Multicomponent Polymer Materials: Photodegradation Mechanism

Dan Rosu, Cristian-Dragos Varganici and Liliana Rosu

Abstract The chapter follows two pathways into polymer photodegradation. The first one consists of an introduction into the obtaining of photodegradable polymers by inserting several photolabile entities, such as o-nitrobenzyl, coumarin-4-ylmethyl, p-hydroxyphenacyl or acetal, with emphasis on the o-nitrobenzyl group. The second and main pathway of the chapter encompasses literature studies related to photochemical decomposition mechanisms occurring in different types of multicomponent polymer systems. UV radiations, oxygen, temperature and humidity represent the main driving forces in polymer irreversible photochemical deterioration, occurring through radical intermediates (hydroperoxides, chromophore carbonyl groups or conjugated double bonds) as chained mechanisms.

1 Introduction

The designing of multicomponent polymeric systems is an interesting research field because of the multiple possibilities for obtaining new materials without resorting to complicated synthesis methods of new polymers. Polymer mixtures, interpenetrated and semi-interpenetrated polymeric networks are some of the most popular multicomponent polymeric systems. Also, the polymeric materials usually contain many other micromolecular substances such as: plasticizers, colorants, antioxidants, fillers and various types of additives that may affect the photochemical stability [1]. Although the interest in photochemical stability of polymeric materials is still limited to some photodegradation topics, such as degradative processes, the linkage

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between the degradative processes and chemoluminescence effects, modifications induced by light on chemical bonds, the sensitivity of polymers to different wavelengths and environmental issues, these still represent state of the art challenges [2]. The interest in photodegradable and/or photosensible polymeric materials significantly increased in recent years due to advantages of ultraviolet or visible light as trigger agent that can be easily controlled both spatially and temporarily [3–5]. Photodegradable polymeric materials are usually designed to check their degradability during exposure to sunlight.

Design of new polymers who are able of splitting into toxic fragments after overcoming their lifetime is, along with recycling, the main technique used to avoid the accumulation of plastic waste in the environment [6]. In the range of degradable plastics photodegradable polymers occupy a special place due to their multiple practical applications in agriculture as ground cover with plastic sheets (plasticulture) [7], in packaging industry and in household where the waste materials left after unpacking and the kitchenware plastics or the trash bags should quickly degrade without negative impact on the environment, in smart materials manufacture for microelectronics devices and in biomedical applications [8]. Hydrogels with photo-degradable bonds have high potential of applications in tissue engineering due to their possibilities of release on demand of bio-active principles or of cells included in the tridimensional polymer structure [9]. Some papers shows that small particles encapsulated in light sensible polymers with different structures have been designed with the purpose to decompose through photo-activation for releasing the active principles [10–12]. A careful handling of several parameters such as wavelength, light intensity, irradiation dose, temperature, exposure time and mechanical stress, the stability of the polymeric material, the degradation rate and its shape may be controlled [13]. By including in the polymer main chain of some photolabile chemical structures, such as o-nitrobenzyl derivatives (I), compounds based on coumarin-4-ylmethyl (II), p-hydroxyphenacyl (III) or acetal (ketal) moieties IV), polymeric materials with controlled photo-degradability have been obtained.
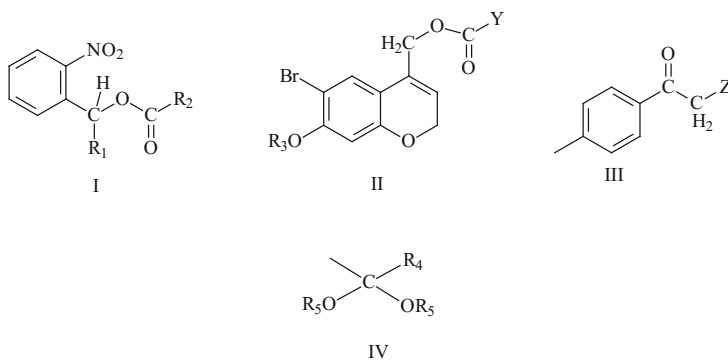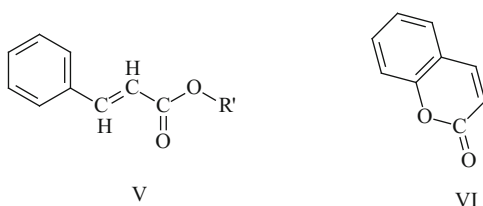
Photo reconfigurable polymeric materials contain some chemical structures such as cinnamate derivatives (V) or functionalized coumarin (VI), which are enabled via reversible photochemical dimerization [13].

Photoizomerization is another type of reversibile structural modification supported by the macromolecular chains during exposure to light [8, 13].

Some examples on photodegradative processes of different photochemical decomposition mechanisms of multicomponent based polymeric materials, either made photodegradable via incorporated specific entities or not, are further depicted in this chapter.

2 Photodegradation Mechanisms of Multifunctional Polymeric Materials

It is first of all worth mentioning that polymeric materials during photodecomposition are not fully degraded to lower molecular mass polymer chains by different photochemical reactions, rather photochemical reactivity introduces different functions, such as aldehyde, carboxylic acid, alcohol or ketone end-groups [14, 15]. Generation of these oxygen based end-groups may also account for further cellular β-oxidation processes occurrence [16, 17].

There are two basic pathways for obtaining photodegradable polymers, either by chemically modifying the polymer main chains with the insertion of a light responsive photodegradable chromophore entity, such as polyolefins or carbonyls [18], or by blending them with specific additives able of initiating photochemical decomposition processes (typically radical autoxidation reactions) within the polymer [6, 19, 20].

As previously discussed in the introductory chapter, the Norrish type reactions account for photodecomposition of polymers with carbonyl moieties, such as polyacrylates, polyesters and polyketones, and through abstraction of the hydrogen atom [21, 22]. After forming of free radicals through Norrish I reactions, photodegradation further proceeds via autoxidation.

Other chromophore entities than carbonyl ones may be used for obtaining photodegradable polymers, such as metal–metal bonds in the main chains, which undergo homolytic scission by absorbtion in the visible light domain [23–26].

Another pathway implied in the obtaining of photodegradable polymers consists in the blending of light responsive radical initiators. A very often used compound in

this sense is TiO_2 which generates free radicals capable of reacting with oxygen to yield hydroperoxides, as shown below.

$$TiO_2 \xrightarrow{\text{hv}} TiO_2^* \xrightarrow{O_2, RH} TiO_2 + R^{\cdot} + HOO^{\cdot}$$
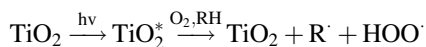
Cleavage of O–O bonds from hydroperoxides further assure photodecomposition together with alkoxy radicals β-scissions afterwards. Another route to polymer photodegradation resides in the further reactions of the hydroperoxides to generate other chromophores and/or new functional entities, such as carbonyls, carboxylic acids, alcohols and olefins, which further contribute to main chain scissions [6] (Scheme 1).

As previously discussed, the generated carbonyl entities further cleave main chains through Norrish reactions, while β-scissions are the main driving force in most polymer backbones photo-oxidative degradation [27] (Scheme 1). Specific UV absorbers may also be blended into the polymer for lowering or retarding the photodecomposition rate by reducing light intensity to carbonyl entities.

Another approach for obtaining photodegradable polymers consists in using the sol–gel technique to covalently couple different inorganic photosensitizers to specific polymer pendant moieties [28, 29], such initiators possessing solid state selectivity regarding inorganic aggregates [6].

Lei et al. [3]. reported the first photodegradable polymers multifunctionalization for micropatterns by firstly obtaining three ortho-nitrobenzaldehyde monomers, containing allyl, propargyl and epoxy entitites, through reacting 5-hydroxy-2-nitrobenzaldehyde with bromides of allyl, propargyl and with epichlorohydrin (Scheme 2) (Reproduced with permission. Copyright 2014, American Chemical Society [3]).

The obtained monomers were further polymerized through the Passerini multi-component polymerization pathway by further reactions with 1,6-hexanedioic acid
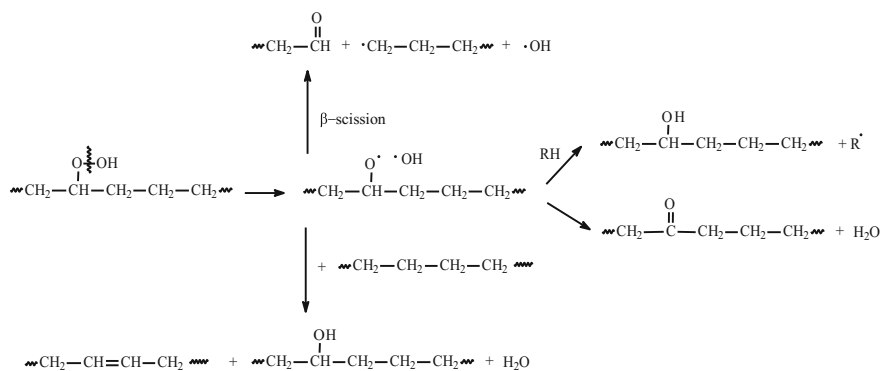

Scheme 1 Different reactions of hydroperoxides
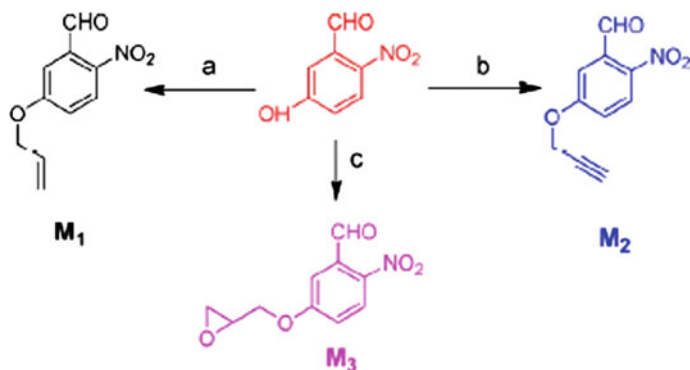
Scheme 2 Obtaining of functional monomers from 5-hydroxy-2-nitrobenzaldehyde. Reactions conditions: (*a*) allyl bromide, K_2CO_3, DMF, room temperature, overnight; (*b*) Propargyl bromide, K_2CO_3, DMF, room temperature, overnight; (*c*) epychlorohydrin, K_2CO_3, DMF, 80 °C, 24 h. Reproduced with permission. Copyright 2014, American Chemical Society [3]

P1 R=allyl
P2 R=propargyl
P3 R=glycidyl
P4 R=allyl / propargyl / glycidyl = 1/1/1
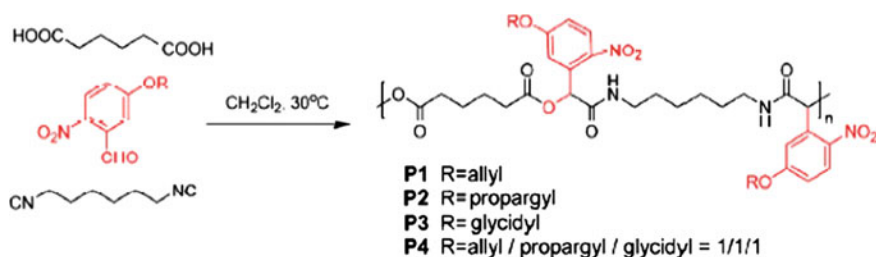
Scheme 3 Photocleavable polymers via the Passerini synthesis pathway. Reproduced with permission. Copyright 2014, American Chemical Society [3]

and 1,6-diisocyanohexane to yield three poly(ester-amides). The obtained polymers are thusly photodegradable through the ester bonds containing ortho-nitrobenzyl entities (Scheme 3) (Reproduced with permission. Copyright 2014, American Chemical Society [3]). Since the obtaining of photocleavable polymers consists of multistage time consuming processes, through the Passerini approach such disadvantages are greatly reduced by directly obtaining the desired polymers from o-nitrobenzaldehyde and further expanding their applications range [30].

The functional groups from the starting monomers may be further modified either by click chemistry, such as thiol-ene, epoxy-amine reaction and copper catalyzed azide–alkyne cycloaddition. Authors also applied the Passerini synthesis pathway to a mixture of the three initial monomers to obtain a combined photodegradable polymer with triple functionality (P4) (Scheme 4). Reproduced with permission. Copyright 2014, American Chemical Society [3]. The photocleavable character may be determined by UV–Vis and gel permeation chromatography (GPC) techniques, when the polymers cleave into the corresponding ortho-nitrosobenzaldehydes and carboxylic acids.
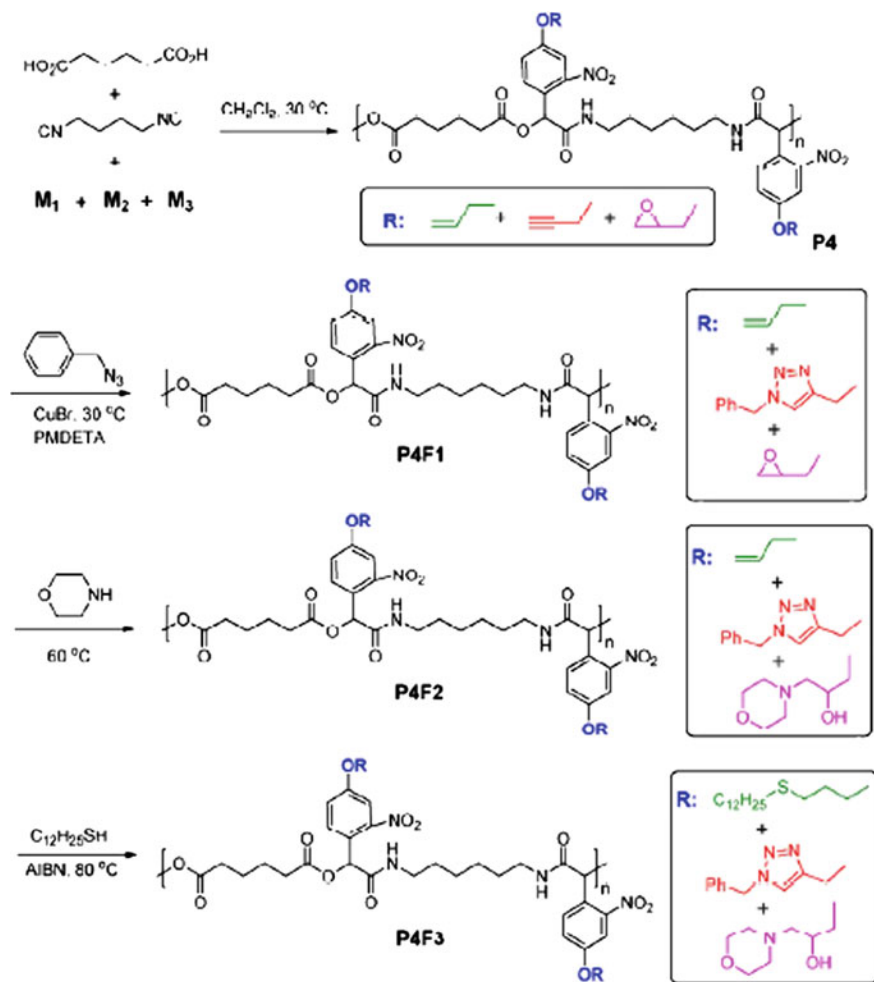
Scheme 4 Obtaining of the photocleavable triple function polymer and the sequential function-alizations. Reproduced with permission. Copyright 2014, American Chemical Society [3]

The modification of different structural properties upon irradiation could lead to polymer disruption or release of different loadings thus making such materials good candidates for a wide palette of applications which range from controlled drug delivery to surface modifications [31–36]. Obtaining of various other such polymers was reported in the literature [37, 38].

The photodegradable characteristic of such polymers may be exploited as photoresists. In this sense, the triply functionalized polymer was tested as photoresist for obtaining reactive patterns, since the multiple groups may be used in surface modification. Photopatterning was undertaken by a UV lamp and a TEM grid photomask. This may be achievable, as previously mentioned, by:
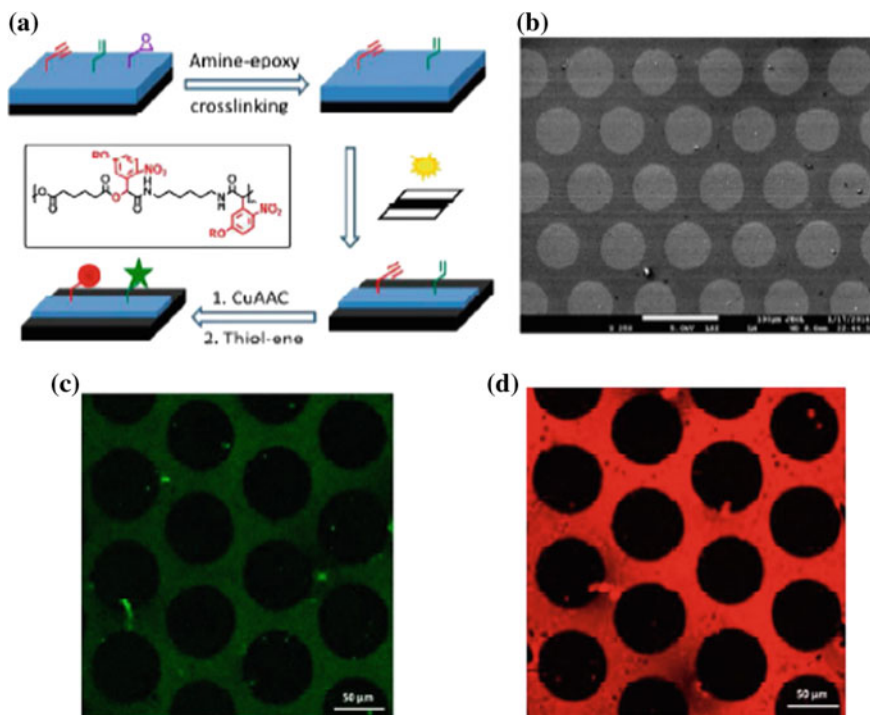
Scheme 5 **a** Multifunctional patterning on a silicon wafer using the photoresist polymer P4. **b** SEM micrograph of the patterned film; **c** Confocal fluorescence of the patterned silicon wafer film functionalized with Azido-FITC and **d** rhodamine dye. Reproduced with permission. Copyright 2014, American Chemical Society [3]

(1) crosslinking the film with amine–epoxy process (2) directly patterning of the surface due to photocleavable property; (3) copper catalyzed azide–alkyne cycloaddition (CuAAC) and (4) thoil-ene reaction. The surface used was a silicon wafer (Scheme 5) Reproduced with permission. Copyright 2014, American Chemical Society [3].

Another challenging and emerging field is that of obtaining phototriggable polymers from renewable bioresources. This is to address the issues surrounding synthetic commercially available polymers (e.g. poor degradability and sustainability) by obtaining biobased polymers with photocleavable units which may be preprogrammed for light decomposition. Two key compounds in doing so are 5-hydroxymethylfurfural (HMF) and one of its oxidation products, 2,5-furandicarboxylic acid (FDCA). For example, terephthalic acid may be replaced by FDCA in PET, with similar final properties. Rajendran et al. obtained a polymer based on FDCA with nitrobenzyl group for triggering photodecomposition upon light irradiation. Firstly, authors obtained model compounds to test the phototriggering efficiency of the widely mentioned 2-nitrobenzyl group. Authors converted
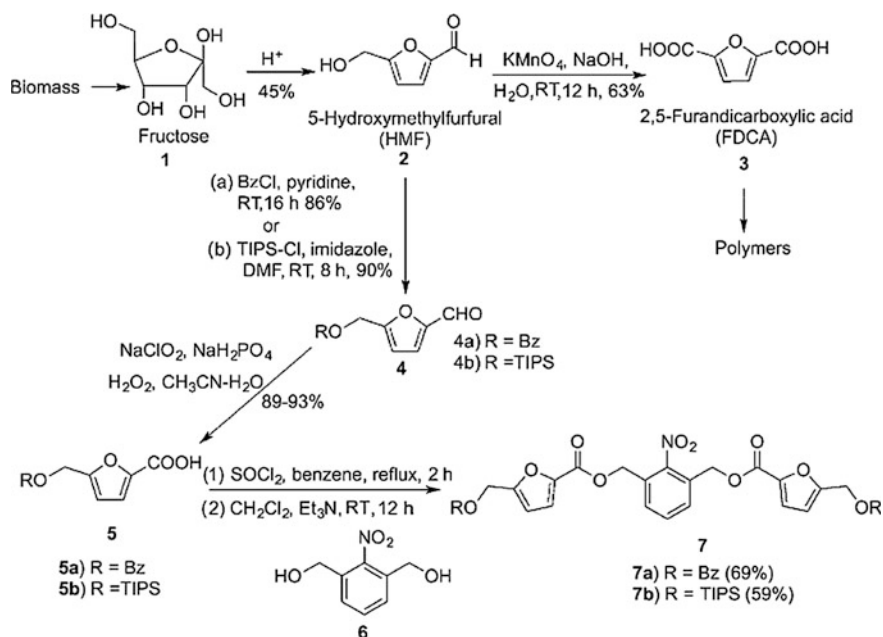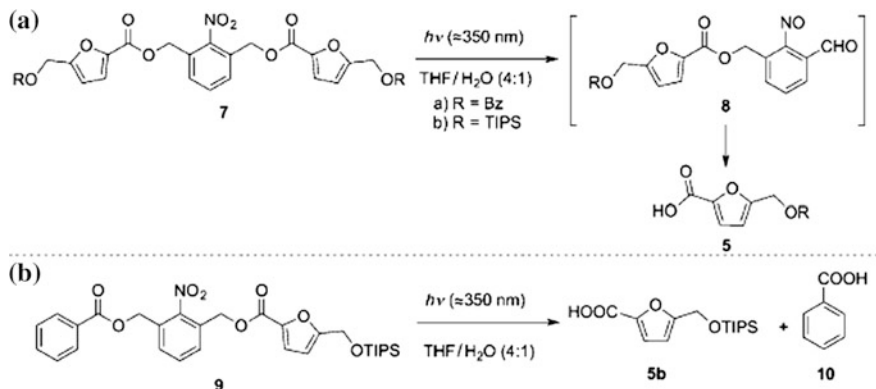
Scheme 6 Synthesis of biobased model compounds for phototriggered degradation, where Bz is benzyl, TIPS is triisopropylsilyl and DMF is N,N-dimethylformamide [39] (reproduced with kind permission from John Wiley and Sons—License no. 3879230249556)

fructose into HMF and FDCA and further functionalized them with 2-nitro-1,3-benzenedimethanol as phototrigger [39]. Photoirradiation of the obtained polymer was undertaken at 350 nm, monitored by ^{1}H–NMR and UV–Vis methods and was reported as being very efficient. There was yielded nitrosoaldehyde which degraded to furan carboxylic acid. (Scheme 6—reproduced with kind permission from John Wiley and Sons—License no. 3879230249556) [39]. Its unsymmetrically substituted ester photodecomposed with the same efficiency (Scheme 7(b)—reproduced with kind permission from John Wiley and Sons—License no. 3879230249556) [39].

With the success obtained after testing the model compounds, authors further synthesized polymer/oligomers from FDCA, not only to assess photocleavage efficiency, but also to attempt monomer recovery. The reaction is given in Scheme 8 [39] (reproduced with kind permission from John Wiley and Sons—License no. 3879230249556). The product was washed with acetone and CH_2Cl_2 for removing the low molecular weight oligomers. Its photodegradability was monitored in both suspension and solid state, in the latter occurring much slower. The photodegradation of the polymer was complete with the yielding of the starting monomer FDCA. Authors further expanded with success their approach to copolymers with glycols as phototriggers [39].

Scheme 7 Photodegradation of biobased model compounds: **a** symmetrical ester; **b** unsymmetrically ester [39] (reproduced with kind permission from John Wiley and Sons—License no. 3879230249556)
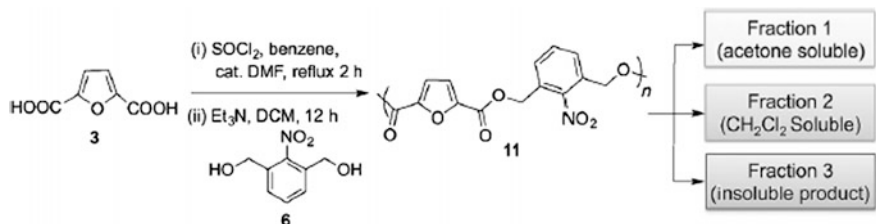
Scheme 8 Synthesis of the biobased polymer/oligomer [39] (reproduced with kind permission from John Wiley and Sons—License no. 3879230249556)

Christensen et al. [40] studied the UV photodecomposition behavior of poly (vinyl chloride) (PVC) and poly(caprolactone) (PCL) polymers in a 1:1 w/w blend and the corresponding homopolymers by monitoring the CO_2 emission during irradiation. The authors observed that the blend yielded lower CO_2 emission, thus the existing of specific beneficial morphological interactions between blend components which reduce photodegradation by a control over photo-oxidation. In individual PCL, chains entanglements reduce the possibility of crystalline regions formation, as opposed to PCL in the 1:1 ratio blend with PVC, in which PVC perturbs carbonyl entities vibration of PCL due to their interactions with chlorine atoms, thus acting as plasticizer. If PCL would have exhibited a higher crystallinity degree as PVC in the blend, then it would reduce oxygen diffusion. If PVC would have exhibited a higher crystallinity degree as PCL in the blend and phase-separated into partially or full crystalline domains, as suspected by the authors, this would greatly reduce the overall oxygen diffusion rate, effect which would be greater enhanced if both polymers would yield phase separation

phenomena. Crystallite shapes are very important, since they cause light to scatter into the blend, thus generating the opposite by favoring photo-oxidation.

Li et al. [41] studied the natural photo–aging for polypropylene (PP) and PP nanocomposites with $CaCO_3$ and SiO_2 exposed for 88 days and characterized them by means of FTIR, high temperature gel permeation chromatography (HGPC) and pyrolysis gas chromatography–mass spectrometry (PGC–MS). It was found that the PP nanocomposites were more prone to photodecomposition than the initial polymers and with higher oxidation rates, through many chain scissions with formation of much lower molecular mass alcohol, ester and ketone entities and unsaturated double bonds which recrystallized and enhanced the nanocomposites crystallinity. Authors gave three possible reasons for the faster photodegradation rate of the PP nanocomposites compared to the unfilled polymers, with further research needing to be conducted on this aspect in the future for confirmation. The first reason refers to the functional groups covering the nanoparticles which may catalyze photo-oxidation. Hydroxyl groups are absorbed on the nano filler surfaces, more pregnant for SiO_2, thus activating photodegradation reactions. The second reason may reside in the agglomeration of filler nanoparticles leading to their weak adhesion to the PP matrix and interfacial incompatibility under stress due to crystallization contraction, more enhanced in the lesser compatible SiO_2 nanoparticles to the PP matrix. The weaker SiO_2 nanoparticles compatibility to the PP matrix is due to a higher number of hydroxyl groups on the surface. Authors based the third reason on their finding of the nanoparticle acting as a nucleation agent. This reduces PP spherulites sizes, enhancing interface crystallinity, which, together with the amorphous domains, is another photo-oxidation site.

Rosu et al. [42]. studied the photochemical stability of a cotton cellulose substrate painted with a series of reactive azo-triazine dyes (Table 1—reproduced with permission of Springer—License no. 3887660087491) [42]. The materials were exposed to UV irradiations with $\lambda > 300$ nm. The purpose of the study consisted in establishing of a photodecomposition mechanism of the dyed textiles, since other studies reported that aryl amines and free radicals, resulted during photodegradation of such dyes, are toxic to human skin after their absorbtion during perspiration. Details of the attachment mechanisms of the dyes to the cellulose substrate, dyeing process and toxicological studies of the dyes were reported in a Ph.D. thesis [43]. The same thesis reports colorimetric analyses of the dyed textiles during the UV irradiation, followed by dye extractions in aqueous media with acid and alkaline pH for human perspiration simulation and spectrophotometric identification of the dyes in solutions.

Colorimetric studies indicated a darkening tendency of surfaces painted with RY-143 and RO-13 dyes (light color dyes) and insignificant color modifications of surfaces painted with RR-2 and RR-183 dyes (dark color dyes), due to accumulation of blue and green chromophores on cellulose surface during 100 h irradiation time due to cellulose surface photo–oxidation reactions. Surface coloring in complementary colors (blue and green) during photoirradiation led to simultaneous hypochrome and bathochrome displacements of the absorbtion maxima. There could also be observed a widening in the absorbtion spectrum towards higher wavelengths, up to

Table 1 Characteristics of the four reactive azo–triazine dyes used in the study [42] (reproduced with permission of Springer—License no. 3887660087491)

Name/manufacturer	Chemical formula	λ_{max}	M_w
Reactive Yellow 143 (RY-143)/Hutsman textile effects		217, 265, 422	742.02
Reactive Orange 13 (RO-13)/Hutsman textile effects		226, 284, 488	762.03
Reactive Red 183 (RR-183)/Hutsman textile effects		227, 280, 503	713.62
Reactive Red 2 (RR-2)/PRO chemical and dye		217, 289, 544	615.33

800 nm, which is a supplementary indication of new chromophores formation on the irradiated surfaces. The darkening of samples surfaces was attributed to C–N bond scissions from amine entities with the resulting of new chromophore structures [42] (Scheme 9—reproduced with permission of Springer—License no. 3887660087491) and was associated with the bathochrome displacement. Also, this darkening was also correlated with the substitution degree and number of amine entities. Scheme 10 [42] (reproduced with permission of Springer—License no. 3887660087491) shows the formation of intermediate blue chromophores from radical IX in Scheme 9 during photoirradiation of RY-143 dye, the other dyes exhibiting similar photochemical behavior [42].

Initiation of the photodegradation process may be undertaken through hydroxyl radical intermediates resulted after hydroperoxides decomposition. The general photodecomposition mechanism of RY-143 dye from the textile substrate is given in Scheme 11 [42] (reproduced with permission of Springer—License no. 3887660087491). The dye's chromophore entities, consisting of azo groups and aromatic rings, are destroyed after the attack of intermediate free radicals with the resulting of nitrogen, process associated with the hypochrome effect. The FTIR spectrum recorded after photoirradiation indicated significant modifications in the absorbtion ranges specific to glucose ring and carbonyl groups for the cellulose substrate painted with RY-143 dye. Results have demonstrated the apparition and intensification of photo-oxidative processes by the appearance of new absorbtion bands specific to carbonyl entities and an increase in absorbance signals specific to
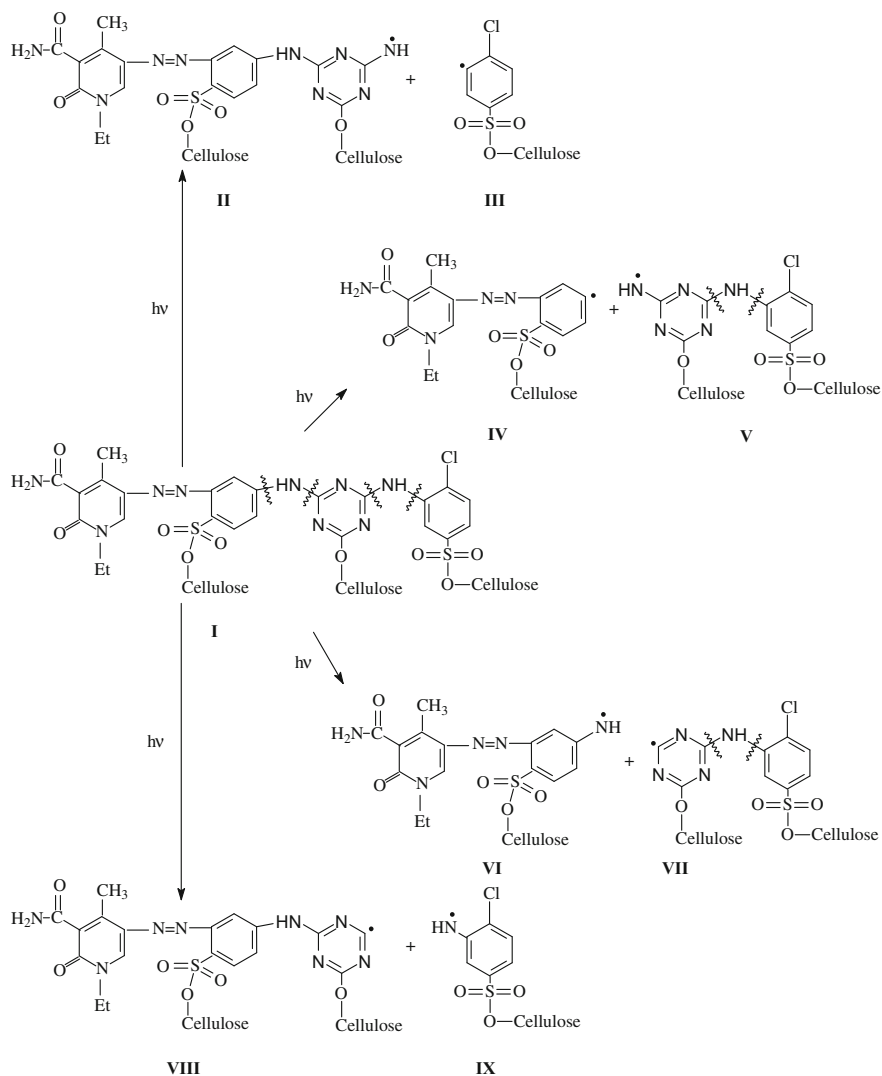
Scheme 9 Scission of C–N bonds during photodecomposition of RY-143 painted cellulose [42] (reproduced with permission of Springer—License no. 3887660087491)

glycosidic rings, suggesting cellulose chain-end initiated depolymerization processes and lowering of molecular mass. The dye molecules from the cellulosic substrate may be dissolved by human perspiration thus provoking hazardous health issues. Authors have observed an increase in the extracted dye quantity with irradiation dose and pH increase [42, 43].

Collagen photochemical behavior in multicomponent polymeric materials is another extensively debated topic. One must first comprehend basic photochemical
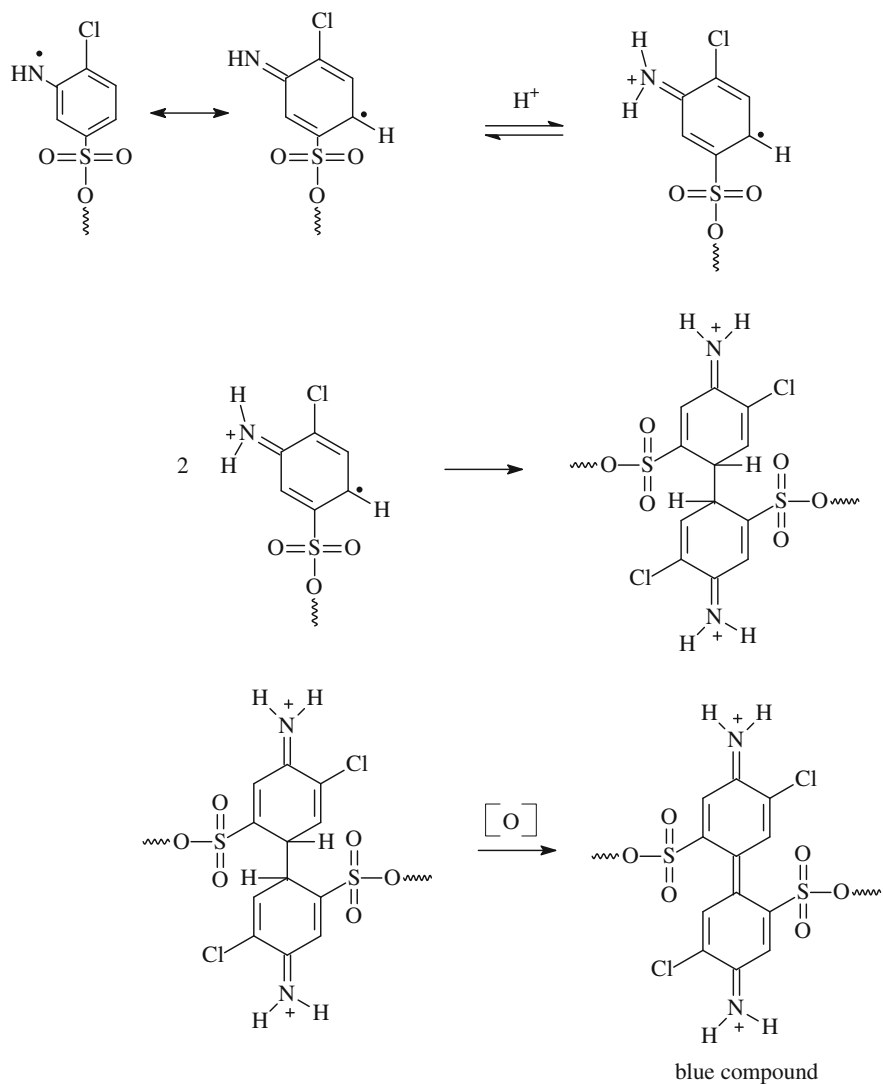
Scheme 10 The generating of blue chromophores during RY-143 dye photoirradiation [42] (reproduced with permission of Springer—License no. 3887660087491)

processes occurring in individual pure collagen. Rabotyagova et al. [44] studied the photochemical behavior of pure collagen irradiated at 254 nm and found changes at every structural level. In early photodegradation stages collagen shifts from the triple helix conformation, protector of single collagen macromolecules against peptide cleavage, to random coil, associated with water elimination (Fig. 1) [44] (Reproduced with permission of Springer—License no. 3890680622983).
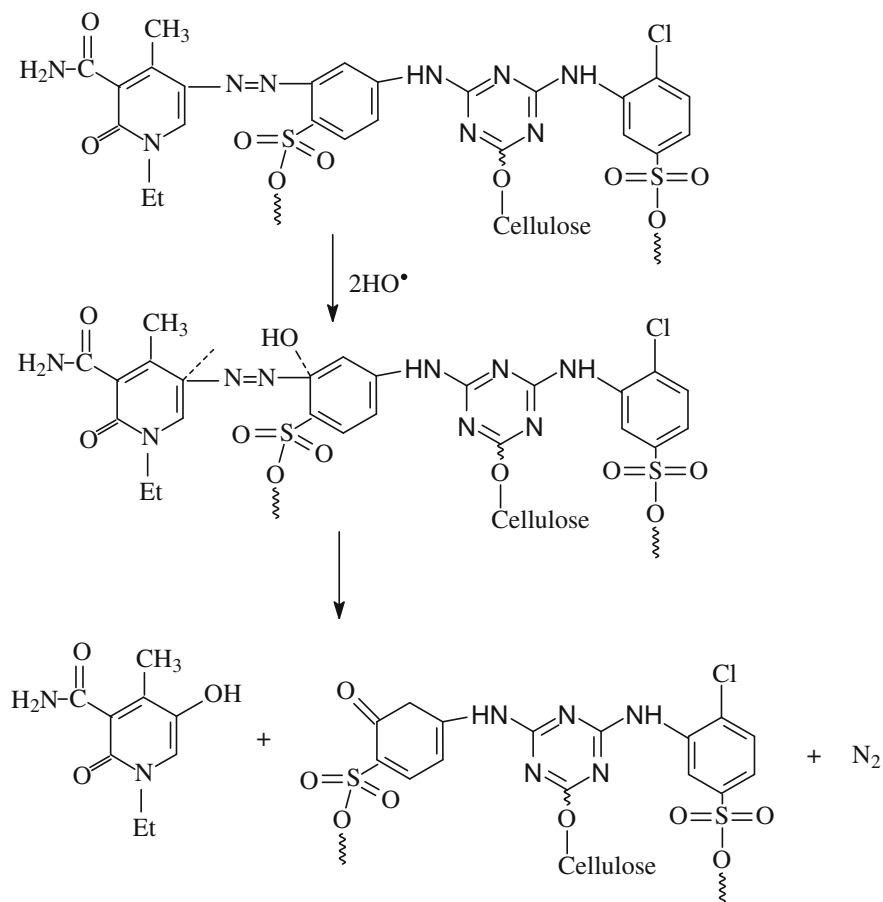
Scheme 11 Photodecomposition mechanism of RY-143 dye [42] (reproduced with permission of Springer—License no. 3887660087491)

With the collagen triple helix once degraded, free radicals generate massive peptide bond scission (Fig. 2) [44] (Reproduced with permission of Springer—License no. 3890680622983. Hydroxyl radicals resulted from the water round the collagen backbone make interactions with its macromolecules to yield new radicals.

The chemically destructive UV irradiation effect on the collagen hierarchical structure was confirmed by FTIR, AFM and sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) studies. These negative effects of electromagnetic radiation on collagen matrices are an important study in tissue remodeling.

Sionkowska [45] studied the photochemical behavior of collagen and PEG based blends by FTIR, UV–Vis, viscometry and microscopy before and after UV irradiation (λ = 254 nm) and observed that the two components were immiscible in the blend, thus exhibiting lower photochemical stability and poor mechanical properties compared to individual components. The photochemical stability of collagen was
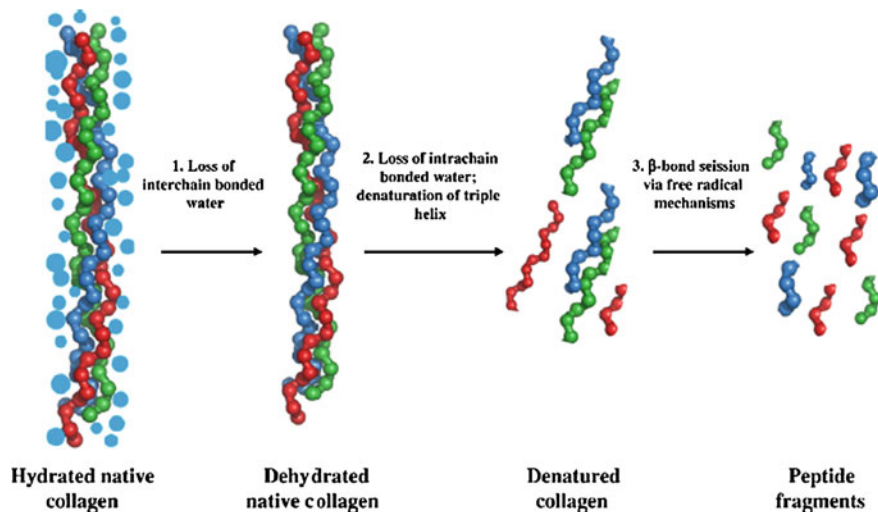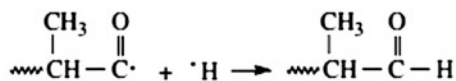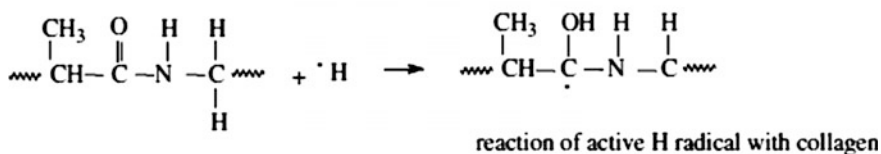
Fig. 1 Possible UV decomposition mechanism of collagen at 254 nm [44] (reproduced with permission of Springer—License no. 3890680622983)
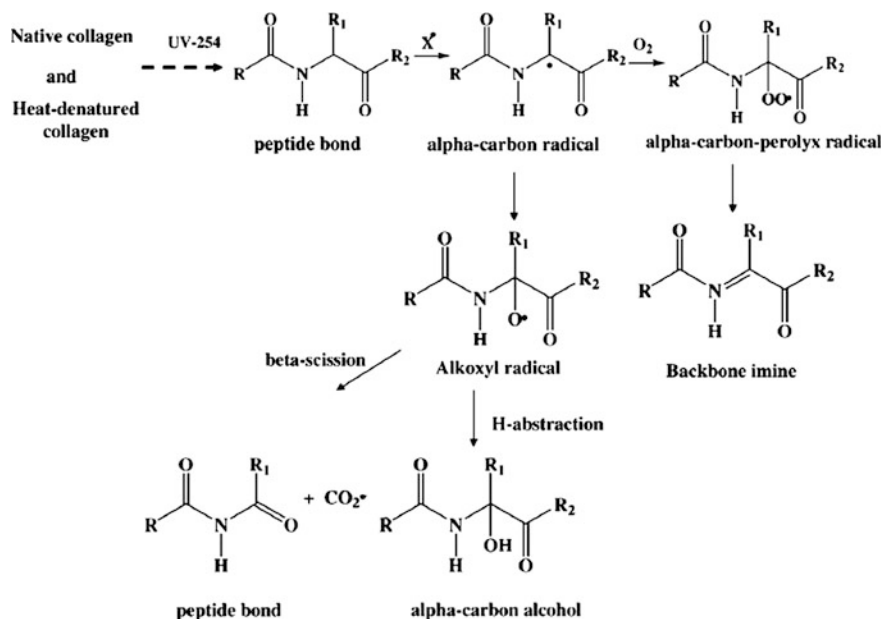
Fig. 2 Collagen backbone scission mechanisms [44] (reproduced with permission of Springer—License no. 3890680622983)

chain scission of collagen
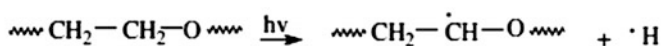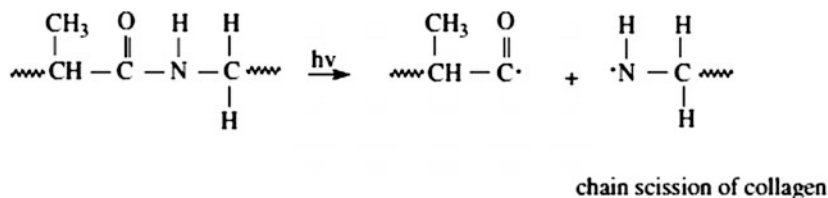
formation of H radical from PEG

reaction of active H radical with collagen

reaction of new formed radicals

Fig. 3 Possible UV degradation mechanism in PEG/collagen films [45] (reproduced with kind permission from Elsevier—License no. 3890091014498)

dependent on PEG concentration in the blend. Photodegradation in collagen is initiated from the side groups through the amino acids tyrosine and phenylalanine chromophores which absorb light under 300 nm, while in PEG photodegradation occurs through main chain scission initiated by weak chemical linkages. Active primary macroradicals are produced during photo–oxidation of one of the blend components and initiate photodegradation of the second component. Free active radicals from both components react with each other leading to blend properties alteration (Fig. 3) [45] (reproduced with kind permission from Elsevier—License no. 3890091014498). FTIR spectra indicated that the films were not so photo-chemically degraded compared to pure collagen and that changes in the properties of blends in solution occur at a lower irradiation time compared to the ones in solid state. Optical micrographs indicated that surface characteristics of collagen and the blends as films are not strongly altered after UV exposure. (Fig. 4) [45] (reproduced with kind permission from Elsevier—License no. 3890091014498).
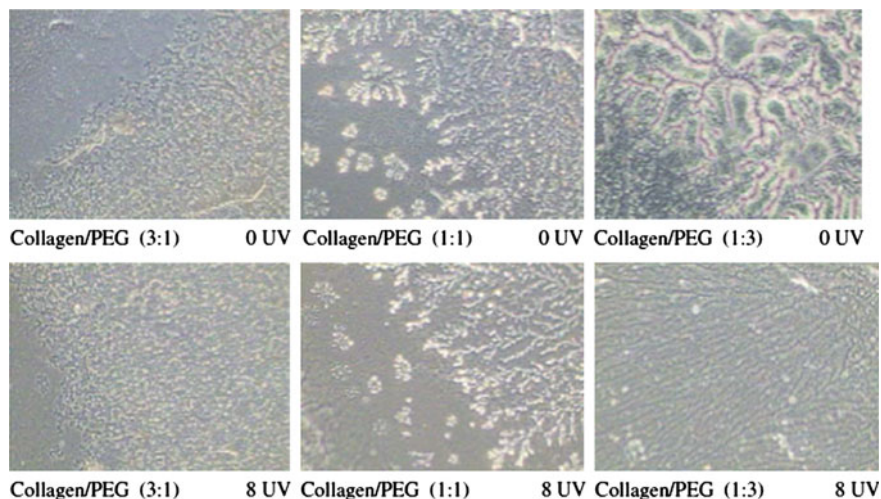
Fig. 4 Optical micrographs of the PEG/collagen films before and after UV irradiation [45] (reproduced with kind permission from Elsevier—License no. 3890091014498)

Fig. 5 Chemical structure of PBI [47] (reproduced with kind permission from Elsevier —License no. 3890161358622)
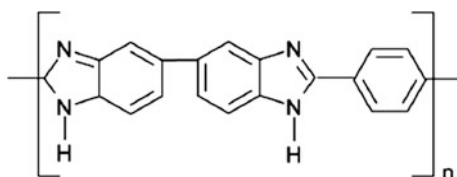

Sionkowska et al. [46] further studied the photochemical stability of poly(vinyl pyrrolidone) in the presence of 1, 3 and 5 % collagen irradiated at $\lambda = 254$ nm in air for 24 h and characterized the samples by by UV–Vis and FTIR spectroscopy and thermal analysis (TGA, DTG). It was observed that PVP was thermally and photochemically less stable in the presence of collagen. Collagen led to crosslinking of PVP and increased its polarity during irradiation, indicating surface photo-oxidation.

Arrieta et al. [47] conducted hydrolytic and photochemical aging studies for a Kevlar–Polybenzimidazole (PBI) blend in yarn form. UV irradiation was conducted at $\lambda = 340$ nm and four different temperatures (50, 60, 70 and 80 °C) between 4 and 31 days. The PBI structure is given in Fig. 5 [47] (reproduced with kind permission from Elsevier—License no. 3890161358622).

The UV exposure led to a decrease in breaking force. New FTIR absorption bands appeared, corresponding to C=O bond vibration in end groups with carboxylic acid. A photodecomposition mechanism was proposed (Fig. 6) [47] (Reproduced with kind permission from Elsevier—License no. 3890161358622), occurred through the Photo-Fries rearrangement, which yielded 2-aminobenzo phenones and carboxylic acid end groups (Fig. 7) [47] (reproduced with kind permission from Elsevier—License no. 3890161358622).
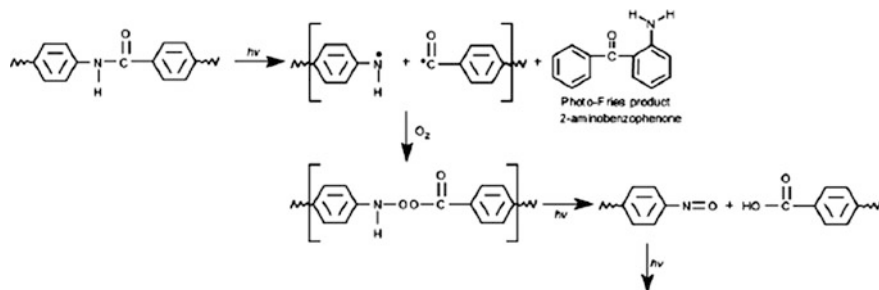
Fig. 6 Photochemical aging mechanism of Kevlar [47] (Reproduced with kind permission from Elsevier—License no. 3890161358622)
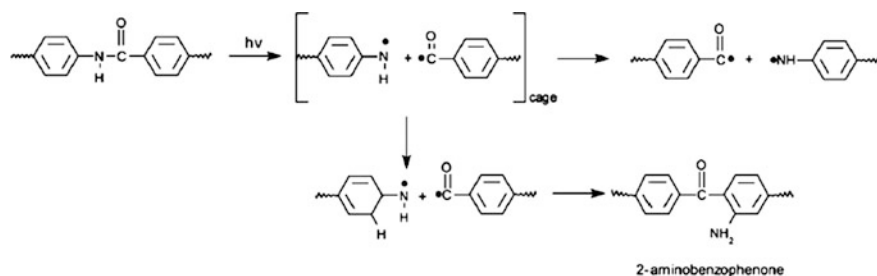

Fig. 7 Photo-Fries rearrangement mechanism in Kevlar [47] (reproduced with kind permission from Elsevier—License no. 3890161358622)

The accumulation of high absorbent products from the Photo–Fries rearrangement led to the occurrence of a "screening" effect at the yarns' surface which protected the Kevlar underlying layers by preventing amide bonds cleavage. The material was afterwards exposed to relative humidity levels of 60 and 80 % and temperatures of 50, 60 and 80 °C) during which the breaking force decreased continuously. FTIR spectra indicated new carboxylic acid groups resulted from amide bond hydrolysis under acid catalyst. Results indicated that hydrolysis competed with a recombination reaction by consuming –COOH containing moieties. Authors elaborated a differential kinetic equation of the aging process based on the amount of resulted –COOH which they solved by analytic methods.

Cui et al. [48] studied UV radiation effect on renewable biobased polymer sheets by SEM and photoacoustic FTIR (PAS-FTIR) (Fig. 8) [48] (reproduced with kind permission from Elsevier—License no. 3891281355385).

UV irradiation was undertaken at 300 nm on a 12 h cycle: of 8 h UV at 60 °C, followed by 4 h condensation at 50 °C, at exposure times of 250, 500, 750, 1000 and 2000 h. UV irradiation and cycled weathering led to crosslinking and surface cracking. The main driving forces of the photodegradation process were hydroperoxide formation and decomposition, the latter occurring through formation of oxidation products, such as ketones, alcohols and aldehydes (Fig. 9) [48]
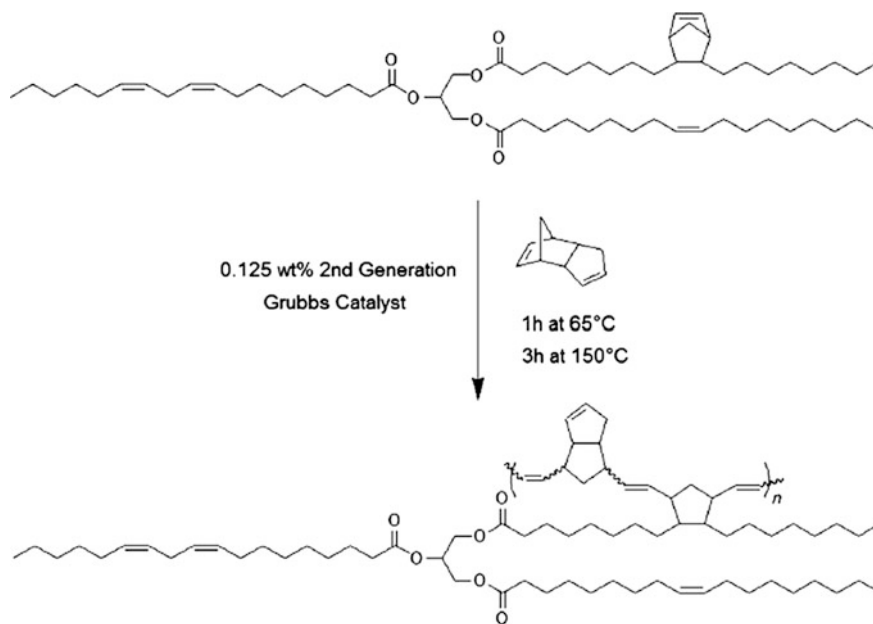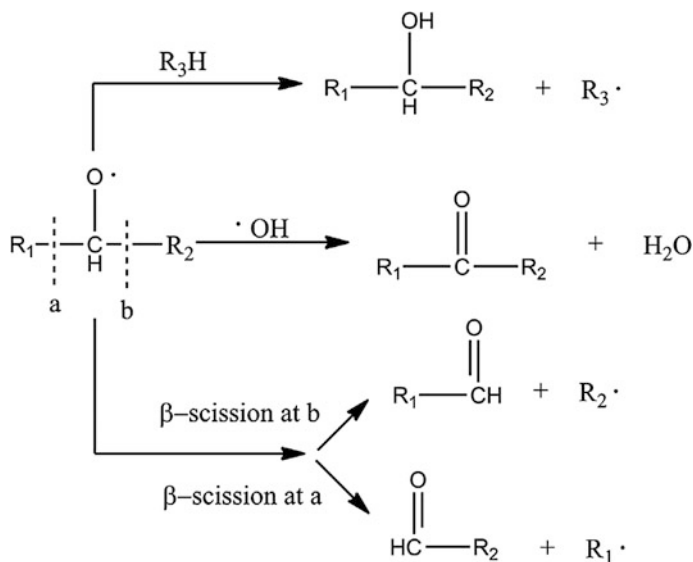
Fig. 8 Ring-opening metathesis polymerization of Dilulin and dicyclopentadiene [48] (reproduced with kind permission from Elsevier—License no. 3891281355385)
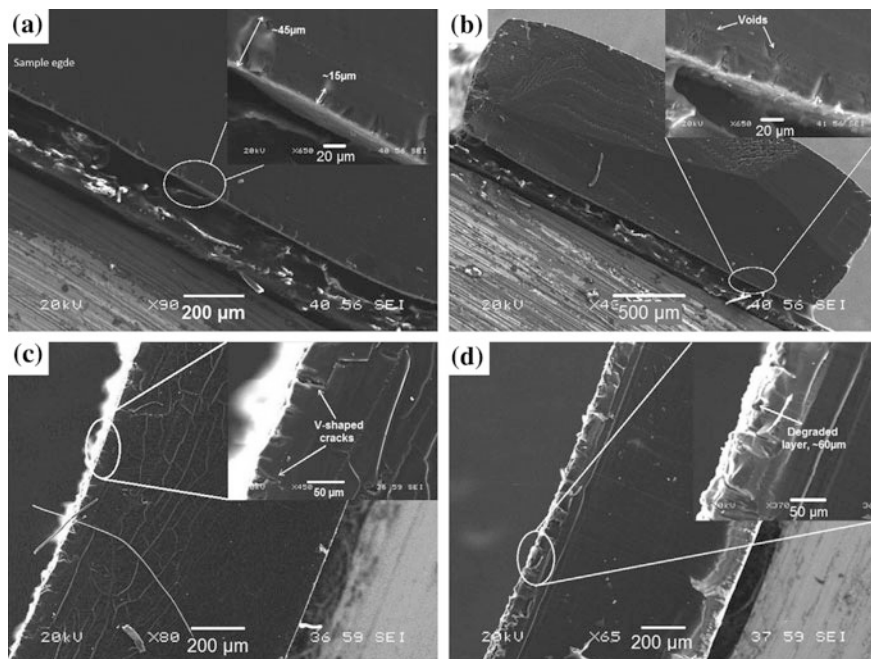
(reproduced with kind permission from Elsevier—License no. 3891281355385), and decreasing with penetration depth increase, due to lowering of oxygen concentration.

Through oxygen consumption, the formed hydrocarbon radicals convert into peroxy radicals which further lead to the formation of hydrocarbon radicals and hydroperoxides via hydrogen atoms abstraction from the polymer chain. The new carbonyl entities generated during photo-oxidation also act as UV absorbers, decomposing afterwards through a Norrish reaction and yielding esters, acids, alkenes and enols, as general products resulted during photodecomposition. SEM and depth profile studies results indicated decomposition occurrence in thin layer surface due to limited oxygen diffusion through the interior layers. (Fig. 10) [48] (reproduced with kind permission from Elsevier—License no. 3891281355385). The formation of hydroperoxides and new carbonyl entities from main chain decomposition was demonstrated by PAS–FTIR.

Further various recent examples on the photochemical behavior of multicomponent polymer based materials were given in *Chap.* 1. *Theoretical aspects regarding polymer photochemistry* and *Chap.* 8. *Lifetime prediction of multicomponent polymeric materials.*

Fig. 9 Second oxidation reactions in alkoxy radical [48] (reproduced with kind permission from Elsevier—License no. 3891281355385)

Fig. 10 Cross-section SEM images of UV-degraded structures at **a** 250 h; **b** 500 h; **c** 1000 h; **d** 2000 h [48] (reproduced with kind permission from Elsevier—License no. 3891281355385)

3   Conclusions

Photodegradable polymers and polymer based materials have witnessed a growing interest in the last two decades, since their properties may be controlled both spatially and temporarily by phototriggering groups or agents. A continuously troubling issue is that of the hazardous environmental impact of polymeric materials. That is why much effort is undertaken into the developing and design of polymers able of splitting into comprising corresponding monomers after service lifetime end. Photodegradable polymers possess a wide palette of applications, such as in agriculture as plastic sheets for ground cover (plasticulture), in the packaging industry and household where they must degrade fast and without an environmentally negative impact, in the obtaining of smart materials for microelectronics and in biomedical applications. Hydrogels with phototriggered controlled release of bioactive principles or cells have high applications potential in tissue engineering. By including photolabile chemical structures in the polymer main chain [o-nitrobenzyl, coumarin-4-ylmethyl, p-hydroxyphenacyl or acetal (ketal)] and by monitoring parameters such as wavelength, light intensity, irradiation dose, temperature, exposure time and mechanical stress, one may control the stability, degradation rate and polymer shape.

References

1. Paul, D.R., Sperling, L.H.: Multicomponent Polymer Materials. American Chemical Society, Washington, DC (1986)
2. Allen, N.: Polymer photochemistry. In: Dunkin, I. (ed.) Photochemistry, vol. 35, p. 206. The Royal Society of Chemistry, London (2005)
3. Li, L., Deng, X.-X., Li, Z.-L., Du, F.-S., Li, Z.-C.: Multifunctional photodegradable polymers for reactive micropatterns. Macromolecules 47, 4660–4667 (2014)
4. Griffin, D.R., Kasko, A.M.: Photo-selective delivery of model therapeutics from hydrogels. ACS Macro Lett. 1(11), 1330–1334 (2012)
5. Griffin, D.R., Kasko, A.M.: Photodegradable macromers and hydrogels for live cell encapsulation and release. J. Am. Chem. Soc. 134(31), 13103–13107 (2012)
6. Daglen, B.C., Tyler, D.R.: Photodegradable plastics: end of life design principle. Green Chem. Lett. Rev. 3(2), 69–82 (2010)
7. Gilead, D.: Photodegradable plastics in agriculture. In: Scott, G., Gilead, D. (eds.) Degradable polymers, p. 186. Springer, Amsterdam (1995)
8. Zhu, C., Ninh, C., Bettinger, C.J.: Photoreconfigurable polymers for biomedical applications: chemistry and macromolecular engineering. Biomacromolecules 15(10), 3474–3494 (2014)
9. Ki, C.S., Shih, H., Lin, C.-C.: Facile preparation of photodegradable hydrogels by photopolymerization. Polymer 54, 2113–2122 (2013)
10. Lv, C., Wang, Z., Wang, P., Tang, X.: Photodegradable polyester for triggered release. Int. J. Mol. Sci. 13(12), 16387–16399 (2012)
11. Fomina, N., McFearin, C., Sermasakdi, M., Edigin, O., Almutairi, A.: UV and near-IR triggered release from polymeric nanoparticles. J. Am. Chem. Soc. 132(28), 9540–9542 (2010)

12. de Gracia, L.C., McFearin, C.L., Almutairi, A.: Single UV or near IR triggered event leads to polymer degradation into small molecules. ASC Macro Lett. **1**(7), 922–936 (2012)

13. Volgraf, M., Banghart, M., Trauner, D.: Switchable proteins and channels. In: Feringa, B. (ed.) Molecular Switches, vol. 2, 2nd edn, p. 563. Wiley, Weinheim (2011)

14. Scott, G., Gilead, D.: Degradable Polymers: Principles and Applications, 2nd edn. Chapman & Hall, New York (2002)

15. Wiles, D.M., Scott, G.: Polyolefins with controlled environmental degradability. Polym. Degrad. Stab. **91**, 1581–1592 (2006)

16. Albertsson, A.-C., Barenstedt, C., Karlsson, S., Lindberg, T.: Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene. Polymer **36**(16), 3075–3083 (1995)

17. Steber, J., Herold, C.P., Limia, J.M.: Comparative evaluation ofanaerobic biodegradability of hydrocarbons and fatty derivatives currently used as drilling fluids. Chemosphere **31**(4), 3105–3118 (1995)

18. Sommazzi, A., Garbassi, F.: Olefin-carbon monoxide copolymers. Prog. Polym. Sci. **22**(8), 1547–1605 (1997)

19. Grassie, N., Scott, G.: Polymer Degradation and Stabilization. Cambridge University Press, New York (1985)

20. Guillet, J.: Polymer Photophysics and Photochemistry: An Introduction to the Study of Photoprocesses in Macromolecules. Cambridge University Press, New York (1985)

21. Schnabel, W.: Polymers and Light: Fundamentals and Technical Aspects. Wiley, Weinheim (2007)

22. Hartley, G.H., Guillet, J.E.: Photochemistry of ketone polymers. I. Studies of ethylene-carbon monoxide copolymers. Macromolecules **1**(2), 165–170 (1968)

23. Tyler, D.R.: Photochemically degradable polymers containing metal–metal bonds along their backbones. Coord. Chem. Rev. **246**(1–2), 291–303 (2003)

24. Chen, R., Tyler, D.R.: Origin of tensile stress-induced rate increases in the photochemical degradation of polymers. Macromolecules **37**, 5430–5436 (2004)

25. Meyer, T.J., Caspar, J.V.: Photochemistry of metal–metal bonds. Chem. Rev. **85**(3), 187–218 (1985)

26. Tenhaeff, S.C., Tyler, D.R.: Photochemically reactive polymers; synthesis and characterization of polyurethanes containing Cp2Mo2(CO)6 or Cp2Fe2(CO)4 molecules along the polymer backbone. Organometallics **10**(2), 473–482 (1991)

27. Rabek, J.F.: Photodegradation of Polymers: Physical Characteristics and Applications. Springer, New York (1996)

28. Matsukawa, K.J.: Development of photo-functional materials from organic/inorganic nano-hybrids. J. Photopolym. Sci. Technol. **18**(2), 203–210 (2005)

29. Xu, J., Shi, W., Gong, M., Yu, F., Yan, L.: Preparation of poly(methyl methacrylate-co-maleic anhydride)/SiO$_2$–TiO$_2$ hybrid materials and their thermo– and photodegradation behaviors. J. Appl. Polym. Sci. **97**(4), 1714–1724 (2005)

30. Li, L., Lv, A., Deng, X.X., Du, F.S., Li, Z.C.: Facile synthesis of photo-cleavable polymers via Passerini reaction. Chem. Commun. **49**(76), 8549–8551 (2013)

31. Koylu, D., Thapa, M., Gumbley, P., Thomas, S.W.I.I.I.: Photochemical disruption of polyelectrolyte multilayers. Adv. Mater. **24**, 1451–1454 (2012)

32. Yamaguchi, S., Yamahira, S., Kikuchi, K., Sumaru, K., Kanamori, T., Nagamune, T.: Photocontrollable dynamic micropatterning of non-adherent mammalian cells using a photocleavable poly(ethylene glycol) lipid. Angew. Chem. Int. Ed. **51**, 128–131(2012)

33. Pauloehrl, T., Delaittre, G., Bruns, M., Meißler, M., Börner, H.G., Bastmeyer, M., Barner-Kowollik, C.: (Bio)Molecular surface patterning by phototriggered oxime ligation. Angew. Chem. Int. Ed. **51**, 9181–9184 (2012)

34. Jiang, J.Q., Tong, X., Zhao, Y.: A new design for light-breakable polymer micelles. J. Am. Chem. Soc. **127**(23), 8290–8291 (2005)

35. Pasparakis, D.G., Manouras, T., Selimis, A., Vamvakaki, M., Argitis, P.: Laser-induced cell detachment and patterning with photodegradable polymer substrates. Angew. Chem. Int. Ed. **50**, 4142–4145 (2011)
36. Cui, J.X., Miguel, V.S., Campo, A.D.: Light-triggered multifunctionality at surfaces mediated by photolabile protecting groups. Macromol. Rapid Commun. **34**, 310–329 (2013)
37. Liu, G., Liu, W., Dong, C.M.: UV- and NIR-responsive polymeric nanomedicines for on-demand drug delivery. Polym. Chem. **4**, 3431–3443 (2013)
38. Gohy, J.F., Zhao, Y.: Photo-responsive block copolymer micelles: design and behavior. Chem. Soc. Rev. **42**, 7117–7129 (2013)
39. Rajendran, S., Raghunathan, R., Hevus, I., Krishnan, R., Ugrinov, A., Sibi, M.P., Webster, D.C., Sivaguru, J.: Programmed photodegradation of polymeric/oligomeric materials derived from renewable bioresources. Angew. Chem. **127**, 1175–1179 (2015)
40. Christensen, P.A., Egerton, T.A., Martins-Franchetti, S.M., Jin, C., White, J.R.: Photodegradation of polycaprolactone/poly(vinyl chloride) blend. Polym. Degrad. Stab. **93**, 305–309 (2008)
41. Li, J., Yang, R., Yu, J., Liu, Y.: Natural photo-aging degradation of polypropylene nanocomposites. Polym. Degrad. Stab. **93**, 84–89 (2008)
42. Rosu, L., Rosu, D., Gavat, C.-C., Varganici, C.-D.: Photochemical stability of cellulose textile surfaces painted with some reactive azo-triazine dyes. J. Mater. Sci. **49**(13), 4469–4480 (2014)
43. Gavat, C.-C.: Contributions for knowledge on some reactive dyes implications in the determination of biological effects, in correlation with their physico-chemical properties. In: Ph.D. Thesis, "Gr. T. Popa" University of Medicine and Pharmacy, Iași, Romania (2011)
44. Rabotyagova, O.S., Cebe, P., Kaplan, D.L.: Collagen structural hierarchy and susceptibility to degradation by ultraviolet radiation. Mater. Sci. Eng. C **28**, 1420–1429 (2008)
45. Sionkowska, A.: The influence of UV light on collagen/poly(ethylene glycol) blends. Polym. Degrad. Stab. **91**, 305–312 (2006)
46. Sionkowska, A., Kozlowska, J., Planecka, A., Skopinska-Wisniewska, J.: Photochemical stability of poly(vinyl pyrrolidone) in the presence of collagen. Polym. Degrad. Stab. **93**, 2127–2132 (2008)
47. Arrieta, C., David, É., Dolez, P., Vu-Khanh, T.: Hydrolytic and photochemical aging studies of a Kevlar–PBI blend. Polym. Degrad. Stab. **96**, 1411–1419 (2011)
48. Cui, H., Hanus, R., Kessler, M.R.: Degradation of ROMP-based bio-renewable polymers by UV radiation. Polym. Degrad. Stab. **98**, 2357–2365 (2013)