illustrates that the presence of coumarin derivatives enabled an increase in conversion and polymerization rate for photopolymerization initiated at 405 nm.

Singh and co-workers investigated the use of 4-hydroxycoumarin in the enzyme-mediated free-radical polymerization of styrene with the aim of finding a more environmentally friendly method to produce polystyrene.[211] The reaction mixture included styrene, horseradish peroxidase, hydrogen peroxide, and the initiator dissolved in a 7:3 mixture of water and THF. Of the initiators used, 4-hydroxycoumarin generated polystyrene at a 14.5% yield with a molecular weight of 57 200 g/mol and a polydispersity of 1.64, the lowest polydispersity of the initiators studied.

Two-photon polymerization affords the ability to achieve higher spatial resolution than conventional photoinitiated polymerizations.[213] Qihuang copolymerized 2-hydroxyethyl acrylate and dipentaerythritol using a three-part initiating system consisting of *N*-phenylglycine, titanocene, and 7-diethylamino-3-(2′-benzimidazyl) coumarin. It was proposed that the coumarin derivative absorbed light from an 800 nm laser and excited the coumarin derivative to the triplet state. The excited coumarin then transferred an electron to the *N*-phenylglycine, which initiated the copolymerization. Using this method, Qihuang's group was able to cure lines as narrow as 1.8 μm.

Walshe et al. utilized 7-hydoxycoumarin during the copolymerization of methacrylic acid and ethylene glycol dimethacrylate to form a molecularly imprinted polymer for solid-phase extraction.[214] Once the cross-linked polymer was isolated and pulverized, the 7-hydoxycoumarin was extracted, yielding the molecularly imprinted polymer. A column prepared with the polymer was utilized to selectively retain 7-hydoxycoumarin from various urine samples with 90% recovery.

6. Concluding Remarks

The use of coumarins in polymeric applications has increased greatly over the past few years and continues to expand. This growth can be attributed to the intriguing properties of the coumarin family, including conventional reaction chemistry to incorporate the groups on a number of different base molecules, tunable absorbance and fluorescence spectra, and the ability to photoreversibly dimerize. When incorporated into polymers, these properties can be exploited to achieve tailored macromolecules that have interesting and wide-reaching properties, a few of which have been highlighted here.

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