

Controlling Photodegradation in Vinyl Ketone Polymers

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Abstract

Polymer degradation has many important applications, ranging from waste management and reuse of polymers, to targeted delivery in nanomedicine. Vinyl ketone (VK) polymers have efficient light driven degradation, due to Norrish chemistry inherent to them. The photodegradation of four RAFT-VK polymers: poly(phenyl vinyl ketone) -poly(PVK), poly(*p*-methoxy phenyl vinyl ketone) -poly(PVK-OMe), poly(*p*-chloro phenyl vinyl ketone) -poly(PVK-Cl), and poly(methyl vinyl ketone) -poly(MVK) was studied. Degradation kinetics were studied under different wavelengths (310, 350, 390, 450, 520 and 630 nm). All poly(PVK) systems showed a rapid degradation under 310 and 350 nm, yielding short oligomers with low molecular weights and broader molecular weight distributions, with minimal degradation under other wavelengths. Among the aromatic poly(VK)s, poly(PVK-Cl) with an electron-withdrawing chloro-group had the highest degradation rate, poly(PVK) had the second highest degradation rate, and poly(PVK-OMe) with an electron-donating methoxy-group had the lowest degradation rate at 350 nm. Photodegradation of poly(MVK) was substantially slower than all of the poly(PVK) derivatives. Using lower polymer concentration and higher targeted chain lengths led to a notable increase in the polymer degradation rate. A scaling model was developed to explain the chain scission events and to gain insight into the underlined degradation process. Finally, photodegradation influenced the thermal and surface properties

of VK materials, with correlation between molecular changes and materials properties highlighting the potential to use these light responsive polymers to change the thermal and surface characteristics of materials.

Introduction

Responsive polymers have unique properties including shape memory[1,2], self-healing[1,3,4], actuation[5,6], and degradability[7,8]. Numerous stimuli have been used to introduce responsiveness to polymers including pH[2,9,10], heat[1,9,11], chemical reagents[9,12], and light[1,13]. Light has emerged as a powerful stimulus due to the mild conditions, simple implementation, and absence of chemical byproducts from the stimulus[14–16]. Light driven polymer degradation has numerous potential applications including plastics waste disposal,[17,18] chemical sustainability[17] and drug delivery[7,8].

Currently, polymer waste is a significant societal concern because of the long lifetime of these plastics in the environment and the slow degradation process to smaller molecules and particles. Therefore, new technologies are being developed for plastics waste management methods[19] such as pyrolysis[20,21], chemical recycling[21–23], and catalytic degradation methods[20,24]. Degradable polymers such as biodegradable[17,25], self-immolative[26] and photodegradable polymer[18,27,28] have received substantial attention to find a solution to plastic waste management while also fulfilling the high demand for polymer materials in commodity and specialty applications[29–31]. One approach to managing and recycling polymer waste involved the depolymerization of commodity polymer to their respective monomers. This approach is advantageous as the monomer is easily recovered and can be used in subsequent reactions[32–35]. However, due to the high ceiling temperature of most commodity polymers, this process requires significant thermal stimulus, which is sometimes coupled to photochemical processes[36]. Photodegradable polymers are appealing because

they can degrade at ambient or near ambient conditions. Typically, the backbone degrades gradually after exposure to sunlight, or a UV based light source and thereby minimizes polymer waste in the environment[18,27,28]. In addition to this, photo degradable polymers are useful in the medical field as photo responsive drug delivery systems (e.g., nanostructures/micelles) which is more attractive because of spatial temporal control, tunability, and ease of controlling the process[7,37].

Recently, depolymerization and polymer degradation have emerged as area of focus for fundamental research and materials applications[19,27–29,32,35,38,39]. Depolymerization yields a one type of monomer, or a mixture of monomers based on the nature of the polymer which can polymerize again, while polymer degradation yields a mixture of different products such as short oligomers, and some other small molecules[32,34]. Both main chain cleavability and side chain cleavability can be introduced to a polymer by incorporating cleavable bonds such as disulfide bonds[40–42], ester bonds[41,42], peptide bonds, Diels-Alder adducts[43], and polysaccharide adducts[29,44]. Similarly, photodegradability can be introduced by incorporating photodegradable links such as nitrobenzyl alcohol (o-NB) groups[45,46], ketone groups[28,47], or coumarin groups[48,49]. Vinyl ketone (VK) monomers and polymers have demonstrated powerful light responsive behavior, with wavelength orthogonal photopolymerization and photodegradation[28,50,51]. As seen in Scheme 1A, photopolymerization of VK monomers occurs efficiently under blue light (450 nm) through a proposed Norrish I reaction. Photodegradation of VK polymers is triggered under UV light (350 or 310 nm) as shown in Scheme 1B through a proposed Norrish II process[27,50,51]. Previous works have focused on the intrinsic photopolymerization of VK monomers and their reversible addition fragmentation chain transfer polymerization (RAFT) kinetics[50,51]. Guillet and coworkers have determined Mark-Houwink parameters of 4-substituted phenyl vinyl ketone polymers and their ability to use as positive photoresists[52]. However, in their

study, uncontrolled polymers were used, without evaluating the effects of chain length, concentration and wavelength on the degradation kinetics, bulk, or surface properties of VK based polymer materials.

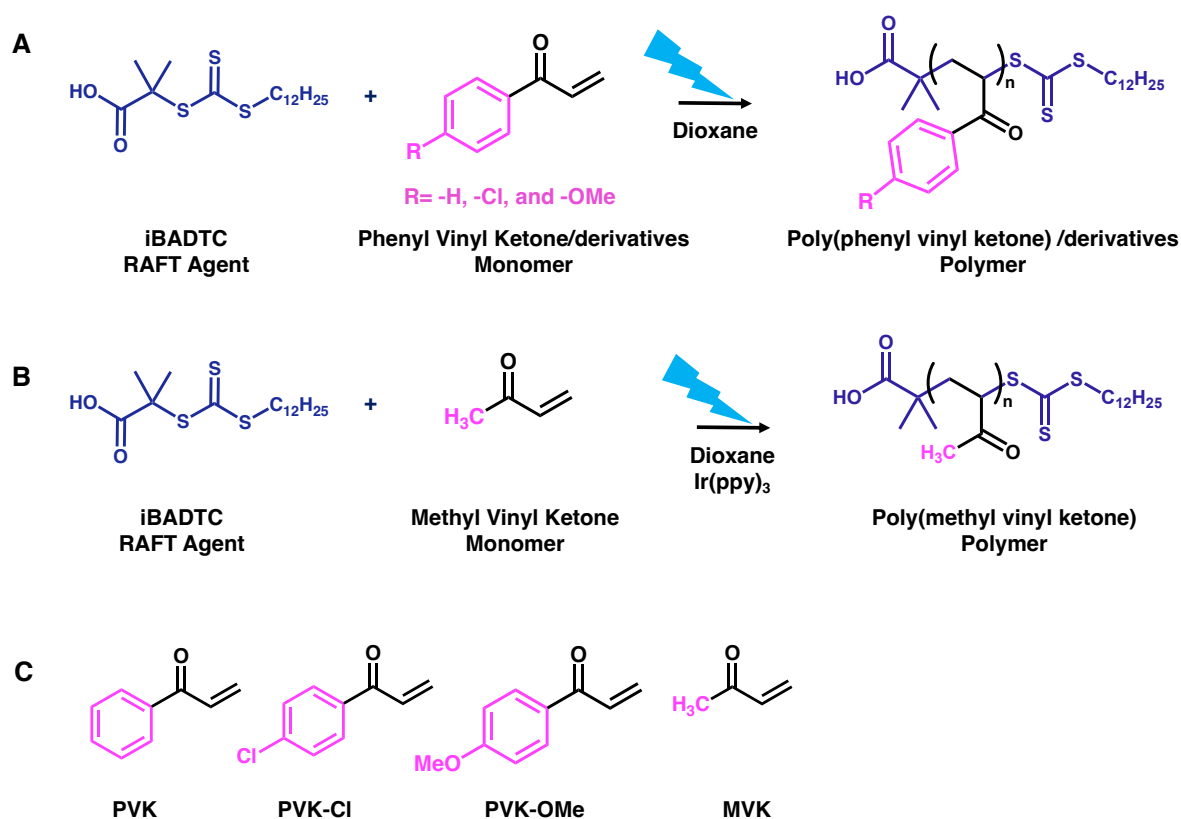
VK polymers contain a ketone group in each repeating unit giving a high density of photo responsive ketone groups in the polymer. Therefore, VK polymers are susceptible to dramatic changes in the polymer backbone through UV degradation. The disruption in the polymer backbone is important for emerging applications including degradable materials[28], targeted delivery[53,54], tuning molecular weight / dispersity[50], and lithography[54]. In the literature there have been several studies of polymer degradation. However, studies based on controlled degradation is limited and those studies have several requirements to achieve the degradation. Therefore, controlled polymer degradation is required to further investigate to broaden their applications. Recently, Ouchi group has achieved successful photocatalyzed hydrogen atom transfer degradation of methyl methacrylate and vinyl ether copolymers under UV. However, they have stated that benzophenone photocatalyst, acetonitrile solvent, vinyl ether comonomer, and UV irradiation at 80 °C are crucial for the degradation and in the absence of any of these conditions no degradation takes place[55].

Ongoing studies have correlated changes in the properties of materials with the photodegradability of vinyl ketone based on thermoplastic elastomers[28] and interpenetrating polymer networks[27]. However, to the best of our knowledge detailed kinetic studies comparing chain cleavability of different VK polymers under different degradation conditions to control the chain cleavability have not been studied in the literature. Especially, control over the rate of photodegradation for a targeted application requires a detailed understanding of the underlying degradation mechanisms and kinetics. Furthermore, tailoring the kinetics of photodegradation of VK polymers with different molecular weights, with different functional groups and especially under different conditions remains poorly understood. In spite of the fact

that, VK polymers are among the most easily photodegraded macromolecules, their photodegradation has received minimal attention over the past years. This contribution studies the impact of polymer structure, functionality, and reaction conditions on the degradation of VK polymers under light. This degradation is captured in an overall scaling law, and thereby opening a door towards sophisticated applications in degradable and responsive materials. Finally, the fundamental photodegradation rates are connected to bulk changes in the material, through thermal analysis and changes in surface morphology.

Results and Discussion

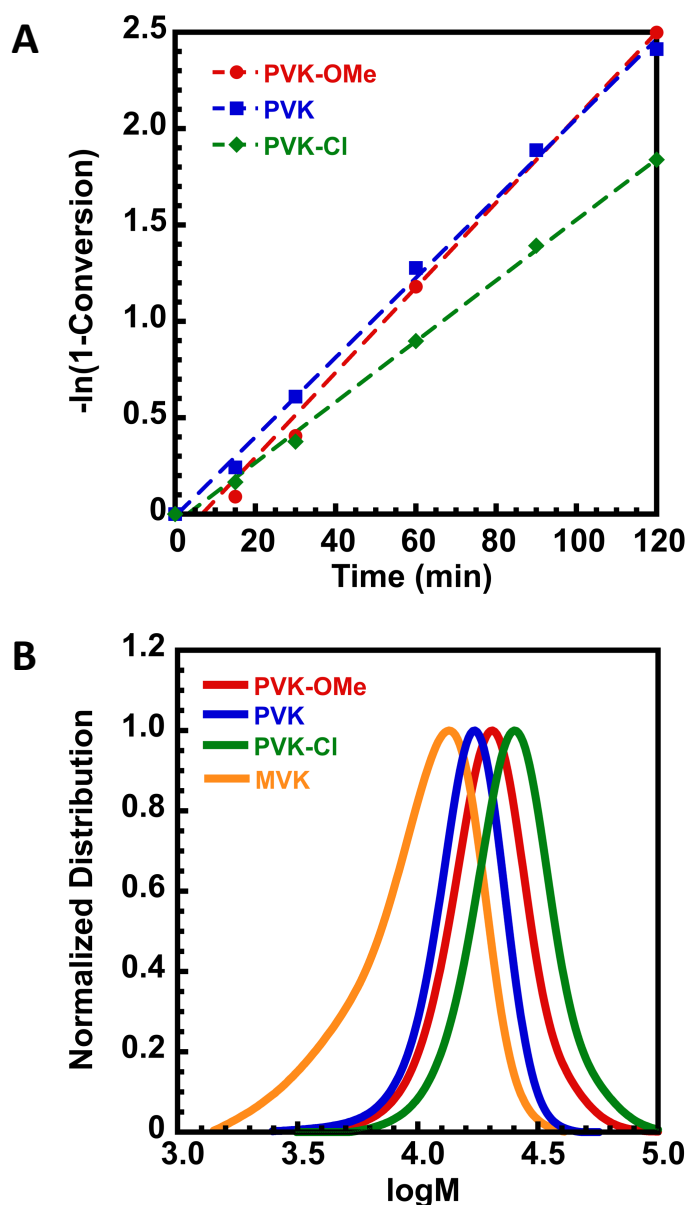
Before investigating photodegradation, polymerization kinetics were performed to evaluate the polymer generation process. Initially the target degree of polymerization (DP) of 200 was studied, as highlighted in Scheme 1. No radical initiators or photocatalysts were used for the polymerization of phenyl vinyl ketone monomers, since the vinyl ketone monomers generate radicals and initiate the polymerization through its intrinsic photochemistry under blue light as shown through the proposed mechanism in Scheme 2A. However, photoinduced electron/energy transfer-RAFT (PET-RAFT) polymerization using iridium(III)trisphenylpyridine ($\text{Ir}(\text{ppy})_3$) was performed to obtain poly(methyl vinyl ketone) (poly(MVK)) (Table S2) because of the lower efficiency of the radical generated from MVK through Norrish I reaction under blue light[50]. Both PET-RAFT polymerization and RAFT-photopolymerization is similar though PET-RAFT mechanism involves photochemically generated radicals by photocatalyst to initiate the polymerization[15] and RAFT-photopolymerization process of other three phenyl vinyl ketone derivatives involves radicals generated by vinyl ketone monomer through the Norrish I mechanism as discussed above.



Scheme 1: (A) RAFT photopolymerization of PVK, PVK-OMe and PVK-Cl. (B) PET-RAFT polymerization of MVK. (C) Structures of VK monomers.

Initially, four different VK polymers, poly(phenyl vinyl ketone)-poly(PVK), poly(4-chlorophenyl vinyl ketone)-poly(PVK-Cl), poly(4-methoxy phenyl vinyl ketone)-poly(PVK-OMe), and poly(methyl vinyl ketone)-poly(MVK) were synthesized via RAFT polymerization as shown in Scheme 1. The RAFT controlled photopolymerization of PVK and MVK have been reported[50,51,56], however, only conventional radical polymerization of PVK-OMe[57] and PVK-Cl[57] have been reported to the best of our knowledge. This presents a unique opportunity to study photopolymerization rate and photodegradation rate as a function of side group donating and withdrawing capability. Radical generation in polymerization is proposed to occur through a Norrish Type I process as highlighted in Scheme 2A. Photodegradation of VK polymers is proposed to occur through a Norrish Type II pathway, as drawn in Scheme 2B[27,28,51].

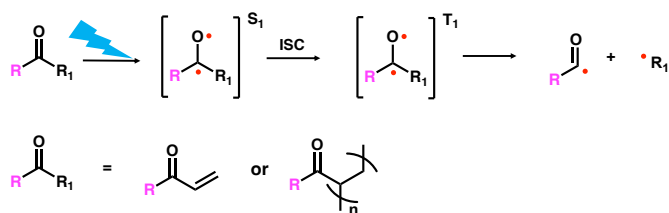
Figure 1A shows the polymerization kinetics of PVK (1-phenylprop-2-en-1-one), PVK-Cl (1-(4-chlorophenyl)-2-propen-1-one) and PVK-OMe (1-(4-methoxyphenyl)-2-propen-1-one) monomers. RAFT photopolymerization was carried out at room temperature under blue light ($\lambda_{\text{max}} = 450 \text{ nm}$ (Intensity= $1.9 \pm 0.20 \text{ mW/cm}^2$, measured as the incident intensity onto a light power meter) and deoxygenated conditions. For all polymerizations, conversion over 85% and narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.14\text{-}1.36$) were achieved within 2 h under blue light irradiation as shown in Table S1. Both PVK and PVK-OMe monomers showed a relatively faster polymerization with an apparent rate of propagation $k_p^{\text{app}} = 0.0221 \text{ min}^{-1}$ and $k_p^{\text{app}} = 0.0206 \text{ min}^{-1}$ respectively, while the apparent rate of propagation of PVK-Cl was somewhat lower at $k_p^{\text{app}} = 0.0158 \text{ min}^{-1}$. However, there was a minimal difference in their polymerization rates. As noted in the literature, MVK polymerizes substantially slower than the PVK derivatives, hence the PET-RAFT approach was used. RAFT polymerization yielded well-defined VK polymers with narrow MWDs for all four systems with dispersities in the order of 1.14-1.38 as seen in Figure 1B.



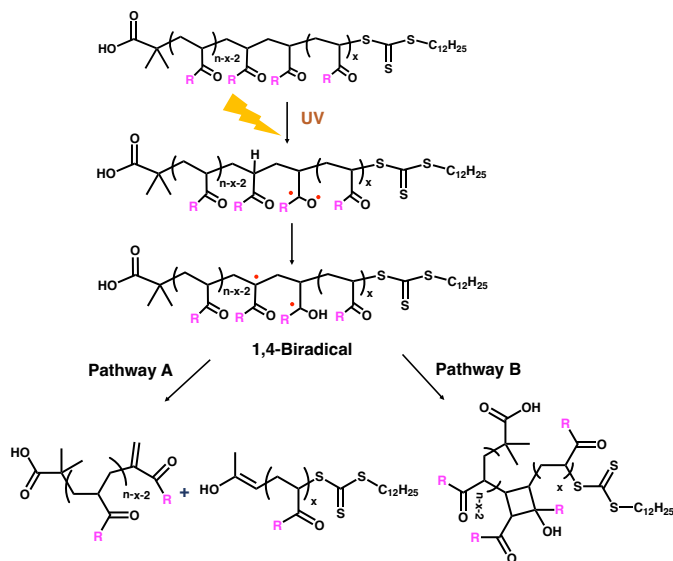
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151 **Figure 1:** (A) Polymerization kinetics of PVK, PVK-Cl and PVK-OMe monomers. (B)
 152 Normalized distributions of PVK, PVK-Cl, PVK-OMe and MVK polymers. Conditions for
 153 PVK, PVK-OMe and PVK-Cl: Molar ratio of [Monomer]: [iBADTC]=200:1, 33 mass% of
 154 monomer under blue light 450 nm (Intensity= 1.9 ± 0.20 mW/cm²), deoxygenated conditions,
 155 and at room temperature for 2 h. Conditions for MVK: Molar ratio of MVK: iBADTC:
 156 Ir(ppy)₃= 200:1:0.002, 33 mass% of monomer under blue light 450 nm (Intensity= 1.9 ± 0.20
 157 mW/cm²), deoxygenated conditions, and at room temperature for 72 h.

A Polymerization - Norrish I



B Degradation - Norrish II



Scheme 2: (A) Radical generation through Norrish I reaction to initiate the polymerization of VK monomers under blue light (450 nm). (B) Radical generation through Norrish II reaction to degrade poly(vinyl ketone) polymers under UV light (310 or 350 nm).

Poly(vinyl ketone) polymers were exposed to various degradation conditions by changing wavelength of light, degradation time, chain length and polymer concentration. The wavelengths explored were in the UV region and visible regions. Initially, all polymers were in dioxane with a fixed ratio of polymer: solvent to keep a constant polymer concentration (0.36 g/mL) throughout all experiments. All photodegradation kinetics occurred under deoxygenated conditions to minimize any potential quenching by triplet oxygen. To analyze the kinetics of degradation, a simple model was developed that estimates the rate of new polymer end group formation through the degradation process. Since to a first approximation

the number of repeat units doesn't change in the degradation process, the ratio of initial number average molecular weight ($M_{n,0}$) to number average molecular weight at time t into the photodegradation process ($M_{n,t}$) can be estimated as follows:

$$\frac{M_{n,0}}{M_{n,t}} = \frac{DP_{n,0}}{DP_{n,t}} = 1 + \frac{C\Phi_{eff}I_{hv}DP_{n,0}t}{[R]} \quad (1)$$

Where C is a constant particular to the geometry and reactor set up, Φ_{eff} is the quantum yield of photocleavage of the backbone, I_{hv} is the photon flux, $DP_{n,0}$ is the initial number average DP and $[R]$ is the concentration of repeat units. The concentration is reported as a mass concentration of g/mL for analysis due to the same polymer mass fractions in solution, but the different repeat unit molar masses in PVK, PVK-Cl and PVK-OMe. However, a similar analysis could be performed using molar repeat unit concentrations. Detailed derivation can be found in the supporting information.

Figure 2 uses the linear scaling of $M_{n,0} / M_{n,t}$ with time (t) in eq 1 to highlight the degradation kinetics of three different types of phenyl vinyl ketone polymers: poly(PVK), poly(PVK-Cl), and poly(PVK-OMe) with para substituted hydrogen (-H), chloro (-Cl) and methoxy (-OMe) groups in the phenyl ring of each repeating unit. Polymers were degraded under 310 nm (Intensity= 2.3 ± 0.35 mW/cm², moles of photons= 5.96×10^{-9} mol cm⁻² s⁻¹), 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹), and 450 nm (Intensity= 1.9 ± 0.20 mW/cm², moles of photons= 7.14×10^{-9} mol cm⁻² s⁻¹) wavelengths. Samples were collected during different time intervals and number average molecular weight (M_n) and dispersity (M_w/M_n) were determined using gel permeation chromatography (GPC). In general, the evolution of $M_{n,0} / M_{n,t}$ with respect to time is linear or close to linear. In all cases the R^2 value for the linear fits was >0.85 , and mostly >0.95 . Variations can be attributed to uncertainties associated with GPC analysis which can be up to $\sim 10\%$ [58].

In all cases, a similar trend was observed with respect to wavelength. As shown in Figure 2A (i) and (ii), there is a significant difference in the degradation kinetics between three different phenyl vinyl ketone polymers under both 310 and 350 nm. This highlights the significant role played by the para substituted group in the degradation process and for Norrish II chemistry in the radical generation process. Among all three phenyl vinyl ketone polymers, poly(PVK-Cl) had the fastest degradation with $3.75 \times 10^{-4} \text{ s}^{-1}$ degradation rate under 350 nm and with $1.53 \times 10^{-4} \text{ s}^{-1}$ under 310 nm. While poly(PVK) had the second fastest degradation with $2.68 \times 10^{-4} \text{ s}^{-1}$ and $0.88 \times 10^{-4} \text{ s}^{-1}$ degradation rates under 350 and 310 nm respectively. However, poly(PVK-OMe) showed notably low degradation rates compared to both poly(PVK-Cl) and poly(PVK). Poly(PVK-OMe) had $0.88 \times 10^{-4} \text{ s}^{-1}$ and $0.15 \times 10^{-4} \text{ s}^{-1}$ degradation rates at 350 nm and 310 nm respectively. Furthermore, UV spectra of VK polymers, before (solid lines) and after degradation (dash lines) were compared as seen in Figure 2C. These UV-Vis spectra were collected on polymers synthesized under conventional radical polymerization (FRP) to ensure there is no RAFT end-group that could overlap with the poly(VK) units. Poly(PVK-OMe) had the highest absorption in the 300 nm-350 nm wavelength range although poly(PVK-OMe) is the least degraded polymer under both 310 and 350 nm among all phenyl vinyl ketone polymers in this study and this implies that absorbance is not the determining factor in degradation rate under UV irradiation[59]. When considering the comparison between before and after degradation, all 24 h degraded poly(vinyl ketone) systems showed a lower absorption indicating a reduction in light absorption efficiency after the degradation. This could be due to some along backbone conjugation of the aromatic rings and ketone groups which is less efficient after photodegradation. However, additional studies beyond the scope of this work would be needed to understand this reduction of chromophore absorption efficiency.

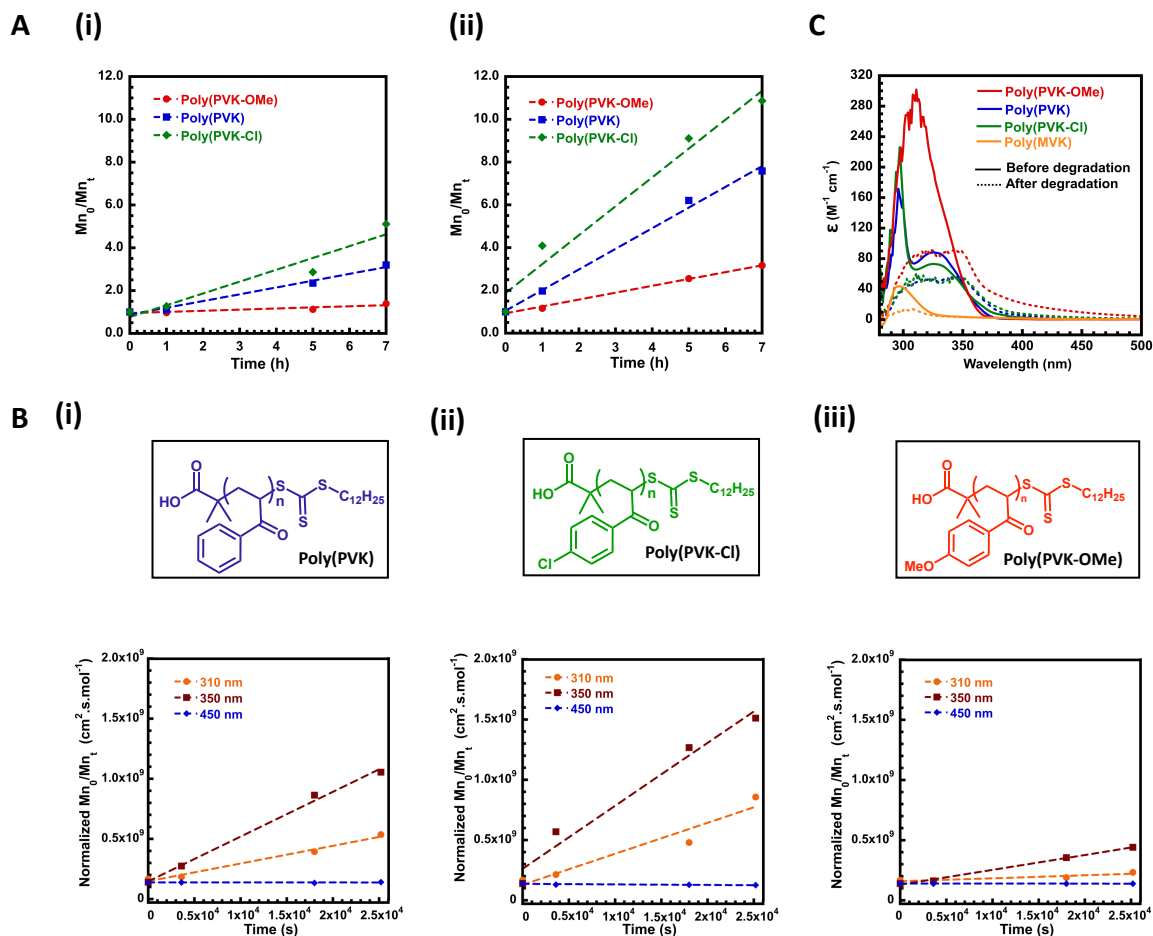


Figure 2: (A) Comparison of degradation kinetics of poly(PVK), poly(PVK-Cl), and poly(PVK-OMe) polymers. (i) Under 310 nm (Intensity= 2.3 ± 0.35 mW/cm², moles of photons= 5.96×10^{-9} mol cm⁻² s⁻¹) and (ii) under 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹). (B) Intensity normalized degradation kinetics of (i) poly(PVK), (ii) poly(PVK-Cl), and (iii) poly(PVK-OMe) under 310 nm (Intensity= 2.3 ± 0.35 mW/cm², moles of photons= 5.96×10^{-9} mol cm⁻² s⁻¹), 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹), and 450 nm (Intensity= 1.9 ± 0.20 mW/cm², moles of photons= 7.14×10^{-9} mol cm⁻² s⁻¹) wavelengths. Conditions for degradation kinetics: 0.36 g/mL of polymers with DP 200 chain length under deoxygenated conditions, and at room temperature. (C) UV spectra of poly(PVK), poly(PVK-Cl), poly(PVK-OMe), and poly(MVK) polymers made by FRP. UV spectra before and after degradation are presented using solid and

dash line respectively. Conditions for degradation: 0.36 g/mL of polymers under 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹), deoxygenated conditions, and at room temperature.

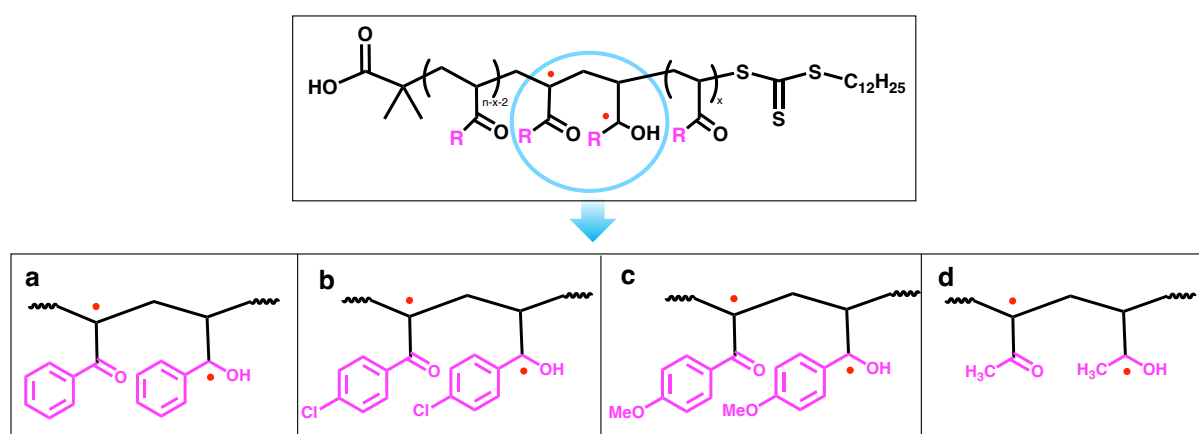
The fastest degradation for all three phenyl vinyl ketone polymers was achieved at 350 nm while the second fastest degradation was achieved under 310 nm. However, each photoreactor produces photons with a slightly different intensity and energy. Therefore, to compare between photoreactors, a normalization procedure was applied. Eq 1 indicates that the change in number average molecular weight ($M_{n,0}/M_{n,t}$) can be divided by the intensity of the photoreactor (I_{hv}) to give an intensity invariant degradation rate, or normalized degradation rate:

$$\text{Normalized } M_{n,0}/M_{n,t} = M_{n,0}/M_{n,t} \times \frac{1}{I_{hv}} \quad (2)$$

Here the molar photon flux per square centimeter is used as the intensity (I_{hv}) in normalization to allow comparison between photoreactors. As seen in Figure 2B kinetics graphs, there is a notable difference between the degradation rates under 310 and 350 nm for all phenyl vinyl ketone polymers. A greater than 50% reduction of initial M_n can be observed for poly(PVK-Cl) and poly(PVK) polymers within 1 h exposure time under 350 nm, whereas this same decrease in M_n required almost 5 h for poly(PVK-OMe). Although both 310 and 350 nm wavelengths in the UV region are capable of degrading all three phenyl vinyl ketone polymers, there was essentially no degradation under 450 nm which is the blue light region. Typically, 450 nm is used to perform polymerization with VK monomers and polymers generating radicals through Norrish I reaction to initiate the polymerization. Therefore, data suggests that 450 nm is not capable of generating radicals in the VK polymer to initiate the

degradation process although it is capable of generating radicals from the VK monomer to initiate the polymerization.

According to the Norrish Type II mechanism, upon excitation, the carbonyl chromophore in ketones goes to excited singlet state (S_1) followed by higher excited triplet state (T_n) through intersystem crossing (ISC) and then undergoes rapid internal conversion into a lower excited triplet state (T_1). From the triplet state, T_1 , initiation or elimination happen as shown in Scheme 2A and 2B. Therefore, the stability of the 1,4-biradical in the triplet state is critical to the efficiency of photoelimination through a Norrish II reaction that results in two fragments with an alkene and a ketone group (Norrish II-Pathway A) [18,51].



Scheme 3: Structure of 1,4-biradical in the triplet excited state (a) 1,4-biradical in poly(PVK) polymer, (b) 1,4-biradical in poly(PVK-Cl) polymer, (c) 1,4-biradical in poly(PVK-OMe) polymer, and (d) 1,4-biradical in poly(MVK) polymer.

Scheme 3 shows the nature of the 1,4-biradical Norrish type II intermediate in each polymer. The difference in degradation rates of poly(PVK), poly(PVK-Cl) and poly(PVK-OMe) can be discussed based on the stability of 1,4-biradical because degradation happens with α - β bond cleavage after 1,4-biradical formation. The 1,4-biradical in poly(PVK-Cl) polymer could be more stable than the 1,4-biradical in both poly(PVK) polymer and poly(PVK-

OMe) polymer because of the electron withdrawing -Cl group. It has been noted previously that electron withdrawing groups (EWGs) are more capable of stabilizing free radicals whereas electron donating groups (EDGs) are less capable of stabilizing free radicals[60]. Further, this has been studied previously using the bromination of para substituted toluene and it was found that EWGs stabilize the benzyl radical while EDGs destabilize the benzyl radical[60]. Similar to that factor, it can be argued that 1,4-biradical in the poly(PVK-Cl) polymer is more stable in the T_1 state and therefore poly(PVK-Cl) polymer degrades fast through Norrish II chemistry. Moreover, this stability can be rationalized using the ability of the chloro group to delocalize the unpaired electron that is conjugated with the phenyl ring. However, the oxygen atom on methoxy group or H group cannot delocalize that unpaired electron ability since it is a first-row element. Therefore, these data suggest a way to control the main-chain cleavability of phenyl vinyl ketone polymers by simply changing the substituent on the phenyl ring's para position in the VK monomer.

The behavior of poly(MVK) under the UV region is totally different from the degradation of phenyl vinyl ketone polymers. As shown in Figure S3, poly(MVK) showed a substantially slower degradation rate in contrast to all three phenyl vinyl ketone polymers even after 48 h under UV. This behavior could arise from the stability of the 1,4-biradical in the triplet state as discussed above. The 1,4-biradical in poly(MVK) polymer has a methyl group which is less efficient towards stabilizing the radical compared to phenyl ring as illustrated in Scheme 3. Therefore, poly(MVK) is a less efficient photodegradable polymer in applications where it needs dramatic changes in the material upon irradiation.

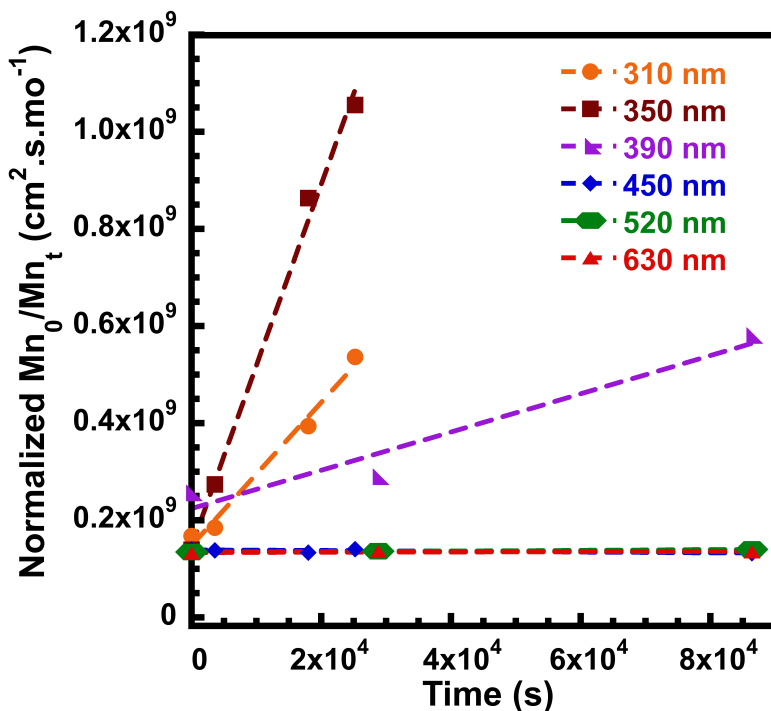
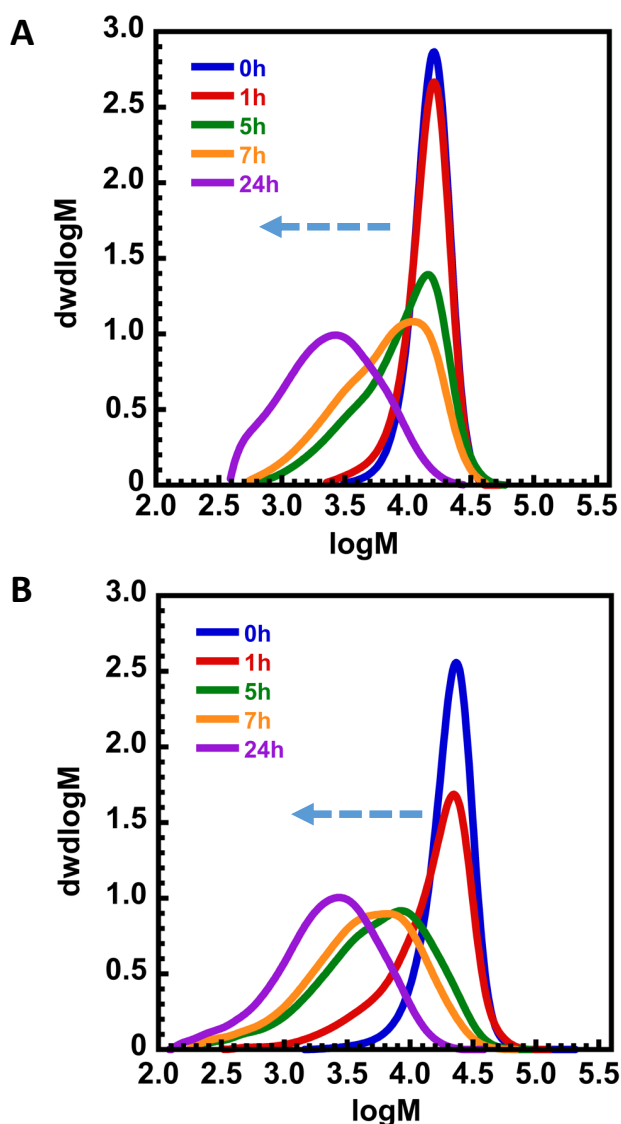


Figure 3: Intensity normalized degradation kinetics of poly(PVK). Conditions: 0.36 g/mL of polymers with DP 200 chain length under 310 nm (Intensity= 2.3 ± 0.35 mW/cm², moles of photons= 5.96×10^{-9} mol cm⁻² s⁻¹), 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹), 390 nm (Intensity= 1.2 ± 0.07 mW/cm², moles of photons= 3.90×10^{-9} mol cm⁻² s⁻¹), 450 nm (Intensity= 1.9 ± 0.20 mW/cm², moles of photons= 7.14×10^{-9} mol cm⁻² s⁻¹), 520 nm (Intensity= 1.7 ± 0.07 mW/cm², moles of photons= 7.43×10^{-9} mol cm⁻² s⁻¹) and 630 nm (Intensity= 1.4 ± 0.06 mW/cm², moles of photons= 7.57×10^{-9} mol cm⁻² s⁻¹) wavelengths, deoxygenated conditions, and at room temperature.

The impact of wavelengths in visible region on the degradation was explored using poly(PVK) polymer. As noted previously, poly(PVK) degraded rapidly under UV irradiation (310 and 350 nm). However, all other wavelengths 450, 520 and 630 nm were not able to degrade the polymer sample even after 24 h irradiation. As shown in both Figure 3 and Table S6, there was a small extent of photodegradation at 390 nm, since this wavelength is at the edge of the visible and UV regions of the electromagnetic spectrum. Therefore, these data

suggest that only UV radiation is capable of degrading PVK polymers efficiently through Norrish chemistry and hence degradation can be modulated by the choice of wavelength.

Beyond M_n analysis, the MWDs for all phenyl vinyl ketone polymers under 310 and 350 nm are shown in Figure 4 and Figure S4 respectively. All degradation studies were started with well controlled narrow molecular weight polymers ($M_w/M_n = 1.2-1.3$) and the degradation process generates short oligomers with low molecular weights and high dispersities ($M_w/M_n = 2.2-2.8$). Each graph in Figure 4 and S4 shows how peaks shifted to the low molecular weight end and how they became broader due to the formation of short fragments through random scission of the backbone. Since poly(PVK-Cl) and poly(PVK) underwent rapid photodegradation under UV region, their MWDs became much broader and shifted to lower molecular weight than poly(PVK-OMe) and shown in Figure S4A-S4D. Further, as shown in Figure S4E and S4F, peaks for poly(PVK-OMe) had a minimal shift in the MWD with the degradation time, and they are centered at almost the same molecular weight region, especially in the graph for 310 nm. Poly(PVK-OMe) also had a small high molecular weight shoulder formed upon UV irradiation, presumably due to the photoiniferter reaction[15] that generates chain end radicals that can couple. Overall, all these findings highlight a simple way to control the main chain cleavability of VK polymers by changing exposure time under UV in addition to wavelength of the light and the nature of the VK monomer.



323

324 **Figure 4:** Evolution of molecular weight distributions with the degradation time. All graphs
 325 are area normalized. (A) Poly(PVK) under 310 nm (Intensity= 2.3 ± 0.35 mW/cm², moles of
 326 photons= 5.96×10^{-9} mol cm⁻² s⁻¹) and (B) poly(PVK) under 350 nm (Intensity= 2.5 ± 0.13
 327 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹). Conditions: 0.36 g/mL of polymers with
 328 DP 200 chain length, under deoxygenated conditions, and at room temperature.

329 Figure 5 explores the impact of the polymer concentration and the initial chain length
 330 for the photodegradation. Experiments were performed under 350 nm where all phenyl vinyl
 331 ketone showed their maximum degradation. Two series of poly(PVK) polymer samples with

DP 100 and DP 200 chain lengths were prepared at polymer concentrations of 0.36, 0.18, 0.09, and 0.04 g/mL. Figure 5A highlights the incredibly fast photo cleavability of samples with 0.09 and 0.04 g/mL concentrations. For instance, as seen in Figure 5 and Figure S5, degradation rate (Degradation rate= $18.50 \times 10^{-4} \text{ s}^{-1}$ and normalized degradation rate= $256958 \text{ cm}^2\text{mol}^{-1}$) of the system with 0.04 g/mL polymer concentration is nearly seven times higher than the degradation rate (Degradation rate= $2.68 \times 10^{-4} \text{ s}^{-1}$ and normalized degradation rate= $37310 \text{ cm}^2\text{mol}^{-1}$) of the system with 0.36 g/mL polymer concentration. Further, as shown in Table S10C and S10D, initial polymer chains were cleaved into smaller fragments with 1/3 or 1/4 of its initial M_n within 10 min exposure time. This is most likely due to the higher ratio of incident photons to vinyl ketone chromophores at low concentration. This is also predicted by the scaling relationship of eq 1, where the concentration of repeat units is in the denominator. As shown in Figure 5B, a similar trend with respect to the polymer concentration can be observed in DP 100 system as in DP 200 system.

The impact of the initial chain length for the degradation was studied using DP 400, 200, 100 and 50 chain lengths under same degradation conditions. As seen in Figure 5C, the degradation at the higher targeted chain length was faster than the degradation at the lower targeted chain length. A gradual increment of degradation rate can be clearly seen in Figure 5C with increasing the initial chain length from DP 50 to DP 400. The degradation rate for DP 400 system (Degradation rate= $5.08 \times 10^{-4} \text{ s}^{-1}$ and normalized degradation rate= $70705 \text{ cm}^2 \text{mol}^{-1}$) is substantially higher than the degradation rate of DP 50 system (Degradation rate= $0.47 \times 10^{-4} \text{ s}^{-1}$ and normalized degradation rate= $6541.8 \text{ cm}^2 \text{mol}^{-1}$). This chain length dependent behavior can be further observed in the presence of different polymer concentrations as in Figure 5A and Figure 5B. For instance, when compared DP 100 and DP 200 systems at 0.04 g/mL polymer concentration, the degradation rate of DP 200 system is nearly two times higher than the degradation rate of DP 100 system. This is predicted by eq 1, and stems from the fact that

357 a photodegradation event creates a relatively larger number of new end groups at a higher chain
358 length, compared to a lower one leading to a faster degradation.

359

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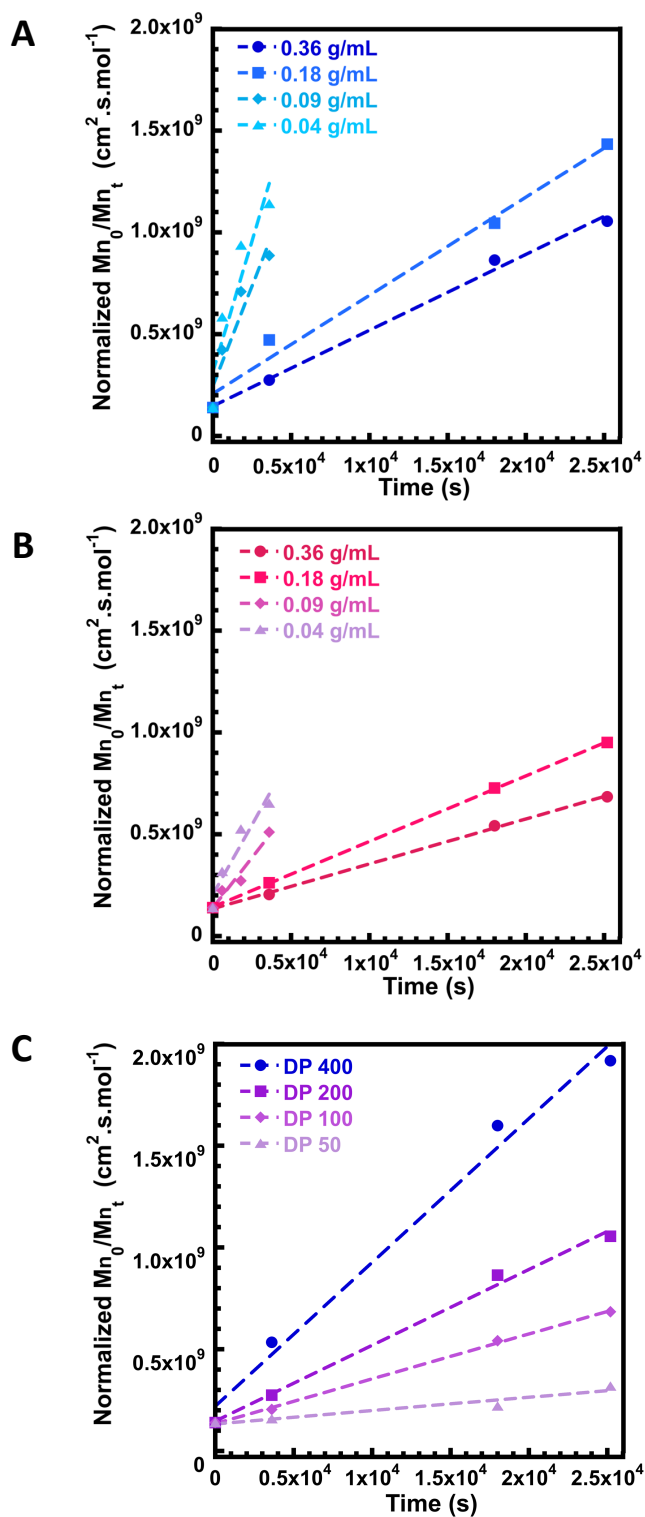


Figure 5: Intensity normalized degradation kinetics of poly(PVK). Conditions: Polymers with (A) DP 200 chain length (B) DP 100 chain length and in the presence of 0.36 g/mL, 0.18 g/mL, 0.09 g/mL, and 0.04 g/mL polymer concentrations. (C) Comparison between DP 400, DP 200, DP 100, and DP 50 system at 0.36 g/mL polymer concentration. All degradations were

366 performed under 350 nm (Intensity= $2.5 \pm 0.13 \text{ mW/cm}^2$, moles of photons= $7.19 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$) wavelength, deoxygenated conditions, and at room temperature.

368 The photochemical nature of the degradation was confirmed following an ON-OFF
369 experiment. As seen in Figure 6A, poly(PVK) polymers undergo an efficient degradation in
370 the light ON period while degradation is ceased in the light OFF period. Further when the light
371 is back ON, the degradation process resumes again. Degradation kinetics under continuous and
372 intermittent irradiations (only irradiated time is used) are compared in Figure 6B and both
373 continuous and intermittent irradiations have almost same degradation rates as a function of
374 irradiation time, since there is no degradation during the dark period. Therefore, Figure 6 shows
375 that poly(PVK) degradation is consistent with photochemically controlled radical generation
376 in Norrish II reaction.

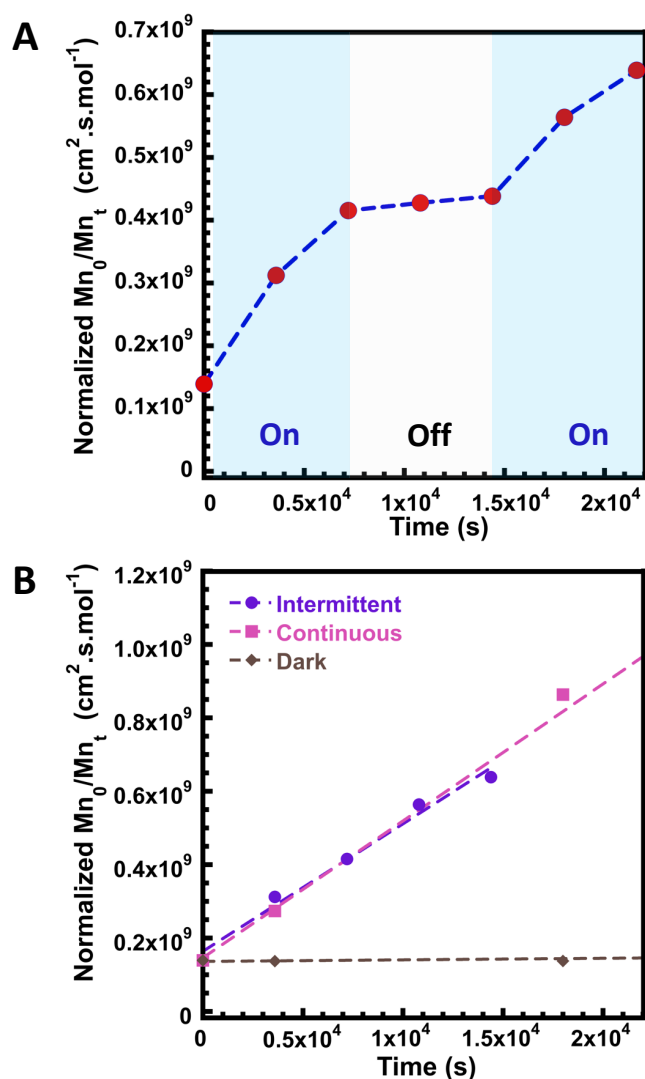


Figure 6: Intensity normalized degradation kinetics of poly(PVK) polymers with DP 200 chain length. Conditions: (A) Under intermittent light irradiation (ON (under 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹) wavelength) and OFF periods), (B) Comparison of degradation reactions under intermittent light irradiation, continuous light irradiation and under dark conditions. All reactions were performed under deoxygenated conditions, and at room temperature. Samples were placed inside the reactor for the dark and OFF reactions in the absence of light irradiation.

In spite of the fact that elimination of oxygen is important in kinetic studies to understand the degradation process of vinyl ketones, the presence of oxygen in lots of

application including waste management or targeted delivery is mostly inevitable. Therefore, the impact of oxygen for the degradation was studied using poly(PVK) polymer under 350 nm. As seen in Figure S1, in the presence of oxygen, poly(PVK) showed a relatively faster degradation with a minimal difference compared to the degradation in the absence of oxygen.

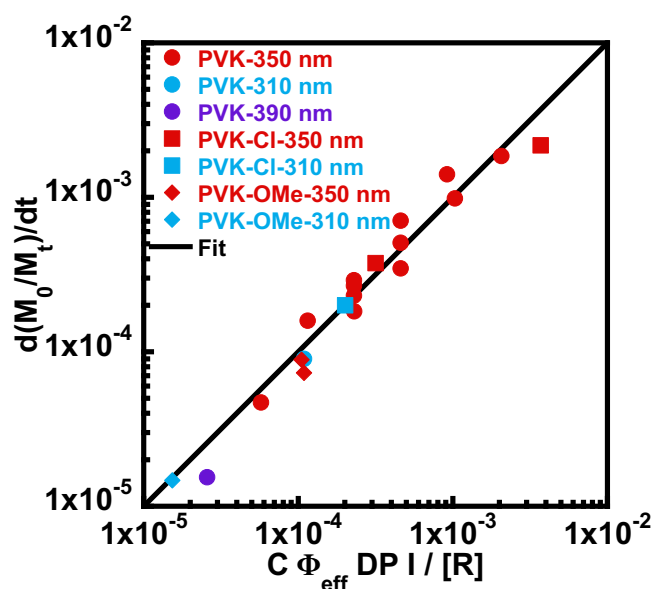
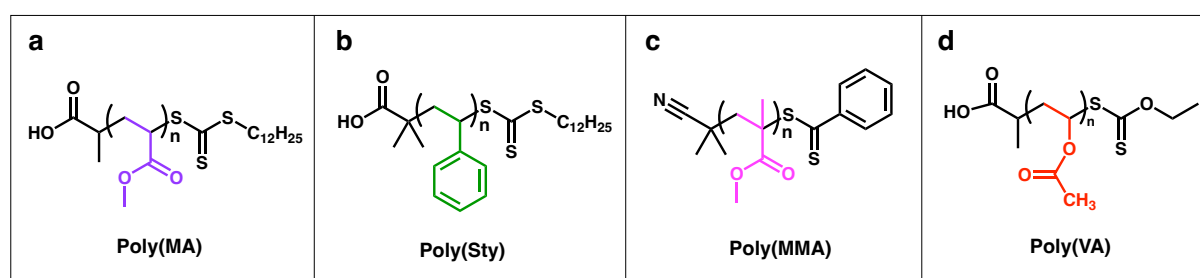


Figure 7: Fitted and experimental degradation rates. Fitted rates were determined by following eq 1.

Degradation rates for poly(PVK), poly(PVK-Cl) and poly(PVK-OMe) under 310, 350 and 390 nm were compared between the experimental values and the fitted values from the model of eq 1 through a kinetics scaling analysis[61,62]. As seen in Figure 7, the experimental degradation rates agree with the degradation rates from the model of eq 1, fitting only the product of C and Φ_{eff} to a given experimental data series. This highlights that a general scaling relationship between polymer degradation rate and the experimentally relevant variables of initial polymer DP, concentration of polymer and light intensity. It is noteworthy that both polymers synthesized by FRP, and RAFT fall on the same scaling relationship without requiring any additional fitting parameters, indicating the degradation mechanism involves

backbone cleavage rather than end-group specific chemistry. This type of scaling analysis could be further performed on other materials that have demonstrated photodegradation such as those based on degradable coumarin units[63], or other vinyl polymers using deep or extended UV irradiation[64].



Scheme 4: Structure of (a) poly(MA), (b) poly(Sty), (c) poly(MMA), and (d) poly(VA) polymers made by RAFT polymerization.

To highlight the unique photodegradation potential of poly(PVK), the photodegradation of four common commodity polymers was studied. These commodity polymers were poly(methyl acrylate)- poly(MA) , poly(styrene)-poly(Sty), poly(methyl methacrylate)-poly(MMA), and poly(vinyl acetate)-poly(VA). All polymers were synthesized by RAFT polymerization to obtain well controlled polymer for the degradation study and structures are drawn in Scheme 4. Conversions, molecular weights and dispersities of all polymers are shown in Table S4. Molecular weights and dispersities of each polymer after 24 h exposure time and under 310, 350, 390, 450, 520, and 630 nm wavelengths are included in Table S14 and molecular weight distributions of poly(MA), poly(Sty), poly(MMA) and poly(VA) before and after the degradation are shown in Figure S2. As seen in Table S14 and Figure S2 none of these commodity polymers showed significant degradation under any of wavelength tested. Both poly(MA) and poly(Sty) polymers have a high molecular weight shoulder peak under 310 and 350 nm because of radical coupling reaction. However, when compared the degradation of commodity polymers in this study with phenyl vinyl ketone

polymers, both poly(PVK) and poly(PVK-Cl) showed fast photodegradation under UV region within 7 h and with a negligible degradation under 450, 520 and 630 nm as shown above in Figure 2B and Figure 3. All these trends can be rationalized using Norrish II chemistry. As shown in Scheme 4, none of these commodity polymers have a ketone group in their structure. Conjugation of the ester carbonyl with the alkoxy group decreases the carbonyl character in poly(VA), poly(MA) and poly(MMA). Therefore, they are not capable of undergoing main chain cleavability under UV light through Norrish chemistry as efficiently as poly(PVK) and its derivatives.

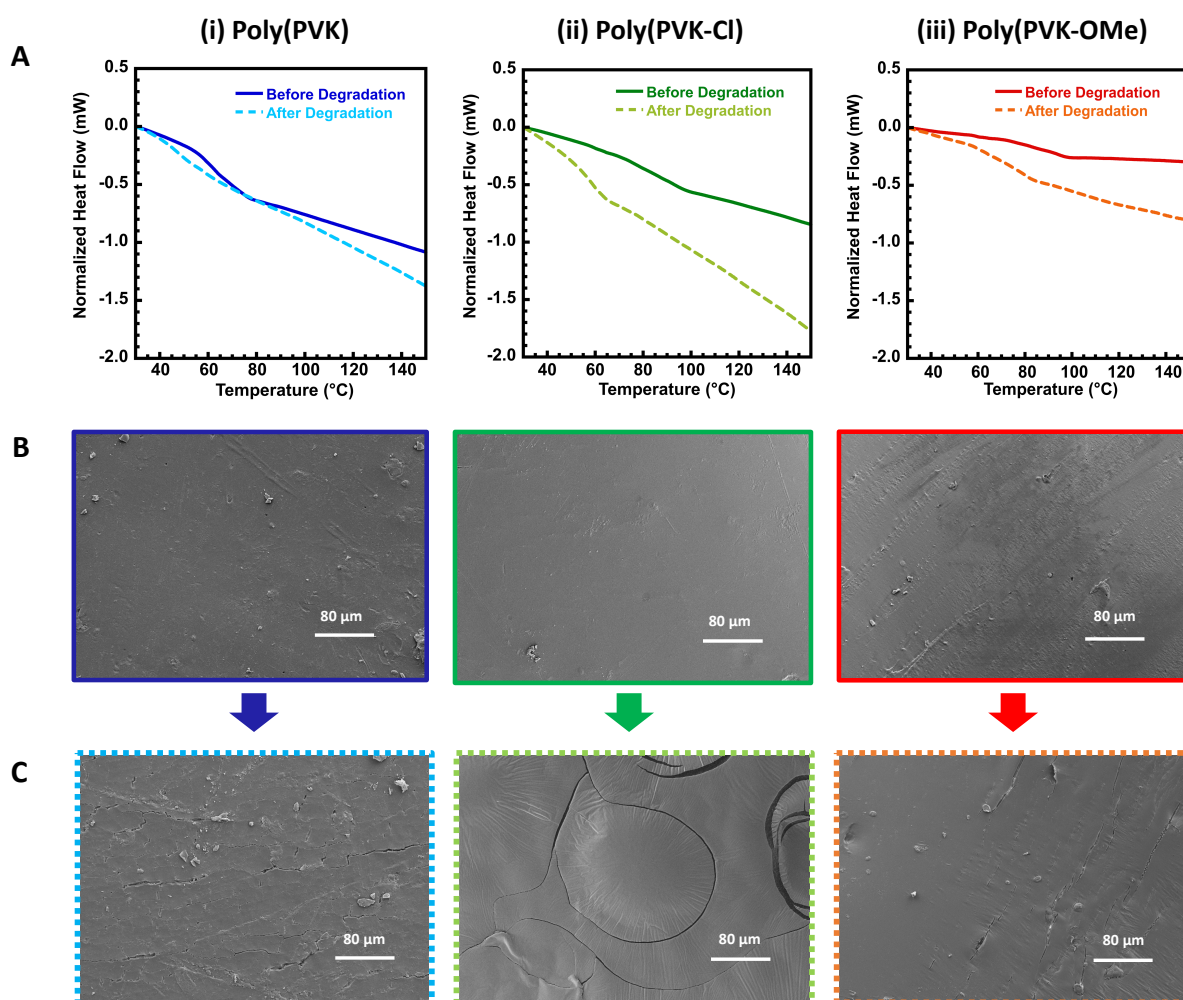


Figure 8: (A) DSC of phenyl vinyl ketone polymers before and after degradation. (B) SEM images of phenyl vinyl ketone polymers before photodegradation. (C) SEM images of phenyl

vinyl ketone polymers after photodegradation. (i) Poly(PVK), (ii) poly(PVK-Cl), and (iii) poly(PVK-OMe). Degraded materials were obtained after the degradation under 350 nm (Intensity= 2.5 ± 0.13 mW/cm², moles of photons= 7.19×10^{-9} mol cm⁻² s⁻¹) for 24 h.

Beyond studying the solution based photodegradation of the PVK based polymers, bulk and surface material properties were studied. Differential scanning calorimetry (DSC) was performed for all phenyl vinyl ketone materials to evaluate the impact of degradation on material's properties. Glass transition temperature (T_g) of materials were compared before and after the degradation, by fitting onset and offset of the T_g as outlined in the SI. Materials were subjected to degradation under 350 nm (Intensity= 2.5 ± 0.13 mW/cm²) for 24 h to obtain degraded materials. Thermograms of each polymer before (solid) and after (dashed) degradation are shown in Figure 8A. T_g values after the degradation clearly move to a lower value compared to the value before the degradation in all three cases because degradation enhances the chain mobility due to formation of shorter polymer fragments. As shown in Figure 8A and Table S15, degraded poly(PVK-Cl) had a dramatic change in T_g values ($T_{g, \text{poly(PVK-Cl) before}} = 82$ °C, $T_{g, \text{poly(PVK-Cl) after}} = 57$ °C) upon degradation compared to poly(PVK-OMe) system ($T_{g, \text{poly(PVK-OMe) before}} = 85$ °C, $T_{g, \text{poly(PVK-OMe) after}} = 74$ °C). This is consistent with the results from degradation kinetic experiments because poly(PVK-Cl) showed faster degradation while poly(PVK-OMe) showed slower degradation. In addition to that poly(PVK) had $T_{g, \text{poly(PVK)}} = 60$ °C before the degradation and $T_{g, \text{poly(PVK)}} = 49$ °C after the degradation which also reveals the impact of photodegradation on bulk properties.

Finally, surface characterization was performed for materials before and after degradation following scanning electron microscopy (SEM). Figure 8B, highlights the difference between uncracked surfaces before the degradation and rough, uneven, and cracked surfaces after the degradation for all phenyl vinyl ketone polymers. Poly(PVK) and poly(PVK-

Cl) show comparatively damaged surfaces with propagated cracks throughout the surface after the degradation while poly(PVK-OMe) shows scattered cracks on the surface. Furthermore, the average sizes of cracks in each system were determined using Image J software with a statistical analysis (Figure S7) and 4.1 μm , 3.2 μm , and 1.9 μm average crack sizes were obtained for poly(PVK-Cl), poly(PVK) and poly(PVK-OMe) respectively with a P-value of 0.0039 using one way ANOVA. It is important to note that the GPC analysis shows significant changes in molecular weight throughout the whole material, indicating that the surface changes and cracking are a result of modifications of the polymers throughout the sample by the photodegradation process. These SEM results are corroborated by atomic force microscopy (AFM) analysis (Figure S8), showing that poly(PVK-Cl) had a substantial increase in surface morphology after photodegradation, poly(PVK) had a small increase in the formation of islands and surface defects, while the overall surface of poly(PVK-OMe) was comparatively smooth before and after photodegradation. Therefore, microscopy supplies additional evidence for the impact of degradation on the surface and for differences in degradation based on the substituent on the phenyl ring.

Conclusion

The photodegradation of four different VK polymers (poly(PVK), poly(PVK-Cl), poly(PVK-OMe) and poly(MVK)) was investigated under different conditions changing substituent, wavelength of the light, degradation time, chain length and polymer concentration. Poly(PVK-Cl) polymer showed the fastest degradation under 350 nm while poly(PVK-OMe) showed the slowest degradation under 350 nm because of the radical stability in the Norrish II mechanism. Additionally, a faster degradation can be achieved in the presence of low polymer concentrations and longer chain lengths which also agrees with the equation in the developed degradation model. Further, degradation was characterized following DSC, SEM and AFM.

483 This work illustrates different ways to control the main chain cleavability and thereby to apply
484 VK materials in different promises applications.

485 **Conflicts of Interest**

486 The authors declare no competing interests.

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491 **Author Contributions**

492 M.A.S.N.W. were involved in experimental design, data acquisition, formal analysis and
493 writing and editing. P.A.M. and M.M. were involved in data acquisition, formal analysis and
494 editing the manuscript. I.O.R was involved in experiment design and formal analysis. P.N,
495 K.Y. and Z.O. were involved in data acquisition, formal analysis and editing the manuscript.
496 D.K. was involved in conceptualization, experimental design, formal analysis, writing and
497 editing.

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