Accepted Manuscript

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PII: S1385-8947(19)31481-0
DOI: <https://doi.org/10.1016/j.cej.2019.122087>
Article Number: 122087
Reference: CEJ 122087

To appear in: *Chemical Engineering Journal*

Received Date: 8 March 2019
Revised Date: 13 May 2019
Accepted Date: 25 June 2019

Please cite this article as: A. Nasresfahani, L.A. Idowu, R.A. Hutchinson, Extractable Content of Functional Acrylic Resins Produced by Radical Copolymerization: A Comparison of Experiment and Stochastic Simulation, *Chemical Engineering Journal* (2019), doi: <https://doi.org/10.1016/j.cej.2019.122087>

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Extractable Content of Functional Acrylic Resins Produced by Radical Copolymerization: A Comparison of Experiment and Stochastic Simulation

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Abstract

A comprehensive stochastic simulator that considers all probable secondary reactions essential for the description of high-temperature radical copolymerization of acrylate/methacrylate is implemented based on previously established accelerating techniques. The comparisons between the predictions and six experimental datasets are detailed for semi-batch copolymerization of 2-hydroxyethyl acrylate (HEA) with *n*-butyl methacrylate (BMA) under starved-feed condition. Macroscopic properties – free monomer and molar mass (MW) average profiles, final polymer molecular mass distributions, and the variation of acrylate composition with time– are reasonably well predicted over the range of initiator and comonomer levels studied. The simulation output also predicts the weight fraction and MW averages of the polymer chains that contain no HEA functionality, results that are compared to the experimental extractables obtained after crosslinking the copolymer resin. The general trends are well-captured, indicating that the model can be utilized in the future to optimize recipe and operating conditions to minimize the production of the non-functional material.

Keywords: radical copolymerization, copolymer composition distribution, kinetic Monte Carlo simulation, starved-feed semi-batch

1. Introduction

The ability to robustly polymerize inexpensive monomers in a variety of reaction media makes radical polymerization (RP) the industrial method of choice to produce functionalized dispersants and surfactants [1]. Acrylates and methacrylates are preferred monomers for binder resins for automotive coatings, providing superior chemical and mechanical properties as well as excellent photostability and resistance to hydrolysis [2–6]. In addition, the ability to equip the polymer backbone with functional groups (hydroxyl, epoxy, amide, carboxylic acid, etc.) simply through monomer choice facilitates a variety of post-polymerization crosslinking options. Led by consumer expectations for improved appearance and longevity without increased cost, the industry is constantly seeking to improve their formulations and methodologies, as well as to reduce the level of solvents and energy required during application [3,7]. Synthesizing low molar mass functional acrylic polymer chains is one solution that has been adopted to face this challenge. For instance, the primary alcohol in 2-hydroxyethyl acrylate (HEA) not only incorporates post-modification capabilities (i.e., crosslinking or grafting) to the resulted resin but boosts the overall polymerization rate [2–7].

The final product resulting from RP synthesis is a mixture of chains with short lifetimes (<1 s) produced at different reaction times over the course of a batch, which typically proceeds for several hours. As it is crucial to tightly control the reaction conditions, these low molar mass polymers are produced via high-temperature (>100 °C) starved-feed radical solution semi-batch copolymerization to improve product uniformity. The concentrations of reactants are kept low by setting the feed rates of monomers and initiator to roughly match their consumption rates in the vessel. Thus, the variation in copolymer composition and molar masses over the course of the reaction is minimized by dictating near steady-state operating conditions [8–13].

Radical acrylate/methacrylate copolymerization under these higher temperature starved-feed conditions favors the formation of acrylate-based mid-chain radicals (MCR) [14,15] as well as the depropagation of methacrylate units on the chain-end of growing radicals [16]. Both phenomena are a strong function of chain composition, as depropagation occurs only with methacrylate diads at the growing radical chain-end. Also, the backbiting mechanism by which a secondary propagating radical (SPR) abstracts a hydrogen atom to create a tertiary MCR radical via a six-membered transition state requires both an acrylate radical and an acrylate unit in the pen-penultimate chain position. A less-frequent pathway leading to

formation of an MCR is intermolecular hydrogen abstraction, by which the radical center is transferred to another macromolecule. Increasing the polymer content in solution increases the occurrence of intermolecular chain transfer (i.e., long chain branching) compared to intramolecular chain transfer, the latter mechanism becoming more probable under solvent-rich conditions to elevate the amounts of short chain branching. Both mechanisms are favored under the low monomer concentrations of starved-feed operation; however, while backbiting occurs at significant rates throughout the entire course of the reaction, intermolecular chain transfer to polymer has an increased influence on chain topologies towards the end of the reaction when polymer concentration is the highest, approaching 60-70 wt.% in the solution. The effect of MCR formation on the product MW and topology is further complicated by the occurrence of β -scission at higher temperatures as a competing pathway to monomer addition to the MCR. While monomer addition creates a branch point, scission yields a product chain that contains terminal unsaturation (i.e., a macromonomer). These macromonomer chains have the propensity to further react under starved-feed conditions [14,15,17–23].

To overcome the design challenges in synthesizing engineered materials, mathematical models and simulators are essential in bridging kinetic and process conditions to the resulting structures. We have recently shown that coupling the so-called scaling method [24,25] with a volume correction approach significantly decreases the computational time required for kinetic Monte Carlo (KMC) simulation, approaching that of the deterministic method known as the method of moments [26]. The KMC output, however, provides detailed information not available from deterministic models, such as the placement of comonomer (often functional) units in the chains across the molar mass distribution [27–30]. Gaining such information becomes pivotal for low molar mass coating resins to balance the desire to reduce the amount of (more expensive) functional monomer in the recipe while also minimizing the fraction of non-functional chains (i.e., chains without a comonomer unit) in the product.

The initial KMC development considered only the basic set of mechanisms defined for solution radical copolymerization (i.e., initiation, propagation, transfer to solvent/monomer, and termination), showing that a significant fraction of chains would not contain the desired functionality if both comonomer content (5 mol.%) and average chain length (20 units) were kept low, even for the case of an ideal copolymerization [26,30]. Herein, we report the expansion of our previous basic model to include all secondary reactions (methacrylate depropagation, MCR formation and consumption, macromonomer formation and consumption) essential for

accurate representation of the radical copolymerization of acrylate with methacrylate under the higher-temperature starved-feed conditions commonly used in the coating industry. After verifying the development through comparison of the stochastic predictions of the accelerated KMC model to the previously established deterministic modeling technique implemented in Predici® [9,12] it is used to analyze a new set of experimental data for the starved-feed copolymerization of HEA with *n*-butyl methacrylate (BMA) conducted with varying HEA and initiator levels. In particular, the utility of the model is assessed by comparing predictions of the properties and amount of non-functional polymer versus that are experimentally determined after extracting material from crosslinked films formed from the copolymers.

2. Materials

n-Butyl methacrylate (BMA, 99% purity containing 10 ppm monomethyl ether hydroquinone as inhibitor), 2-hydroxyethyl acrylate (HEA, 96% purity containing 200-650 ppm monomethyl ether hydroquinone as inhibitor), *tert*-butyl peracetate solution (TBPA, 50 wt.% in mineral spirits), 5-methyl-2-hexanone (MIAK, 99% purity), tetrahydrofuran (THF, 99% purity containing 250 ppm butylated hydroxytoluene as stabilizer), anhydrous dimethyl sulfoxide d-6 (DMSO-d₆, containing 99.9% D), and HPLC-grade acetone ($\geq 99.8\%$ purity) were purchased from Sigma-Aldrich. 4-Methoxyphenol (MEHQ, 98% purity) was purchased from Alfa Aesar. All materials were used as received without further purification to mimic industrial practices.

3. Description of Experimental Procedures and Analyses

In total, there are six cases studied theoretically and experimentally challenging our understanding of the process. The impact of different comonomer and initiator content at 138 °C under the semi-batch starved-feed policy on the amount of extractable polymer chains is explored. The resins were synthesized in a LabMax reactor with automatic stirring, heat control, reflux system, and reagent flow control through gravimetric feed, with the amounts of extractable species determined after isocyanate-based crosslinking of the resins boosted with a tin catalyst.

As a brief summary of the semi-batch procedure, 242 g total mass consisting of TBPA initiator solution and a homogeneous mixture of BMA and HEA is fed at a constant rate over 6 h to the stirred reactor. The reaction vessel is initially filled with 130 g of MIAK and maintained at 138 ± 0.5 °C. Assuming 100% monomer conversion, the reactor reaches a total mass of 372 g, with 65 wt.% polymer content, at the end of

the feeding period. Both the comonomer composition (6.25, 12.5 and 25.0 wt.% HEA) and the amount of initiator (2.0 and 4.0 mol.% relative to total monomer fed) are varied within the experimental set. Based on the duration of feeding process, the flow rate into the 0.6 L reactor is $0.7 \text{ g}\cdot\text{min}^{-1}$. Up to ten samples of 2–3 mL are acquired over the course of reactions to monitor the time-varying behaviors. All samples are immediately quenched by the addition of MEHQ inhibitor ($1 \text{ g}\cdot\text{L}^{-1}$ in xylene) and stored in the freezer before being subjected to gas chromatography (GC) and size exclusion chromatography (SEC) to obtain residual monomer concentrations and polymer molar mass distributions (MMD), respectively.

Both the operating procedure and sample analyses are carried out according to the previous studies [11,12,16]. GC-samples are diluted (1/300 w/w ratio) in acetone and analyzed using a Varian CP-3800 GC setup, consisting of a CP-8410 auto-sampler, CP-117 isothermal split/splitless injector (with a 9:1 split), 30M Agilent Varian (Chrompack) GC Columns (CP-Sil 8CB), oven, and flame ionization detector (FID). The quantitative analysis of residual monomers is based on the calibration curves shown as **Figure S1** and **Figure S2** (Supplementary Information). SEC samples, prepared in tetrahydrofuran (THF) at $\sim 3 \text{ mg}\cdot\text{mL}^{-1}$, are analyzed with a Waters 2960 separation module with a Waters 410 differential refractometer (DRI) and a Wyatt Instruments Dawn EOS 690 nm laser photometer multi-angle light scattering (LS) detector. For relative molar masses, polystyrene standards between 300 and 875 000 g mol^{-1} are used for the calibration of the separation performed by 4 Styragel columns (HR 0.5, 1, 3, 4) maintained at 35°C , with a sample solution flow rate of $0.3 \text{ mL}\cdot\text{min}^{-1}$. Proper transformation of relative molar masses with known Mark–Houwink–Sakurada parameters allows for a suitable comparison and verification between RI and LS results. The results presented are from DRI detection, due to the superior signal to noise response [12]. The copolymer MMDs were calculated using a weight-averaged treatment of the calibration parameters, as described previously [31]. Since the polymers are methacrylate-rich, the level of long-chain branching is expected to be low and is not accounted for in the analysis.

A standard clear-coat testing formulation is performed to extract the non-functional oligomers using hexamethylene diisocyanate (Desmodur® N 3300 A) as the curing agent [32–34]. After purifying the acquired resins from the reactor, the solids are dissolved in butyl acetate to prepare 45 wt.% solutions. To enhance the diisocyanate reactivity, 700 ppm dibutyltin dilaurate is added with a small molar excess of -NCO relative to the hydroxyl groups, -OH, in the system (i.e., ~ 1.05). For wetting the substrates, 0.25 wt.% BYK-306, a

commercial silicone-containing additive from BYK Additives & Instruments, is applied to the surface. Drawdowns are prepared on thermoplastic polyolefin panels using easy film removal via 8 mm blade. Prior to being exposed to 60 °C for 30 min and 140.6 °C for 30 min, the panels are cured at ambient. After 30 days, analytical extraction is performed on the panels by scraping an approximately 25.4×76.2 mm² portion of the coating and placing it into a scintillation vial containing 25 g dichloromethane (DCM). The extracted solutions are filtered before evaporating the DCM. At this point, the samples weights are precisely measured, verifying by GC that no volatile component remained. Accordingly, weight percentages of the non-volatiles extracted species from the coated films are determined and the samples subjected to SEC analysis. ¹H nuclear magnetic resonance (NMR) was carried out on a Bruker 400 MHz spectrometer at room temperature to further assess the extractables in DMSO-d₆, following procedures outlined elsewhere [31].

Samples for ESI mass spectroscopy – both the original resin and the extractable materials – are dried before dissolving 0.1 g of material in 10 mL of methanol for analysis using an Orbitrap Velos Pro (Thermo Scientific, Bremen, Germany) mass spectrometer coupled to a heated-electrospray ionization (HESI) source. The sample spray needle temperature was set to 275 °C and an ion spray voltage of 5.0 kV was applied. MS scans were acquired at an Orbitrap resolution of 60k for an m/z range from 0.2k to 4k. The resulting spectra were examined using Xcalibur Qual Browser software (Thermo Scientific).

Simulations are performed in both Predici® and the developed kinetic Monte Carlo (KMC) stochastic simulator. A reliable stochastic representation can be achieved in about 20 minutes (32 GB RAM, Core-i7 4790 3.60 GHz). The detailed information regarding the acceleration techniques established in the KMC model can be found in our previous publication [26].

4. Results and Discussion

Implementation of Gillespie's Algorithm

Table 1 provides the set of primary reactions – initiation, propagation, termination, and chain transfer to solvent and monomer – needed to describe any radical copolymerization system, with the added complication of considering the influence of penultimate units on both propagation and termination rates. $P_{(n,m)}^{ij,[B]}$ is the growing secondary (chain end) radical, possessing n/m methacrylate/acrylate units with [B] branches. The terminal and penultimate units can be recognized by j and i , respectively, with δ_i the unit vector specifying the initiated polymer chain ($P_{\delta_i}^{ii,[0]}$). The termination products are differentiated as to whether they

carry a reactive double bond ($U_{(n,m)}^{[B]}$; i.e., a macromonomer) or not ($D_{(n,m)}^{[B]}$). The set of basic mechanisms is augmented by the secondary reactions summarized in **Table 2** that include the depropagation of methacrylates [16] and the formation and consumption of both macromonomer chains and acrylate MCRs, the latter denoted as $Q_{(n,m)}^{xili,[B]}$ with *xili* being the monomeric sequence adjacent to the radical center; in general format, the mid-chain radicals are referred as $Q_{(n,m)}^{[B]}$. The depropagation requires at least two consecutive methacrylate units on the radical chain-end, while backbiting occurs with three consecutive acrylate units or with a methacrylate unit sandwiched between the two acrylate units, as shown in **Table 2**. The addition of a macromonomer (formed from termination by disproportionation as well as scission of an MCR) to an SPR leads to an MCR structure, raising the probability of scission which is addressed via a treatment originally introduced by Wang et al. [10]. Intermolecular chain transfer to polymer is not included, as its contribution to branching under these reaction conditions is small compared to that of macromonomer incorporation in acrylate homopolymerization [10], with the influence diminished further for the current methacrylate-rich recipes considered in this work. This comprehensive set of mechanisms was previously accomplished in a deterministic-based model implemented in Predici® [9,12]. The kinetic coefficients specific to BMA/HEA copolymerization were taken from previous work [8,9], as summarized in **Table S1** (Supplementary Information).

The improved Gillespie's direct method is adapted to implement the stochastic algorithm, where if N elementary reactions shape the stochastic events, the chosen reaction is the one with the closest higher cumulative probability compared to a first randomly-generated number. The radical species are randomly selected from the ensemble, with the random numbers selected from a uniform distribution bounded between 0 and 1. Simulation details regarding the initial number of molecules (i.e., ensemble size), accuracy of results, recognition of different species, and acceleration techniques are described within the context of our recent publication [26].

Data storage is a vital aspect in KMC simulations as it allows the tracking of species with respect to the reaction channels defined. Since macromonomer can be transformed into a propagating radical, the storage scheme should provide the minimum required info (i.e., the total number of monomer/comonomer units and branches), referred to as "history" in the storage schemes tabulated in **Table S2**. The overall vector of repeat units, which includes the total number of monomer and comonomer denoted as n and m , are distinguished

from the SPR active branch by n_p and m_p . Also, the depropagation or backbiting flag indicates the capacity of a given SPR to become involved in the depropagation or backbiting channel. The storage structure for an MCR, $Q_{(n,m)}^{[B]}$, considers that its type (l) that can be either 1 or 2, specifying the penultimate unit. This method of storing species enables the stochastic model to rapidly track, distinguish, and, if needed, select the different categories of radicals in the growing reaction volume. The macromonomers and dead polymer chains are grouped under the title of “dead species”, sorted and categorized based on their degree of polymerization and number of comonomer units. For example, $F_{[m]}$ (acrylate functionality) is the frequency of dead species with m comonomer units for a given degree of polymerization (DP_n).

The output of KMC model perfectly overlaps the previously developed deterministic model implemented in Predici [12] for all six cases studied in this paper, confirming that the complex set of mechanisms has been properly implemented in the stochastic model, and that the simulation volume is sufficiently large to accurately represent the system. As an advantage of utilizing the accelerated stochastic model, the functionality of all dead chains is readily accessible at any given time of the polymerization. The number of branches is also available for each individual chain, as the considered set of mechanisms (**Table 1** and **2**) fully captures the most probable scenarios leading to short or long chain branching. The extended description of the reactions along with the associated assumptions can be found in our previous publications [8,9].

Table 1. Primary radical copolymerization reactions included in the KMC model, with indices 1 and 2 indicating BMA and HEA, respectively. δ_1 and δ_2 represent unit vectors (1,0) and (0,1), respectively. The penultimate model coupled with the geometric mean approximation are considered to model the termination reactions.[9,35] The expanded version of the schemes can be found elsewhere [8,9].

Primary Reactions k, l, j and $i = \langle 1 \therefore \text{Methacrylate} \rangle$ or $\langle 2 \therefore \text{Acrylate} \rangle$	
Reaction Type	Scheme
Initiation	$I_2 \xrightarrow{k_d} 2f_d I$ $I + M_i \xrightarrow{k_p^{ii,i}} P_{\delta_i}^{ii,[0]}$
Propagation	$P_{(n,m)}^{ij,[B]} + M_k \xrightarrow{k_p^{ijk}} P_{(n,m)}^{jk,[B]} + \delta_k$
Chain Transfer to Solvent	$P_{(n,m)}^{ij,[B]} + S \xrightarrow{C_s^{ijk}} D_{(n,m)}^{[B]} + I$
Chain Transfer to Monomer	$P_{(n,m)}^{ij,[B]} + M_k \xrightarrow{k_{trM}^{jk}} D_{(n,m)}^{[B]} + P_{\delta_k}^{kk,[0]}$
Termination	$P_{(n,m)}^{ij,[B]} + P_{(n,m)}^{lk,[B]} \xrightarrow{k_{td}^{ij,ls}} U_{(n,m)}^{[B]} + D_{(n,m)}^{[B]}$

Table 2. Secondary reactions included in the KMC model, with 1 and 2 indicating BMA and HEA, respectively. The expanded version of the schemes can be found elsewhere [8,9].

Secondary Reactions	$j = 1 \blacksquare i = 2 \blacksquare k, l$ and $x = 1$ or 2 (1 ∴ Methacrylate) or (2 ∴ Acrylate)
Reaction Type	Scheme
Depropagation	$P_{(n,m)}^{ij,[B]} \xrightarrow{k_{dp}} P_{(n,m)-\delta_j}^{ij,[B]} + M_j, m \geq 2$
Backbiting	$P_{(n,m)}^{ili,[B]} \xrightarrow{f_b^{lk_b}} Q_{(n,m)}^{ili,[B]}, n + m \geq 4$
MCR Scission	$Q_{(n,m)}^{ili,[B]} \xrightarrow{f_{sci}^{lk_{sci}}} U_{(n,m)-\delta_i-\delta_l}^{[B]} + P_{\delta_i+\delta_l}^{li,[0]}$ $Q_{(n,m)}^{xili,[B]} \xrightarrow{f_{sci}^{lk_{sci}}} U_{2\delta_i+\delta_l}^{[0]} + P_{(n,m)-2\delta_i-\delta_l}^{kx,[B]}$
Propagation of MCR	$Q_{(n,m)}^{[B]} + M_k \xrightarrow{k_p^t/r_{ik}} P_{(n,m)+\delta_k}^{kk,[B+1]}$
Termination of MCR	$Q_{(n,m)}^{[B]} + Q_{(n',m')}^{[B']} \xrightarrow{k_{tc}^{qq}} D_{(n+n',m+m')}^{[B+B'+2]}$ $P_{(n,m)}^{kl,[B]} + Q_{(n',m')}^{[B']} \xrightarrow{k_{tc}^{pq}} D_{(n+n',m+m')}^{[B+B'+1]}$ $Q_{(n,m)}^{[B]} + Q_{(n',m')}^{[B']} \xrightarrow{k_{td}^{qq}} D_{(n,m)}^{[B]} + D_{(n',m')}^{[B']}$ $P_{(n,m)}^{kl,[B]} + Q_{(n',m')}^{[B']} \xrightarrow{k_{td}^{pq}} D_{(n,m)}^{[B]} + D_{(n',m')}^{[B']}$
Simplified Treatment for Macromonomer Reactions [10]	$P_{(n,m)}^{kl,[B]} + U_{(n,m)}^{[B']} \xrightarrow{k_{macro}^{lx}} P_{(n+n',m+m')}^{xx,[B'+B+1]} + \delta_x$ $P_{(n,m)}^{kl,[B]} + U_{(n,m)}^{[B']} \xrightarrow{k_{exchange}^{lx}} U_{(n,m)}^{[B]} + P_{(n,m)}^{xx,[B]}$
Primary Radical Termination	$I + P_{(n,m)}^{ij,[B]} \text{ or } Q_{(n,m)}^{[B]} \xrightarrow{k_{ts}} D_{(n,m)}^{[B]}$

Secondary Reactions Imprints

The imprint of a secondary reaction on the characteristics of the copolymerization system is dependent upon operating conditions and copolymer composition, as well as the relative values of the associated rate coefficients. For example, reducing the amount of acrylate in the recipe decreases the significance of the secondary MCR reactions but increases the impact of methacrylate depropagation, while increasing reaction temperature increases the importance of all secondary reactions. One of the experimental recipes examined in this study, a feed consisting of 25 wt.% HEA (remainder BMA) and 2 mol.% TBPA relative to the total monomer, is simulated to demonstrate the influence of the secondary reactions known to be important for

acrylate and methacrylate radical polymerizations. The feed is added at a constant rate over 6 h to a reactor with MIAK solvent maintained at 138 °C, such that the final mixture contains 35 wt.% solvent.

Figure 1. Impacts of secondary reactions on A) free monomer levels, B) number-average (M_n) and weight-average (M_w) polymer molar masses, and C) molar mass distribution of the final product for BMA/HEA (75/25 w/w) polymerization conducted under starved-feed semi-batch conditions.

The simulated output shown in **Figure 1** consists of the concentration profiles of free monomer – both BMA and HEA – in the reactor (A), the number- (M_n) and weight- (M_w) average polymer molar mass profiles (B), and the molar mass distributions (MMD) of the final polymer product (C). Four simulations of the system

were done, starting with the basic set of radical polymerization mechanisms (initiation, propagation, termination, transfer to solvent and monomer, as summarized by **Table 1**), then sequentially adding in methacrylate depropagation, acrylate MCR formation and consumption (denoted as scission), and finally the reactions involving macromonomer as a reactant.

For this methacrylate-rich recipe, adding depropagation to the mechanistic set has a clear effect on the consumption of methacrylate, as reflected by the increase in the level of unreacted BMA in the reactor from ~ 0.1 to $0.3 \text{ mole}\cdot\text{L}^{-1}$. It takes a longer period of time to build up to a “steady-state” BMA concentration in the system, with the reduced rate leading to the formation of lower MW material during the transient period early in the reaction. However, the influence of depropagation on MW averages at later times and the final polymer MMD is minimal, as the high instantaneous monomer and initiator conversion means that roughly the same number of total monomer units is being incorporated into the same number of polymer chains. With only 25 wt.% acrylate in the system, the addition of MCR reactions has little influence on rate or polymer MW, as the fraction of chains that undergo backbiting (a reaction that requires an acrylate unit in both the ultimate and pen-penultimate positions of the growing radical) is small. However, a significant number of macromonomer chains in the system are still formed through termination by disproportionation, such that when the reaction of those chains is considered, both M_n and M_w (and the final product MMD) are elevated to higher values (**Figure 1**).

Macroscopic Model Predictions versus Experimental

Although it is feasible to improve the predictions of the model for a certain case study through optimization of the related parameters, the emphasis here is to present predictions using a comprehensive model for radical copolymerization of acrylate/methacrylate through previously assessed kinetic coefficients. The kinetic coefficients summarized in **Table S1** result from over a decade of experimental and theoretical research on the primary/secondary reaction mechanisms of acrylate and methacrylate families partially referenced here [8–12,16,31,36–40].

The six cases studied differ only in the amounts of HEA comonomer (25.0, 12.5, or 6.25 wt.%) and TBPA initiator (2.0 or 4.0 mol.% relative to monomer) fed to the reactor. **Figure 2** illustrates the capacity of the model to capture the experimental trends observed for the free monomer/comonomer (i.e., BMA/HEA) levels in the reactor as well as the average comonomer composition (F_{HEA}) with respect to the reaction time.

While there are minor mismatches, the consumption and incorporation behaviors of the reactive species are well depicted by the model. Noteworthy to mention, the incorporation of HEA becomes nearly constant after passing 100 min of the total 6 h reaction time, indicating the starved-condition is successfully achieved (**Figure 2**). Moreover, the average polymer molar masses are adequately estimated by the model, as shown in **Figure 3**. While free monomer levels decrease only slightly when the initiator level is increased from 2 to 4 mol.% TBPA (a result of the starved-feed operation), the polymer average molar masses decrease significantly.

Increasing the HEA level from 6.25 to 25.0 wt.% in the recipe results in a slight decrease in the level of free BMA in the reactor, as the influence of depropagation lessens. A slight influence on polymer molar masses can also be observed: as the probability of MCR formation increases with increased acrylate content, there is a subsequent increase in both the formation of short-chain branches and the rate of chain scission, the latter leading to lowered average chain lengths. However, this effect is mitigated by the propagation of the resulting macromonomers, which introduces long chain branches to the topologies of the macromolecules.

Figure 2. Comparison of the simulated monomer/comonomer concentrations in the reaction media and mol fraction of HEA in the copolymer, F_{HEA} , with the experimental data obtained via gas chromatography. The plots are titled according to the weight percentage of comonomer and the molar percentage of the initiator in each recipe. Note that the scale for F_{HEA} (right axes) decreases from top to bottom, in order to improve the clarity of data presentation.

Figure 3. Simulated evolution of polymer molar-mass averages compared to the SEC-measured experimental data. The plots are titled according to the weight percentage of comonomer and the molar percentage of the initiator in each recipe.

Figure 4 compares the modeled MMDs (without accounting for broadening) of the final polymer product to those measured by SEC. As expected from the examination of M_n and M_w values, decreasing the amount of comonomer or initiator shifts the distribution towards higher values, stretching the high molar mass tail from 4.50 to 4.75 on the logarithmic scale. It should be noted that SEC is relatively insensitive to the oligomers having less than four repeat units such that the low molar mass tails within the experimental data are roughly indifferent to the amount of comonomer and initiator included in the polymerization recipes.

As mentioned above, the simulation results shown in **Figures 2-4** are identical for the deterministic model implemented in Predici® and the KMC simulator. Lowering the amount of HEA causes a decrease in chain branching, as fewer radicals are present with acrylate units in both the penultimate and pen-penultimate position. According to the stochastic calculations, there are 1.0 and 2.0 (25 wt.% HEA), 0.8 and 1.6 (12.5 wt.% HEA), and 0.65 and 1.5 (6.25 wt.% HEA) branches per hundred repeat units, with the higher branching level in each pair resulting from the higher initiator loading (2.0 vs. 4.0 mol.% relative to monomer). As methacrylate termination is predominantly by disproportionation, the higher TBPA levels lead to greater levels of macromonomer formation, which in return increases branching levels through macromonomer addition. Although not a focus of the current investigation, the use of KMC provides additional information about the distribution of branches, as captured through plots of the branching density (ρ_B) as a function of chain length (**Figure S14**); the branch distributions follow a Gaussian behavior, $f(x) = \sum_i \left(a_i \exp \left(- \left(\frac{x - b_i}{c_i} \right)^2 \right) \right)$, similar to the molar mass distributions plotted in **Figure 4**. As branched chains have a lower viscosity than the linear chains of equivalent molar mass, such information may be useful when tuning the viscosity of the resin to reduce the amount of volatile solvent required for its application.

Figure 4. Simulation versus the normalized experimental MMDs. Each subplot is titled according to the weight percentage of comonomer and the molar percentage of the initiator.

Modeling of Extractables Versus Experimental

While overall copolymer composition may be well-controlled by the semi-batch operation, previous KMC studies have shown that the probability of generating chains without the desired functionality increases with decreasing chain-length in the distribution [26,30]. Thus, both lowering the average polymer molar mass (by increasing initiator level), and lowering the amount of functional comonomer in the recipe should increase the non-functional polymer fraction in the product. As described in the experimental section, an isocyanate-based crosslinker assisted with a tin catalyst allows extraction of the non-reactive portion of the synthesized resins. As summarized in **Table 3**, the experimental results follow these expectations, with the mass fraction of extractables increasing from 0.6 wt.% for the recipe with 25 wt.% HEA produced using 2 mol.% TBPA to 8.1 wt.% for the recipe with 6.25 wt.% HEA produced using 4 mol.% TBPA. The average molar masses of the extractables are also summarized in **Table 3**, with the MMDs compared to those of the original resins in **Figure 5**. Note that low molar mass species with chain lengths below four can be partially/fully evaporated during the purification of the resins, or not measured accurately during SEC analysis, as calibration standards start at 300 g mol⁻¹. Despite these uncertainties, it is evident that the MMDs of the extractables shift to lower values as the HEA content in the original resin increases from 6.25 to 25.0 wt.%, with corresponding M_n values decreasing from ~1800 to ~800 g mol⁻¹. Surprisingly, there is not a significant difference in the MMDs of the extractables from the resins produced using different initiator levels at a constant HEA level; as seen in **Figure 5**, clear differences are seen in the MMDs of the original resins produced with high (4 mol.%) and low (2 mol.%) initiator, and the fraction of extractable material is higher for the resins produced with 4 mol.% TBPA. This behavior is also observable by comparing the estimated or experimental average molecular weights in **Table 3**. Therefore, chain-length range of the non-functional chains is more strongly governed by the comonomer amount rather than the initiator level.

Figure 5. Experimentally obtained SEC distributions of the original polymer resins (bottom) and extractable materials (top).

During the crosslinking reaction via the tri-functional-isocyanate catalyzed with tin, the chains containing hydroxyls ($F \geq 1$) become a part of the generated polymeric network. No evidence of hydroxyl groups could be detected by proton NMR, confirming the efficiency of the crosslinking reaction performed on the functional groups. In addition, ESI-MS spectra from the extractable materials are compared to those of the base resins (**Figure S3-S5**). Initiating and terminating species, summarized in **Table S3**, are assigned based upon a previous ESI-MS study of TBPA-initiated poly(BMA) produced under identical starved-feed conditions [41]. Normalizing the peak heights relative to a value of 100 for the most intense signal (corresponding to $\text{CH}_3\text{-BMA}_7\text{-H}$), all of the other peaks with relative intensities of 10 or greater in the mass/charge region between $\text{CH}_3\text{-BMA}_7\text{-H}$ and $\text{CH}_3\text{-BMA}_8\text{-H}$ for the extractable sample could be assigned to homopolymer BMA structures. In contrast, the spectra for the original resin contained clear evidence of chains containing HEA, with the relative ratios of $\text{CH}_3\text{-BMA}_8\text{-H}$, $\text{CH}_3\text{-BMA}_7\text{-HEA-H}$, and $\text{CH}_3\text{-BMA}_6\text{-HEA}_2\text{-H}$ species, for example, varying in the expected fashion depending on the HEA content (6.25, 12.5 or 25.0 wt.%) in the resin (**Figure S6, Table S4**).

While the complete absence of HEA units in the extractable material cannot be claimed, the ESI-MS and NMR measurements show that the content is lower than detectable limits. Thus, it is reasonable to compare the amounts and molar masses of these materials to predictions from the KMC simulations, equating the population of chains without any hydroxyl functionality to the experimental extractables.

As depicted in **Figure 6**, decreasing the amount of HEA from 25.0 to 6.25 wt.% causes a noticeable increase in the cumulative mol fraction of BMA homopolymer chains (i.e., non-functional chains) in the system, with the amount also increasing as the MW of the resin is lowered at a constant HEA level by increasing initiator amount. It is interesting to note that the fraction of non-functional chains is lowered at the start of the reaction; as shown in **Figure 6**, the first 2 hours is characterized by the production of material with higher HEA content than average. However, the values level out for the latter part of the reaction, as relative concentrations of reactants (TBPA, HEA, and BMA) become invariant with time. While the predicted mol fraction of non-functional material reaches close to 30% for the resin produced with 4 mol.% TBPA and 6.25 wt.% HEA, it is the mass fraction of material that must be compared to the extractable quantity. This amount is easier to visualize by examining **Figure 7**, which compares the entire simulated MMD to the sub-distributions containing exactly 0, 1, 2 and >2 HEA units for the two extreme cases – the resin containing 25 wt.% HEA produced with 2 mol.% TBPA, and that produced with 4 mol.% TBPA containing 6.25 wt.% HEA. For both cases, the non-functional chains are, as might be expected, found in the low molar mass tail of the distribution. The full set of the simulated MMDs is presented in **Figure S7**, with **Figures S8-S13** providing further details of the sub-distributions for each simulation case.

Figure 6. Evolution of the mol fraction of non-functional chains (i.e., BMA homopolymer) over the course of polymerization, as stochastically determined. The case studies are numbered according to **Table 3**.

Table 3. Comparison of the average characteristics of the material extracted from the crosslinked films formed from HEA/BMA copolymer (superscript “Exp.”) versus predictions from the stochastic model (superscript “Est.”) for the non-functional chains. The column attributed to case study details the wt.% HEA and the mol.% TBPA relative to the total monomer fed.

#	Case Study	$*M_w^{Exp.}$	$*M_n^{Exp.}$	$*M_w^{Est.}$	$*M_n^{Est.}$	$**w_{[0]}^{Exp.}$ %	$***w_{[0]}^{Est.}$ %
1	25 wt.% - 2 mol%	1045	796	551	346	0.6	0.13
2	25 wt.% - 4 mol%	1036	821	533	336	0.7	0.39
3	12.5 wt.% - 2 mol%	1291	965	1318	711	1.4	1.06
4	12.5 wt.% - 4 mol%	1639	1175	1199	657	2.3	2.69
5	6.25 wt.% - 2 mol%	3349	1780	2529	1286	3.4	4.87
6	6.25 wt.% - 4 mol%	3587	1952	2185	1118	8.1	10.17

*Number and weight average molar mass values reported in $g \cdot mol^{-1}$.

** Mass percentage extracted after forming crosslinked films from HEA/BMA copolymers

*** Mass percentage of non-functional (i.e., BMA homopolymer) material stochastically estimated.

Figure 7. Final molar mass distributions showing populations containing non-functional ($F=0$) chains, as well as chains with exactly 1, 2, or greater than 2 HEA units calculated for Case 1 (left) and Case 6 (right), as detailed in **Table 3**.

The predicted mass fractions of chains in the final product containing 0, 1, 2, or greater than 2 HEA units for the six experiments are summarized in **Figure 8**, with the mass fraction of non-functional material in polymer product ($w_{[0]}^{Est.}$) compared to the experimentally determined extractable fractions in **Table 3**. The predictions are quite reasonable, capturing the increase from <1 wt.% extractables measured for the two resins containing 25.0 wt.% HEA, to the much higher level (>8 wt.%) seen for the resin containing 6.25 wt.% HEA produced with 4 mol.% TBPA. As the amount extracted from samples with comonomer content higher than 6.25 wt.% are extremely low, the experimental values may be slightly biased by components such as the 0.25 wt.% silicone-containing additive used in the coating procedure described in **Experimental Section**. Thus,

the relative mismatches become progressively smaller as higher amounts of extractables are obtained. As seen in **Figure 6**, a fifty-percent reduction in the comonomer content increases the percentage of non-functional chains by a factor of three whereas the same reduction in the amount of initiator results in a fifty-percent decrease. This theoretical characteristic is observed in the experimental data summarized in **Table 3**, with the mass fraction of extractables varying from 0.6% to 8.1 wt.% as the HEA and TBPA were varied from 25.0 to 6.25 wt.% and 2.0 to 4.0 mol.%, respectively.

Figure 8. Final weight percentages determined for populations of chains classified by their comonomer functionality computed through the accelerated KMC simulator.

Additional validation of the modeling approach and predictions is seen in the average molar mass values of the extractable materials, also compared to experimental results in **Table 3**. In agreement with experiment, the predicted M_n and M_w values of the non-functional material increases as the HEA content is lowered from 25.0 to 6.25 wt.%, but do not vary significantly with the TBPA initiator level. While some differences in the predicted and measured average MM values are observed, these might be expected due to the difficulties in using SEC on such low MW material. **Figure 9** provides a visual comparison between the experimental extractables and estimated SEC distributions of the non-functional chains, with the predicted peak positions reasonably matching the experiments. The best predictions of the shape of the experimental distributions are seen for the 6.25 wt.% HEA cases, for which the extractable amounts are the greatest; simulations do not match the multi-modalities measured for the experiments in which the extractable content

was very low, <2 wt.%. Thus, while higher sensitivity to contamination may be associated with the low extractables content from the resins produced with 12.5 and 25.0 wt.% HEA, the trends are well-predicted,

Figure 9. Molar mass distributions of the extractables compared with the distributions of the non-functional material stochastically derived. Each subplot is titled according to the weight percentage of comonomer and the molar percentage of the initiator relative to the total monomer.

with both the amounts and the MMDs of the experiment with 6.25 wt.% HEA and extractable amount higher than 3 wt.% are in good agreement with the predictions.

5. Conclusions

Reducing the amount of volatile solvent used for application of coatings can be achieved at lower viscosities by reducing the molar mass of the polymeric binder resin. However, the stochastic nature of radical polymerization penalizes this approach by decreasing the fraction of chains containing the functional comonomer units needed for the crosslinking reactions upon application.

We have developed and applied a stochastic modeling technique that includes all of the mechanistic complexities – penultimate copolymerization kinetics, depropagation, and reactions involving the formation and consumption of mid-chain radicals – required to capture the characteristics of acrylate/methacrylate free radical high-temperature copolymerization. Despite the introduction of these additional reaction pathways, efficient data storage and acceleration techniques reduce the computational time required for the solution of the full model to reasonable times, ~20 min for a typical 6-hour semi-batch copolymerization run under starved-feed conditions. After verification by comparing to the output (monomer concentration, copolymer composition, and polymer average MM profiles as well as MMDs) calculated using a previously-formulated deterministic model, the KMC model is utilized to simulate six BMA/HEA experiments conducted with varying comonomer and initiator levels.

As well as providing reasonable predictions of polymer average molar masses and MMDs, free monomer levels and copolymer composition for the series of experiments, predictions of both the mass fraction and molar masses of non-functionalized chains are in good agreement with the experimental investigation of the properties of the polymeric material extracted from crosslinked films formed from the BMA/HEA copolymer resins. It is found that decreasing HEA from 25.0 to 6.25 wt.% in the comonomer mixture and increasing initiator level from 2 to 4 mol.% increased the fraction of extractables from 0.6 to 8.1 wt.%. These results are well-predicted by the KMC model assuming that the extractable material is entirely BMA homopolymer chains, an assumption supported by NMR and ESI-MS characterization of the experimental samples. In addition, the changes in polymer MMs of the extractables measured by SEC with synthesis conditions are also well-predicted by the KMC model. With this experimental verification, the model formulation provides a solid ground for optimizing the production of acrylic resins to obtain the desired

population of polymer chains synthesized under industrial conditions. In the future, the modeling approach will be used to develop nonlinear feeding strategies to decrease the total polymerization time traditionally required by a starved-feed policy while also minimizing the production of non-reactive chains.

6. Supporting Information

Further documentation of the results can be found in **Supporting Information**.

7. Acknowledgments

The authors would like to thank Dr. Matthew Hunley and Nicole Gardner of Axalta Coating Systems for performing the crosslinking and extractables determination, as well as Axalta Coating Systems and the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

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Graphical Abstract for Table of Contents:

Highlights

A stochastic model describes acrylic copolymerization under semi-batch starved-feed policy

The model considers all reactions important under industrial conditions

Acceleration strategies implemented provide accurate results within twenty minutes

The model predicts chain microstructure including fraction of non-functional material

The model provides an excellent representation of experimental results