

Comparison of UV- and EB-initiated Polymerizations Based on Equivalent Radical Concentration

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Abstract.

In this study, a protocol was developed to investigate UV- and EB-polymerized films of equivalent radical concentrations. This protocol was then applied to an acrylate/methacrylate pair to characterize the impact of the initiation mechanism. Raman spectroscopy was used to determine differences in polymer conversion. Monomer chemistry was shown to be a key variable in the comparison of the two initiation mechanisms.

Introduction.

Two common techniques for radiation-induced polymerization are ultraviolet (UV) and electron-beam (EB). Both techniques have advantages over thermal initiation and can be used to create similar products,^{1,2} including inks, adhesives, and coatings.³ Although UV and EB polymerization techniques are similar in many respects, there are differences between the two initiation mechanisms that can affect the polymerization kinetics and polymer properties.⁴⁻⁷

A major difference in UV and EB initiation is how primary radicals are formed. UV requires a photoinitiator, which absorbs light and decomposes to form predictable radical structures.^{8,9} In contrast, EB has enough energy to form radicals on any molecule in the formulation – even on the body of a polymer chain – and does not require an initiator.^{10,11} Radical formation during EB exposure is much less predictable than during UV exposure due to this ability to form radicals nearly anywhere. Non-selectivity can result in secondary reactions, such as crosslinking, instead of the desired secondary initiation reaction that is required for polymer formation.¹²

Other studies have shown that monomer chemistry is a key factor in radical formation and secondary reactions during EB polymerization.^{12,13} In one study, an increase in labile bonds in a monomer led to a higher concentration of primary radicals. However, this increase in primary radical concentration did not necessarily lead to an increase in the rate of polymerization or a higher final conversion.¹² Furthermore, this study also showed differences when comparing the conversion of acrylates and methacrylates. These differences are consistent with major kinetic differences observed during UV-initiation of acrylates and methacrylates in the past.¹⁴⁻¹⁸ These previous studies show there is a difference between the kinetics of acrylate and methacrylate polymerization; however, the authors have not found any studies that compare the impact of

initiation mechanism on the kinetics of radiation-induced polymerization of acrylates and methacrylates.

In fact, few studies have focused on comparing the kinetics of UV and EB polymerization in general.⁵⁻⁷ Schissel et al. found differences in conversion and physical properties of polymers initiated with UV and EB using equal energy deposition.¹⁹ Comparing UV and EB with equal initiation energy highlighted some of the differences in the initiation methods, but other questions remained unanswered.

It is known that radical formation, concentration, and secondary reactions are reliant on monomer chemistry, which affects polymerization kinetics. The comparison of UV and EB polymerization at equal primary radical concentrations will reveal the differences in kinetics and network formation driven by monomer chemistry and initiation mechanism. To compare initiation mechanisms, an acrylate/methacrylate pair was exposed to UV and EB resulting in equal primary radical concentrations. Using Raman microscopy to measure conversion, a relationship among formulation chemistry, initiation mechanism, and polymerization kinetics was elucidated for these acrylate/methacrylate systems.

Experimental.

Materials.

An acrylate/methacrylate pair was chosen to further study the significance of monomer chemistry and initiation mechanism on radiation-induced polymerization kinetics:^{12,19} 2-phenylethyl acrylate (PEA, TCI America) and 2-phenylethylmethacrylate (PEMA, Polysciences) (Figure 1). To induce UV polymerization, the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Sartomer) was used. The free-radical inhibitor 2,2,1-diphenyl-1-picrylhydrazyl (DPPH, TCI America) was used to quantify radical formation. All materials were used as received and stored at room temperature.



Figure 1. Chemical structures of the acrylate/methacrylate monomers used in this study: (A) PEA and (B) PEMA.

Methods.

Radical concentration.

The method to quantify primary radical concentration during EB exposure has been described in detail previously,²⁰ and only a brief outline of the method is presented here. In previous ionizing radiation literature, the radical concentration was reported in terms of a radiation chemical yield or *G*-value. Here, radical concentration is reported in mol/L as opposed to radicals per 100 eV or mol/J, as are typically used to report *G*-values. The unit change was made to

accommodate discussion of both EB and UV initiation mechanisms since G -values are associated with EB polymerization, but not with UV polymerization.

To determine the primary radical concentration in mol/L, the rate of radical formation (R_R) was multiplied by the reaction time. R_R was determined by adding an inhibitor to the monomer formulations, which reacted with primary radicals upon their formation during EB exposure. The disappearance of inhibitor, marked by a color change, was directly proportional to the rate of radical formation (R_R) and was monitored using UV-Vis spectroscopy (DU-62 Spectrophotometer, Beckman).

Once the primary radical concentration of each monomer was determined for EB exposure, a program written by Kenning et al. was used to determine the UV requirements necessary to match the radical concentration during UV exposure.²¹ This program used a set of differential equations to model polychromatic illumination based on initiator concentration, absorbance, and efficiency. For each monomer, the concentration of photoinitiator was set at 0.14 mol/L, which was the lowest concentration that allowed the UV radical concentration targets to be achieved with the available lamp. Low initiator concentration was desirable because high concentration of initiator is known to block UV light penetration.⁸ The exposure time was set at 1 s to match the exposure time of the EB reactions. Matching the exposure time meant that not only would the total radical concentration of the UV and EB reactions be the same, but the average rate of radical formation would also be equivalent. For the program, the quantum yield of DMPA was estimated to be 0.2.²²

Table 1. Effective irradiance of the UV lamp required to match the radical concentrations for each monomer during EB exposure.

Monomer	PEA	PEMA
Effective Irradiance (mW/cm ²)	600	675

Conversion measurements.

EB sample preparation. Neat monomer was pipetted onto a glass slide, and a tape spacer was used to achieve a sample thickness of ~100 μ m. Samples were polymerized using an EBLab unit (Comet Technologies, Inc.) or an EB Pilot Line (BroadBeam EP Series, PCT Ebeam and Integration, LLC). The voltage of both EB units was set at 200 kV to ensure uniform energy deposition throughout each sample. Nitrogen flow was used to reduce the oxygen concentration to less than 200 ppm to minimize the effects of oxygen inhibition. Ten exposure conditions were used for the EBLab experiments; all at a constant dose rate of 197 \pm 4 kGy/s. The dose rate was held constant because altering the dose rate has been shown to have an impact on conversion.^{13,23,24} The dose and line speed combinations match those used to determine the G -values on the EBLab unit and are shown in Table 2. A single 400 kGy exposure at 1.5 m/min was carried out on the EB Pilot line, which was used to gather conversion data rather than determine radical concentration.

Table 2. Dose and line speed combinations used to create EB samples for conversion profiles.

Dose (kGy)	200	100	67	50	40	33	29	25	22	20
Line speed (m/min)	3	6	9	12	15	18	21	24	27	30

UV sample preparation. Monomer containing 0.14 mol/L DMPA was pipetted onto glass slides with a tape spacer used to achieve a sample thickness of ~ 100 μm . Samples were polymerized using an Omnicure $\text{\textcircled{R}}$ S1000 Ultraviolet/Visible Spot Cure System (Excelitas, 250-450 nm band pass filter) with a 3-mm, liquid light guide at ambient temperature. The tip of the light guide was inserted into a nitrogen-purging chamber. The air gap between the sample surface and the light guide was ~ 1 mm. Nitrogen flow was used to reduce the oxygen level below 200 ppm to minimize the effects of oxygen inhibition. The effective irradiance was measured by a radiometer (Versaprobe Pro, Con-Trol Cure).

Raman microscopy. Raman microscopy was used to determine conversion of the samples after polymerization. In order to eliminate error from instrumental variation and EB bombardment, a reference peak was used. Previous work has established the reaction peak at 1636 cm^{-1} (indicative of the $-\text{C}=\text{C}-$ bond in the (meth)acrylate moiety) and a reference peak at 1613 cm^{-1} (indicative of the $-\text{C}=\text{C}-$ bonds in the phenyl ring).²⁵ Fractional conversion, α , was calculated using the following equation:

$$\alpha = \left(1 - \frac{I_{rxn}(P)}{I_{ref}(P)} \bigg/ \frac{I_{rxn}(M)}{I_{ref}(M)} \right) \quad (1)$$

where $I_{rxn}(P)$ and $I_{ref}(P)$ are the peak intensities of the reaction and reference peak of the polymer, respectively; $I_{rxn}(M)$ and $I_{ref}(M)$ are the peak intensities of the reaction and reference peak of the monomer, respectively.²⁶

Samples were transferred to aluminum Q-panels for analysis. Raman spectra of the samples were collected using an optical microscope (DMLP Leica) connected to a modular research Raman spectrograph (HoloLab 5000R, Kaiser Optical Systems, Inc.) *via* a $100\text{-}\mu\text{m}$ collection fiber. A single-mode excitation fiber carried an incident beam of 785-nm near-infrared laser to the sample through a $10\times$ objective with a numerical aperture of 0.25 and a working distance of 5.8 mm. Laser power at the samples was ~ 8 mW. Spectra were collected with an exposure time of 30 s and 3 accumulations. Ten monomer spectra were collected and averaged to provide accurate values for $I_{rxn}(M)$ and $I_{ref}(M)$ to use in Equation 1. The error in the conversion measurements due to instrumental variation is expected to be ± 0.05 .

Results and Discussion

To compare UV- and EB-initiated polymerizations, an acrylate/methacrylate pair was examined. Polymerization kinetics were studied for UV and EB initiation with equal primary radical concentration. After samples were exposed to either UV or EB radiation, Raman microscopy was used to determine monomer conversion.

Comparison of radical concentration and initiating energy.

Using the free-radical inhibitor (as described in the Methods section), primary radical concentration during EB exposure was quantified (Table 3). The methacrylate PEMA has three additional labile C-H bonds compared to its otherwise identical acrylate counterpart (PEA) due to the added methyl group. Although these additional labile bonds provide additional locations for

primary radical formation, PEA forms approximately the same concentration of radicals (within error) as PEMA.

Table 3. The primary radical concentration for the monomers used for both UV and EB initiation. Note that the error values are for EB initiation. There are no error values associated with UV initiation because equivalent radical concentrations were determined through theoretical modeling.

	Radical Concentration (mol/L)
PEA	0.0115±0.0007
PEMA	0.0122±0.0006

In order to generate this same number of primary radicals, the energy required for EB is much different than that required for UV. For EB, the monomers received a dose of ~200 J/g. When using UV, the energy was varied to match the radical concentration of the EB samples. The more radicals produced during EB exposure, the higher the effective irradiance required to form the same amount of radicals. The effective irradiance (I) in $\frac{mW}{cm^2}$ was converted to dose (D) in $\frac{J}{g}$ using the exposure time (t), sample mass (m), and area (A) as follows:¹⁹

$$D = \frac{IAt}{1000m} \quad (2)$$

Note that Equation 2 contains the implicit unit conversions: $\left(\frac{mJ/s}{mW}\right)$ and $\left(\frac{J}{1000mj}\right)$. The EB and UV equivalent doses are compared in Table 4.

Table 4. The EB and UV equivalent doses required for initiation with equivalent primary radical concentration.

	EB Energy (J/g)	UV Energy (J/g)
PEA	200	58
PEMA	200	69

EB initiation requires ~3 to 4 times the amount of energy than that required by UV to form the same number of primary radicals. The smaller energy requirements for UV initiation are likely the result of differences in bond lability of photoinitiators compared to monomers. For example, the photoinitiator DMPA requires 52.1 kcal/mol to generate radicals during UV exposure;²⁷ breaking relatively weak C-H bonds on monomer molecules requires ~100 kcal/mol during EB irradiation.¹² Additionally, there are many other reactions that can happen besides radical formation when electrons interact with matter.¹¹ The inefficiency of accelerated electrons is not well established; however, photon loss to other reactions is characterized through the quantum yield of the photoinitiator.

Comparison of monomer conversion.

For this study, EB and UV polymerizations were initiated at conditions to produce equal primary radical concentrations in order to compare the impact of initiation mechanisms on radiation-induced polymerization kinetics. The conversion was then measured using Raman microscopy (Figure 2). UV initiation of PEA was faster than EB initiation. Additionally, higher final conversion was observed for UV initiation compared to EB initiation (Figure 2A).

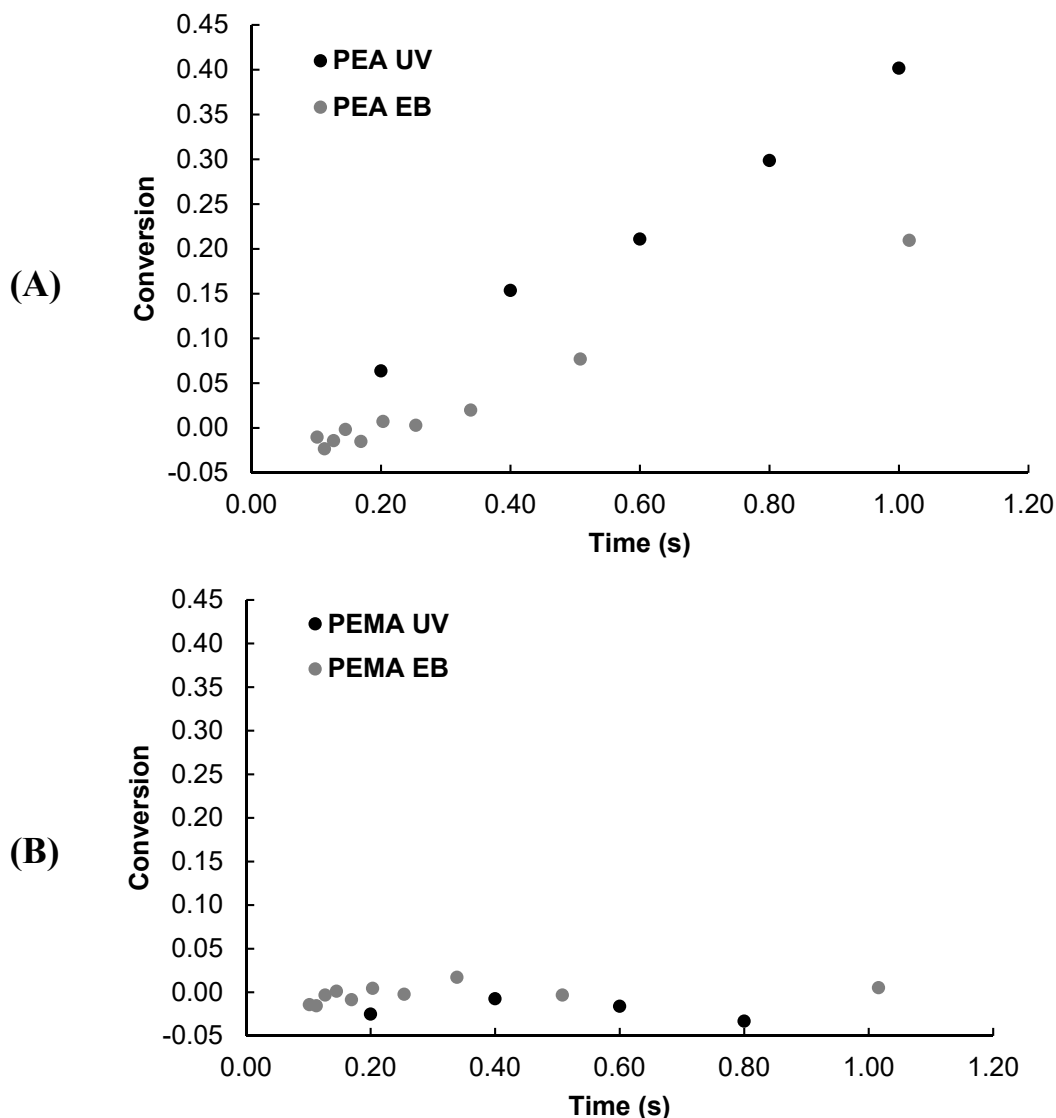


Figure 2. Conversion profiles for UV- and EB-initiated PEA (A) and PEMA (B). UV initiation results in faster reactions and higher final conversion compared to initiation with EB for PEA, while PEMA is essentially unreactive for both UV and EB initiation. Note that the x- and y-axis do not intersect at zero and the negative conversion values are within the error of the measurement technique and indicate essentially no reaction.

The lower conversion of PEA during EB initiation compared to UV initiation could be the result of differences in primary radical structures that cause differences in secondary radical reactions. UV initiation typically results in predictable radical structures, while EB initiation tends to form many radicals with structures that are much harder to predict.^{8,10} During EB polymerization, some of the primary radical structures may undergo secondary radical reactions, such as crosslinking, recombination, or termination, which do not lead to chain initiation.²⁸ If fewer primary radicals are used to initiate polymerization, conversion is suppressed.

In contrast to PEA, PEMA achieved nearly zero conversion regardless of initiation mechanism (Figure 2B). Previous studies have shown that methacrylates typically react much slower than their acrylate counterparts during UV illumination,¹⁴⁻¹⁸ and this trend holds under EB exposure as well. The lack of conversion of PEMA compared to PEA is likely due to the stability of the initiating methacrylate radical compared to the initiating acrylate radical.

Conclusions.

The conversion of an acrylate/methacrylate pair was studied for UV and EB polymerization initiated with equal radical concentrations. Higher conversion of the acrylate monomer was achieved with UV initiation when compared with EB initiation. Although both monomers start with equivalent primary radical concentration, EB may be less likely to form initiating radicals compared to UV because of the non-selectivity of the accelerated electrons, which results in less secondary reactions leading to monomer conversion.

For both UV and EB initiation, monomer chemistry has a large impact on polymerization kinetics. Methacrylates had significantly lower conversion than their acrylate counterpart due to the increased stability of the tertiary methacrylate propagating radical compared to the secondary acrylate propagating radical. Knowing the differences that initiation mechanisms and monomer chemistry can make on polymer development can help guide formulation practices and extend the use of radiation-cured materials in industrial processes.

Acknowledgements.

This work was supported by the National Science Foundation [grant number 1264622]. The authors would like to acknowledge Stan Howell for his contribution to the development of the nitrogen inerting chamber for UV polymerization.

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