

Predicting Dose Rate Effects in EB Polymerizations Based on Monomer Structure

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Abstract

Dose rate effects (DREs), or changes in polymer properties due to changes in dose rate, can be problematic during scale-up of electron-beam-initiated polymerization. DREs are not apparent for all formulation chemistries and processing parameters, and predicting when they will occur is challenging. Using glass transition temperature as measured by dynamic mechanical analysis, DREs were characterized for various acrylate monomers polymerized at different dose rates. Results show monomers with more easily abstractable hydrogens have smaller DREs.

Introduction

Formulations for electron-beam (EB) polymerization are often perfected on a small lab unit or pilot line before being scaled to an industrial beam. The dose (*i.e.*, the energy absorbed by the sample) delivered by each EB unit is often comparable, but the speed at which the dose is delivered – dose rate – changes. Altering the dose rate can cause property changes in the cured polymer, known as dose rate effects (DREs).

Previous work has established a protocol for measuring DREs in the glass transition temperature (T_g) for a polymer system by determining the difference in T_g at two different line speeds at a constant dose (Equation 1).¹

$$T_g DRE(dose) = |T_{g,200 \text{ ft/min}} - T_{g,20 \text{ ft/min}}| \quad (1)$$

The previous study compared the DREs of five phenyl acrylate monomers and determined DREs were minimized as dose and monomer size increased across the five monomer series. It was hypothesized that the decrease in DREs for the larger monomers could be attributed to the greater number of labile bonds (primarily abstractable hydrogens) on the molecule, which increases the likelihood of chain transfer. The chain transfer mechanism provides a means of freeing trapped radicals by transferring the tethered radical to a more mobile chain and thus increasing propagation. Involving both chain transfer and propagation helps to balance radical consumption by termination at high radical concentrations (*i.e.*, high dose rates), promoting polymer conversion and lessening DREs.

This work is a follow-up to studies presented at RadTech 2016² and published in 2017.¹ Here, we further confirm that DRE is a function of the number of abstractable hydrogens by comparing additional monomers. These additional monomers were selected to complement data from the initial series, as well as to further investigate the importance of bond energy. Dynamic mechanical analysis was used to determine the T_g of samples polymerized at different doses and dose rates, from which data

the T_g DREs were calculated.

Experimental

Materials

Six acrylate monomers were chosen to study the effect of dose rate on T_g : phenyl acrylate (PA, MP Biomedical); cyclohexyl acrylate (CHA, TCI America); benzyl acrylate (BA, MP Biomedical); tetrahydrofurfuryl acrylate (THFA, Aldrich); dodecyl acrylate (DDA, TCI America); and 2-(2-ethoxyethoxy)ethyl acrylate (EEEEA, TCI America) (Figure 1). Monomers PA and BA were a part of the previous study and were initially chosen because the phenyl ring provided a stable bond in Raman spectroscopy measurements for determining polymer conversion.^{1,3} CHA and THFA were selected for this study because of their structural similarity to PA and BA, respectively; the major difference between the two sets being the conjugation of their aromatic ring structures. DDA and EEEEA were chosen to examine the impact of electron-withdrawing groups (here, the ether groups).

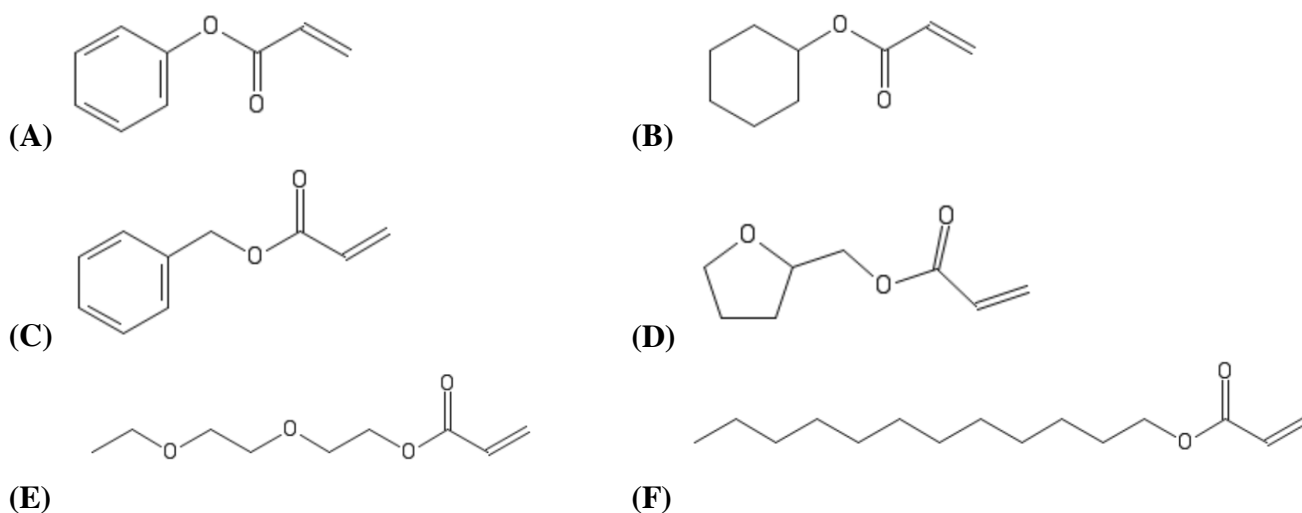


Figure 1. The chemical structures of the acrylate monomers used in this study: (A) PA, (B) CHA, (C) BA, (D) THFA, (E) EEEEA, and (F) DDA.

An aliphatic urethane diacrylate oligomer, Ebecryl 8807 (proprietary structure, Allnex), was added to each of the monomer formulations to achieve the necessary film properties for mechanical-property testing. All materials were used as received and stored at room temperature.

Methods

EB Film Preparation

Each formulation consisted of a 50/50, by weight, mixture of monomer and oligomer. Because of the high viscosity of the oligomer, the formulations were heated to approximately 60°C to allow mixing of the monomer and oligomer. Once heated, formulations were stirred using a drill with a paddle mixer attachment.

Samples for EB curing were prepared by first treating 4 × 3.25 inch glass slides using two coats of Rain-X® 2-in-1 glass cleaner and rain repellent. Next, two layers of lab tape (total thickness ~180 μm) were placed on either side of the glass to be used as spacers. A large droplet, approximately 1 mL, of a formulation was then placed near the top of the slide, between the pieces of tape, and covered with a piece of silicone-coated, 34-μm thick polyethylene terephthalate (PET). A straight edge was drawn across the PET to form a uniform film underneath.

The samples on the glass slides were polymerized by EB irradiation through the PET film using an EB accelerator equipped with a variable-speed, fiberglass carrier web (BroadBeam EP Series, PCT Engineered Systems, Inc.). Three different doses (15, 30, and 60 kGy) and three different line speeds (20, 100, and 200 ft/min) were used to cure the films. Accelerating voltage and N₂ flow rate were held constant at 250 kV and 17 SCFM, respectively. Once polymerized, the films were removed from the glass slides and cut into rectangles measuring 6.25 × 25 mm for characterization. The use of silanized (Rain-X®-treated) glass and silicone-coated PET assisted in the release of the polymer film.

Dynamic Mechanical Analysis

A dynamic mechanical analyzer (DMA, Q800 TA Instruments) equipped with a film tension clamp was used to find the T_g of the polymer films. A mono-frequency strain, temperature ramp sequence was used to collect tan δ values as a function of temperature. Temperature was increased at a rate of 3°C/min over a broad temperature range at a constant oscillating frequency of 1 Hz and a sinusoidal strain of 0.05%. The polymer T_g was taken as the maximum of the tan δ peak. Measurements were not repeated for these data; however, previous research with similar polymer films demonstrated that the standard deviation of three averaged T_g values was ± 2.2°C.

Results and Discussion

This study investigated the impact of bond energy, specifically abstractable hydrogens, on the magnitude of the dose rate effect. Dose rate effects were monitored by polymer T_g, which was measured by DMA. The results of this study show DREs are influenced by not only the number of abstractable hydrogens but also the ease of abstraction.

In order to understand the impact of dose on dose rate effects, both dose and line speed were systematically varied, and the effect on the polymer T_g was recorded (Table 1). As a general trend, the T_g of the polymers studied increases with increasing dose at a constant line speed. Exceptions to this trend (EEEA at 20 and 100 ft/min) are attributed to the values being within the standard deviation of the instrument. This result is consistent with previous work and is ascribed to increases in conversion.¹ With an increase in initiating energy (dose), it follows via traditional kinetics that conversion is also increased.^{4,5} Conversion and T_g are well known to be correlated: at low conversions, the threshold molecular weight needed to reach a polymer's maximum T_g may have not yet been reached, and the remaining monomer may also suppress the T_g by plasticizing the film.⁴ Thus, films polymerized with higher doses should have higher conversions and T_g values. Conversion measurements were not included in these studies because not all monomers contained an EB-radiation stable bond, which is needed for accurate Raman measurements.³

Table 1. Comparison of T_g values for six acrylate monomers at three different doses and line speeds. DMA was used to collect T_g data. (*Film weakness prevented data collection for DDA at 15 kGy, 200 ft/min.)

	20 ft/min			100 ft/min			200 ft/min		
	15 kGy	30 kGy	60 kGy	15 kGy	30 kGy	60 kGy	15 kGy	30 kGy	60 kGy
PA	26	49	57	3	31	50	-21	6	19
CHA	53	52	55	47	49	52	40	49	51
BA	21	24	27	-3	2	14	-26	-19	14
THFA	11	23	23	12	23	21	15	20	22
EEEA	-5	-8	-9	-7	-8	-9	-9	-7	-8
DDA	4	4	4	-3	-4	2	*	-6	-5

To more effectively demonstrate the impact of dose rate on T_g , Equation 1 was used to calculate the $T_g DRE$ from Table 1 data for the studied monomer formulations (Figures 2-4). PA and CHA are identical monomers, save for the conjugation of the aromatic ring. Because of this conjugation, PA not only has fewer hydrogens than CHA, but the hydrogens on the phenyl ring are also less prone to abstraction because of the stabilizing effects of resonance. Comparison of the T_g data for PA and CHA shows the greater number of abstractable hydrogens on the cyclohexyl moiety of CHA significantly lessens the magnitude of the $T_g DRE$ for all dose and line speed combinations (Figure 2). At 60 kGy for example, the $T_g DRE$ is reduced by 34°C between the two formulations. Despite having a lower magnitude $T_g DRE$ than PA, CHA does continue to follow the established trend of having its largest $T_g DRE$ at 15 kGy.¹

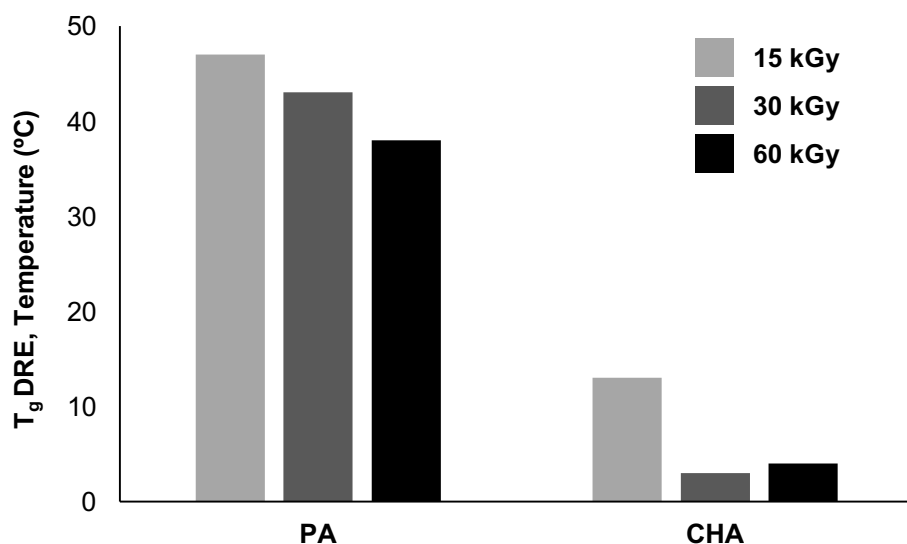


Figure 2. The glass transition temperature DREs, at three different doses, for PA and CHA. The larger number of abstractable hydrogens on CHA decreases the DRE.

It was previously hypothesized that the chain transfer mechanism influences the magnitude of a

monomer's DRE.¹ At a set dose, the overall concentration of radicals should be the same independent of the dose rate; however, at high dose rates, the radical concentration is larger at any given instant in time during the EB reaction, in comparison to low dose rates, because the same initiating energy must be delivered over a shorter time period. Since the rate of propagation (R_p , Equation 2) is first order with respect to radical concentration ($[M^*]$) and the rate of termination (R_t , Equation 3) is second order, a higher concentration of radicals preferentially increases R_t over R_p .⁴

$$R_p = k_p[M][M^*] \quad (2)$$

$$R_t = k_t[M^*]^2 \quad (3)$$

Increasing R_t over R_p favors lower polymer conversions and thus lower T_g and larger DREs. Conversely, chain transfer allows radicals trapped by entangled polymer chains an alternative path to increased conversion, and it competes with termination for radicals (Equation 4).

$$R_{ct} = k_{ct}[M^*][MH] \quad (4)$$

The increased conversion provided by the chain transfer mechanism has less impact at low dose rates, where polymers already achieve high conversions. However, at high dose rates, promoting chain transfer by increasing the concentration of abstractable hydrogens or other similarly labile bonds ($[MH]$) can restore the balance between termination and conversion, thereby reducing DREs. The T_g DRE comparison of PA and CHA supports this theory, since CHA has the lower T_g DRE magnitude and a larger concentration of abstractable hydrogens to increase the rate of chain transfer (R_{ct}).

Similarly, a comparison of BA and THFA T_g DREs shows that THFA, with a greater number of abstractable hydrogens, has a lower DRE (Figure 3). BA has a $\geq 40^\circ\text{C}$ difference in T_g DRE magnitude over THFA at both 15 and 30 kGy.

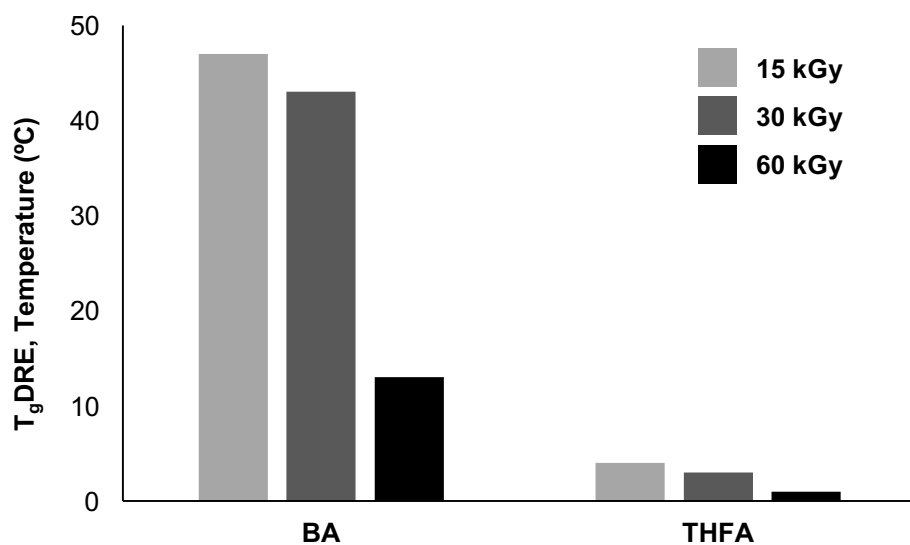


Figure 3. The glass transition temperature DREs, at three different doses, for BA and THFA. The larger number of abstractable hydrogens on THFA decreases the DRE.

These comparisons – PA/CHA and BA/THFA – not only continue to support the hypothesis that the presence of labile bonds on a monomer reduces DREs, but also work to eliminate monomer size as a valid argument for affecting DREs. In previous work with the five-monomer series, both the size of the monomer molecule and the number of labile bonds increased with increasing monomer size.¹ In this study, these two pairs of monomers were selected to be of similar size to facilitate a focused validation of the abstractable hydrogen theory. Table 2 lists the molecular weight (MW) and molar volume of the monomers to demonstrate their similarity. The molecular weight and molar volume of PA are 96% and 87%, respectively, of that of CHA. For the BA/THFA pair, THFA is actually slightly smaller than BA although it has more abstractable hydrogens; THFA is 96% of the weight of BA and 93% of the molar volume. Relating the monomer size and $T_g DRE$ data shows no correlation between the two properties (Figures 2 and 3).

Table 2. Properties of the monomers used in this study. Molar volume was calculated using the density (at 20°C) provided by the manufacturer.

	Formula	MW (g/mol)	Molar Volume (cm³/mol)
PA	C ₉ H ₈ O ₂	148.16	137.4
CHA	C ₉ H ₁₄ O ₂	154.21	157.5
BA	C ₁₀ H ₁₀ O ₂	162.19	153.3
THFA	C ₈ H ₁₂ O ₃	156.20	142.9
EEEA	C ₉ H ₁₆ O ₄	188.20	185.6
DDA	C ₁₅ H ₂₈ O ₂	240.39	275.4

Comparison of $T_g DRE$ data for DDA and EEEA indicates not only is the number of abstractable hydrogens in a monomer important, but the bond strength of the hydrogens also influences DREs (Figure 4, note the y-axis magnitude compared to previous figures). Setting aside the hydrogens within the acrylate moiety (which both monomers have in common), DDA contains 25 hydrogens while EEEA only contains 13 hydrogens (Figure 1); however, the $T_g DRE$ for EEEA is smaller than that of DDA.

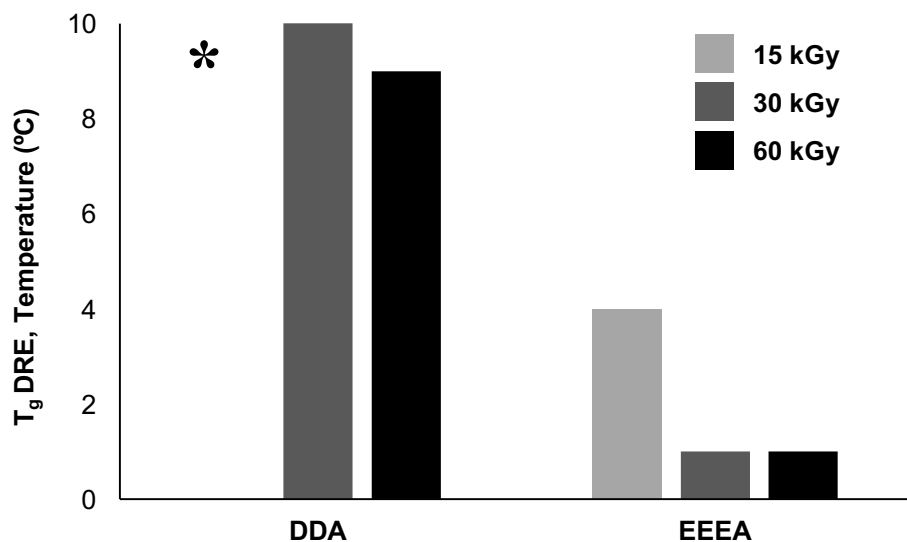


Figure 4. The glass transition temperature DREs, at three different doses, for DDA and EEEA. The more easily abstractable hydrogens in the backbone of EEEA decreases the DRE. (*Film weakness prevented data collection for DDA at 15 kGy, 200 ft/min.)

The lower $T_g DRE$ in EEEA can be attributed to the oxygen within the backbone. The oxygens are strong electron-withdrawing groups, and they weaken the surrounding C-H bonds, making the hydrogens in the adjacent bonds more easily abstractable (Table 3).

Table 3. Bond dissociation energies.⁶

Bond	Dissociation Energy (eV)
H – CH ₂ CH ₃	4.25
H – CH ₂ CH ₂ CH ₃	4.25
H – COCH ₂ CH ₃	3.78

Although the bond energy is only reduced by approximately 0.5 eV in oxygen-adjacent C-H bonds, EEEA is able to achieve almost no $T_g DRE$ (1°C) at 30 and 60 kGy, while DDA has a ~10°C $T_g DRE$ at the same energies with twice as many abstractable hydrogens available. The lower bond dissociation energy not only increases the probability that an accelerated electron will have sufficient energy to break the bond, but it also saves energy to be used on other bonds.

Conclusions

Monomer chemistry plays an important role in the magnitude of DREs experienced during EB polymerization. This work confirms monomer structure trends found in past studies, namely that increasing the number of abstractable hydrogens on a monomer molecule can lessen the DRE. It was also demonstrated that monomer size does not correlate with the magnitude of a monomer's DRE. Additionally, new insight was gained about the effect of bond energy on DREs. Electron-withdrawing groups within a monomer weaken the adjacent bonds and increase the ease of hydrogen abstraction, thereby reducing DREs. Future investigations into the cause of DREs will continue to explore the effect

of bond dissociation energy and how lower dissociation energies can compensate for a fewer number of abstractable hydrogens.

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References

- (1) Schissel, S.M., Lapin, S.C., Jessop, J.L.P. "Characterization and Prediction of Monomer-based Dose Rate Effects in Electron-beam Polymerization," *Radiation Physics & Chemistry*, Vol. 141, 2017, 41-49.
- (2) Schissel, S.M., Lapin, S.C., Jessop, J.L.P., "Accelerating EB's Potential: Understanding the Effects of Dose Rate in Electron-beam Polymerization," *RadTech 2016 UV/EB Technology Conference Proceedings*, On-line, May 2016.
- (3) Schissel, S., Lapin, S.C., Jessop, J.L.P., "Depth/Conversion Characterization of Electron-beam Initiated Polymerization," *RadTech 2014 UV/EB Technology Conference Proceedings*, On-line, May 2014.
- (4) Odian, G. *Principles of Polymerization*, 4 ed.; John Wiley and Sons, Inc., 2004.
- (5) Chapiro, A., *Radiation Chemistry of Polymeric Systems*. John Wiley & Sons, Inc.: New York, 1962.
- (6) Dean, John A., *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill Inc., 1999.