How monomer chemistry and radical formation impact EB polymer development

Nicole L. K. Thiher,[1] Sage M. Schissel,[*2] and Julie L. P. Jessop[3]

[1]Department of Chemical & Biochemical Engineering, University of Iowa, Iowa City, IA
[2]PCT Ebeam and Integration, LLC, Davenport, IA
[3]Mississippi State University, School of Chemical Engineering, Mississippi State, MS

Abstract.

Radical reactions facilitate polymer development during EB polymerization. To better understand the kinetics of EB polymerization, primary radicals were quantified for pairs of acrylate and methacrylate monomers. Monomer chemistry was shown to impact primary radical formation; however, increased primary radical concentration did not necessarily correlate to increased polymer development.

Introduction.

In previous work,[1] the primary radical formation was quantified for a series of (meth)acrylates by calculating radiation chemical yields, also known as G-values.[2,3] In early literature, G-values were defined in terms of $G(A)$, where "$G(A)$ represents the number of events or chemical species of type A formed per 100 eV of energy absorbed".[4] (The definition of the G-value has been updated to conform with SI units and is now reported in mol/J.[5]) In this past work, the primary radical radiation chemical yield, $G(R^\bullet)$, was shown to increase as the number of labile bonds in a monomer increased. Additionally, acrylate and methacrylate analogs were compared, as both chemistries are important to industrial processes. Methacrylates were able to produce greater $G(R^\bullet)$ values than their acrylate counterparts but had no appreciable conversion.

Here, two new pairs of (meth)acrylate monomers were investigated in an effort to continue developing an understanding of how monomer chemistry is impacted by radical formation and secondary radical reactions. In contrast to the previous work, these new pairs of monomers do not contain a phenyl ring. Without this phenyl ring, quantitative conversion measurements using Raman spectroscopy is not possible;[6] therefore, qualitative measures were used to determine relative monomer conversion. A correlation was found between monomer chemical structure and primary radical radiation chemical yield, $G(R^\bullet)$. This research provides a foundation for future investigations that can aid in the development of structure/processing conditions/properties relationships that are currently underdeveloped for EB polymerizations.

Experimental.

Materials.

Three acrylate monomers were used in this study. The series of acrylates was augmented with three analogous methacrylate monomers to investigate the impact of chemistry on primary radical formation: 2-phenoxyethyl acrylate (POEA, Aldrich); 2-phenoxyethyl methacrylate

(POEMA, TCI America); isobornyl acrylate (IBOA, Sartomer); isobornyl methacrylate (IBOMA, Sartomer); 2-hydroxyethyl acrylate (HEA, Aldrich); and 2-hydroxyethyl methacrylate (HEMA, Aldrich) (Figure 1). The POEA/POEMA pair was included in the study for comparison to previous work.[1] The monomers were not washed of inhibitor because the impact of inhibitor was determined to be below the error of the measurements in this study. A free-radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl (DPPH, Millipore Sigma), was used to quantify primary radicals. All materials were used as received and stored at room temperature.
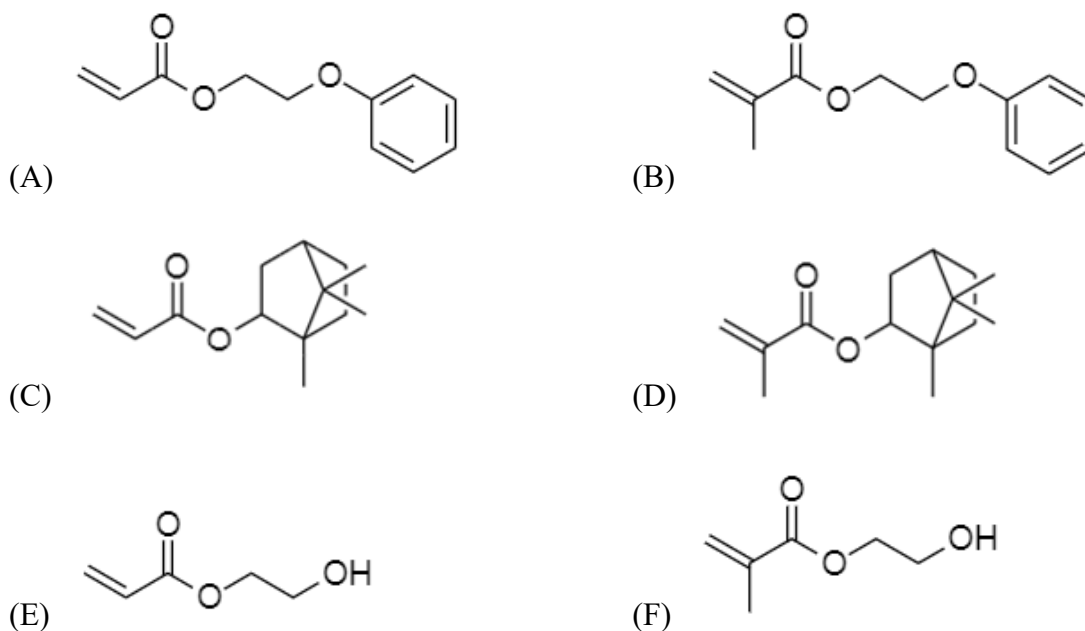
Figure 1. The chemical structures of the monomers used in this study: (A) POEA, (B) POEMA, (C) IBOA, (D) IBOMA, (E) HEA, and (F) HEMA.

Methods.

Primary radical radiation chemical yield, $G(R^\bullet)$

The methods used to determine primary radical radiation chemical yield have been described in detail previously,[3] and only a brief outline of the method is presented here. (Note that the units of the G-value have been updated from radicals per 100 eV (used in early literature) to mol/J (the modern definition) by multiplying by 1.03 x 10⁻⁷.) To quantify primary radicals, a free-radical inhibitor was added to the formulation. When the inhibited formulation was exposed to the EB, primary radicals formed. These primary radicals then reacted with the inhibitor, inducing a color change. The disappearance of inhibitor is directly proportional to the rate of radical formation (R_R) and was monitored using UV-Vis spectroscopy (DU-62 Spectrophotometer, Beckman). After determining the rate of radical formation, Equation 1 was used to calculate $G(R^\bullet)$, since the density (ρ) and dose rate $\left(\frac{dD}{dt}\right)$ were known.

$$G(R^\bullet) = \frac{R_R}{\rho \frac{dD}{dt}}$$

(1)

2

Quantitative conversion measurements.

    Sample Preparation. Neat monomer was pipetted onto a glass slide, and a tape spacer was used to achieve a sample thickness of ~100 µm. EB polymerization took place on an EBLab unit (Comet Technologies, Inc.). The voltage was set at 200 kV to ensure uniform energy deposition through the entire depth of each sample. Nitrogen flow was used to reduce the oxygen concentration to less than 200 ppm to minimize the effect of oxygen inhibition. Ten exposure conditions were used for these experiments, all at a constant dose rate of 197±4 kGy/s. The dose and line speed combinations match those used to determine the radiation yield values and are shown in Table 1.

Table 1. Dose and line speed combinations used to create 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

    Raman microscopy. Raman microscopy was used to determine conversion of the samples after EB exposure. 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 -C=C- bond in the acrylate moiety) and a reference peak at 1613 cm^{-1} (indicative of the -C=C- bonds in the phenyl ring).[6] Fractional conversion, α, was calculated using the following equation:

$$\alpha = \left(1 - \frac{I_{rxn}(P)/I_{ref}(P)}{I_{rxn}(M)/I_{ref}(M)} \right) \tag{2}$$

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.[7]

    EB-exposed 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-µm collection fiber. A single-mode excitation fiber carried an incident beam of 785-nm near-infrared laser to the sample through a 10x 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 seconds 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 2. The error in the conversion measurements due to instrumental variation is expected to be ±0.05.

Qualitative conversion measurements.

    Sample Preparation. Neat monomer was pipetted onto a Leneta chart, and a Mayer rod was used to achieve a sample thickness of ~100 µm. EB polymerization took place on an EBLab unit (Comet Technologies, Inc.). The voltage was set at 200 kV to ensure uniform energy deposition through the entire depth of each sample. Nitrogen flow was used to reduce the oxygen concentration to less than 200 ppm to minimize the effect of oxygen inhibition. Samples were exposed to 200 kGy at 3 m/min; these conditions are consistent with the 197 kGy/s dose rate used for conversion measurements.

Tack / Cotton Ball Test. Adhesion of cotton strands from a cotton ball was used to estimate the degree of conversion. This qualitative test was used because several of the monomers lack the phenyl ring necessary for quantitative Raman conversion measurements. A 4-point scale was used to differentiate conversion levels (Table 2). The cotton ball was held on the coating by a 2-pound hammer for 15 seconds.

Table 2. Scale used to estimate the degree of conversion using the cotton ball test.

Score	Description
1	Full coverage of cotton
2	Mostly full coverage of cotton
3	Partial coverage of cotton
4	No cotton fibers adhere

Wetness / Tissue Paper Test. One failing of the cotton ball test is that the conversion of the monomer may be so low as to be completely wet to the touch and not have enough tack to adhere any cotton strands. In order to overcoming this failing, a second test was used in conjunction with the cotton ball test to qualitatively estimate conversion. Tissue paper was laid on the coating, and the absorption of the coating into tissue paper was scaled (Table 3).

Table 3. Scale used to estimate the degree of conversion using the tissue paper test.

Score	Description
0	Completely wet tissue paper
0.5	Damp/partially wet tissue paper
1	Dry tissue paper

Results and Discussion.

Primary radical reactions.

Primary radical formation was quantified by calculating $G(R^{\bullet})$ for each monomer using the inhibitor method described above. IBOA had the largest $G(R^{\bullet})$ value of the acrylates; this result falls in line with previous research,[1] where monomers with more labile bonds had greater $G(R^{\bullet})$ values (Figure 2).
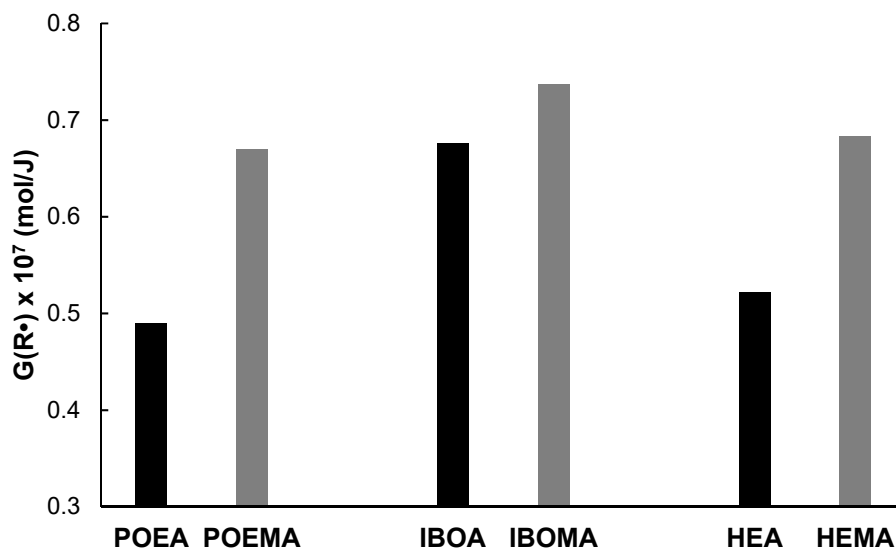
Figure 2. Primary radical formation quantified by measuring $G(R^\bullet)$ for each monomer. Methacrylates (gray bars) form more primary radicals upon EB exposure compared to their acrylate counterparts (black bars).

POEA and HEA also follow this trend, though it might not be readily apparent. POEA has a slightly smaller $G(R^\bullet)$ value than HEA although it has 12 hydrogens compared to HEA's 8; however, 5 of POEA's hydrogens are situated on the conjugated phenyl ring and are expected to not be as labile due to the higher bond energy.[8]

Methacrylates exhibited greater values of $G(R^\bullet)$ compared to their acrylate counterparts (Figure 2). This trend, too, has been demonstrated in previous research[1] and is expected since the addition of the methyl group adds 3 more abstractable hydrogens. Yet, while the methyl group gives each pair the same boost, the resulting increase in $G(R^\bullet)$ values is not proportional for the 3 studied pairs. The POEA/POEMA and HEA/HEMA pairs both see a similar increase: 175% and 160% respectively, in $G(R^\bullet)$ values from acrylate to methacrylate; comparatively, the increase in $G(R^\bullet)$ value from IBOA to IBOMA is only 117%. Considering that IBOA has significantly more abstractable hydrogens than POEA or HEA, the impact of the methyl group may correlate to the percent increase of labile bonds rather than the number of bonds increased. For example, excluding the phenyl ring hydrogens, POEA's hydrogen count increases from 7 to 10 when it becomes POEMA, a 143% increase. Just as with the similar increase in $G(R^\bullet)$ values with the POEA/POEMA pair, the HEA to HEMA transition results in a 138% increase in hydrogens. Finally, IBOA to IBOMA only results in a 114% increase in abstractable hydrogens. Comparing the percent increase in labile bonds to the increase in $G(R^\bullet)$ values establishes a clear trend.

Conversion of acrylates *vs.* methacrylates.

Raman microscopy was used to measure conversion of the POEA and POEMA after EB exposure to investigate the impact of primary radical concentration on conversion (Figure 3).[1] Overall, there was not a strong correlation between primary radical concentration and conversion for this pair.
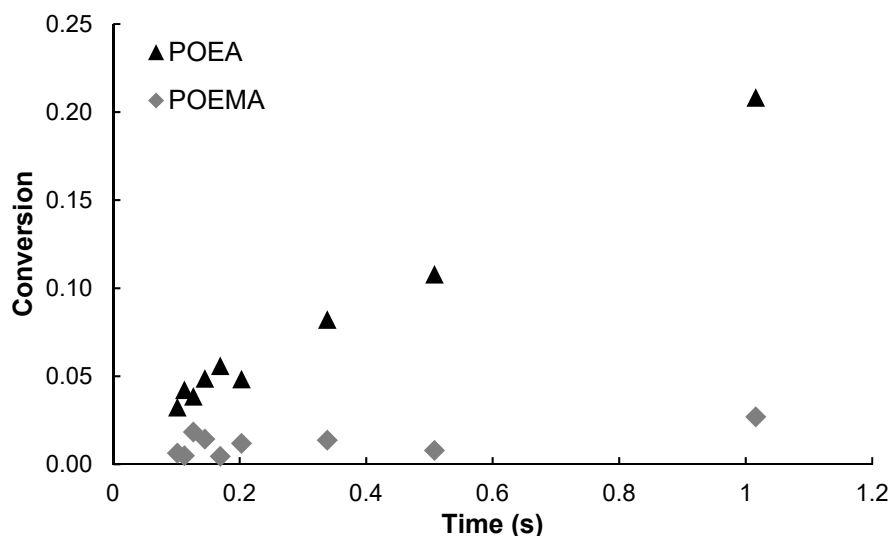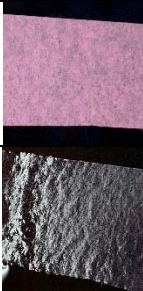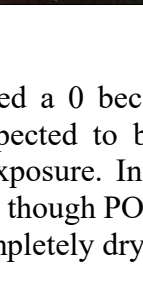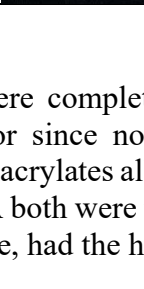
Figure 3. Piecewise conversion profile of the acrylate POEA and its methacrylate analogs POEMA. The acrylate is able to achieve significant conversion upon EB exposure, while the conversion of the methacrylate is near zero. Adapted from Ref. 1.
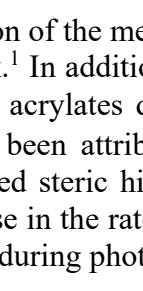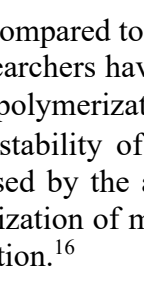
The acrylate conversion profile, as anticipated, increased with increasing dose and time. The fractional conversion of POEA reached nearly 0.21 at a dose of 200 kGy (t = 1 s). The methacrylate conversion profile, however, only reached a fractional conversion of 0.03. Since POEMA has a greater $G(R^\bullet)$ value than POEA, these results indicate that neither the final conversion values nor the speed of reaction seem to be related to the primary radical concentrations quantified by calculating $G(R^\bullet)$.[1]

To explore this conclusion further, the other two pairs of (meth)acrylates were compared on a more qualitative basis, since the lack of a phenyl moiety prevented accurate Raman results (Table 4). The POEA/POEMA pair was also included in this analysis for comparison. Cotton balls were used to check the tack of the monomer coating, after EB exposure, and tissue paper was used to demonstrate the wetness of the coating. The results indicate that the methacrylates have lower conversion than their acrylate analogs, as seen with the quantitative POEA/POEMA comparison.

6

Table 4. Qualitative conversion results of the three (meth)acrylate pairs. For each pair, the methacrylate appears to have a lower conversion than its acrylate analog.

Monomer	Cotton Ball Test (CBT)		Tissue Paper Test (TPT)		Final Score (CBT x TPT)
POEA					1 x 1 = **1**
POEMA					4 x 0 = **0**
IBOA					4 x 1 = **4**
IBOMA					4 x 0 = **0**
HEA					3 x 1 = **3**
HEMA					4 x 0 = **0**

All of the methacrylates scored a 0 because they were completely wet to the touch. If any conversion occurred, it is expected to be very minor since no appreciable differences were observed before and after EB exposure. In contrast, the acrylates all experienced some conversion. All three were dry to the touch, though POEA and HEA both were tacky. Based on the qualitative scoring, IBOA, which was completely dry and tack-free, had the highest level of conversion.

The low final conversion of the methacrylates compared to the acrylates is consistent with results from the previous work.[1] In addition, other researchers have observed slow reaction rates of methacrylates compared to acrylates during photopolymerization reactions.[9-13] The slow R_p values of methacrylates have been attributed to the stability of the propagating methacrylate radical, as well as the increased steric hindrance caused by the additional C-H bonds.[14,15] One study reported a 7-fold decrease in the rate of polymerization of methacrylates compared to their identical acrylate counterparts during photopolymerization.[16]

Conclusions.

Radical formation and secondary radical reactions initiated *via* EB exposure are dependent on monomer chemistry. However, high concentrations of primary radicals did not necessarily translate into increased conversion. The methacrylates in this study had higher values of $G(R^\bullet)$ than their acrylate counterparts, but the methacrylates failed to achieve any appreciable conversion during EB exposure.

Ultimately, understanding radical formation and secondary radical reactions is critical to developing structure/processing conditions/properties relationships for EB polymerization. Future work should focus on expanding the radical relationships beyond one-component formulations of acrylates and methacrylates into mixtures of monomers and oligomers, which are widely used in industry, in order to guide EB formulation development.

References.

1. Thiher NLK, Schissel SM, Jessop JLP. The Influence of Monomer Chemistry on Radical Formation and Secondary Reactions During Electron-beam Polymerization. *J. Polym. Sci.*, in press. doi:10.1002/pol.20190113.

2. Thiher NLK, Schissel SM, Jessop JLP. Analysis of methods to determine G-values of monomers polymerized via ionizing radiation. *Rad. Phys. Chem.* 2019; 165, 108394. doi:10.1016/j.radphyschem.2019.108394.

3. Thiher NLK, Schissel SM, Jessop JLP. Counting Radicals: Methods to Measure Radiation Yields of Monomers in EB Polymerization. *UV+EB Technology*, 2019; 5(2), 32-40. https://uvebtech.com/articles/2019/counting-radicals-methods-to-measure-radiation-yields-of-monomers-in-eb-polymerization/.

4. McNair A. ICRU Report 33 - Radiation Quantities and Units Pub: International Commission on Radiation Units and Measurements, Washington D.C. USA issued 15 April 1980, pp.25. *Journal of Labelled Compounds and Radiopharmaceuticals*. 1981; 18(9), 1398-1398. doi:10.1002/jlcr.2580180918.

5. Makuuchi K, Cheng S. *Radiation processing of polymer materials and its industrial applications*. 2011, Hoboken, NJ: John Wiley & Sons, Inc.

6. Schissel SM, Lapin SC, Jessop JLP. Internal Reference Validation for EB-Cured Polymer Conversions Measured via Raman Spectroscopy. *RadTech Report*. 2014; 28(4), 46-50. https://www.radtech.org/magazinearchives/Publications/RadTechReport/dec-2014/InternalReferenceValidationforEB-CuredPolymerConversionsMeasuredviaRamanSpectroscopy.pdf.

7. Cai Y, Jessop JLP. Decreased oxygen inhibition in photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy. *Polymer*. 2006; 47(19), 6560-6566. doi: 10.1016/j.polymer.2006.07.031.

8. Schissel SM, Kloepfer N, Lapin SC, Jessop JLP. Predicting Dose Rate Effects in EB Polymerizations Based on Monomer Structure. *RadTech 2018 UV/EB Technology Conference Proceedings*, on-line edition, May 2018.

9. Anseth KS, Wang CM, Bowman CN. Reaction behaviour and kinetic constants for photopolymerizations of multi(meth)acrylate monomers. *Polymer*. 1994; 35(15), 3243-3250. doi:10.1016/0032-3861(94)90129-5.

10. Scherzer T. VUV-Induced Photopolymerization of Acrylates. *Macromolecular Chemistry and Physics*. 2012; 213(3), 324-334. doi:10.1002/macp.201100485.

11. Ghorpade RV, Bhosle SM, Ponrathnam S, Rajan CR, Chavan NN, Harikrishna R. Photopolymerization kinetics of 2-phenylethyl (meth)acrylates studied by photo DSC. *J. Polym. Res.* 2012; 19(2), 1-8. doi:10.1007/s10965-011-9811-3.

12. Takács E, Wojnárovits L. Comparison of the reactivity of acrylate and methacrylate monomers. *Rad. Phys. Chem.* 1995; 46(4, Part 2), 1007-1010. doi:10.1016/0969-806X(95)00310-T.

13. McCurdy KG, Laidler KJ. Rates of polymerization of acrylates and methacrylates in emulsion systems. *Canadian Journal of Chemistry*. 1964; 42(4), 825-829. doi:10.1139/v64-122.

14. Doetschman DC, Mehlenbacher RC, Cywar D. Stable free radicals produced in acrylate and methacrylate free radical polymerization: Comparative EPR studies of structure and the effects of cross-linking. *Macromolecules*. 1996; 29(5), 1807-1816. doi:10.1021/ma951444w.

15. Matyjaszewski K, Davis TP. *Handbook of radical polymerization*. 2002: Hoboken, NJ: Wiley-Interscience.

16. Kurdikar DL, Peppas NA. A kinetic study of diacrylate photopolymerizations. *Polymer*. 1994; 35(5), 1004-1011. doi:10.1016/0032-3861(94)90945-8.