Hydrogen bonding in radical solution copolymerization kinetics of acrylates and methacrylates: A comparison of hydroxy- and methoxy- functionality

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The pulsed-laser polymerization technique in combination with size exclusion chromatography and nuclear magnetic resonance is used to study the influences of solvent choice and monomer structure on the copolymerization propagation kinetics of 2-hydroxyethyl acrylate (HEA) and 2-methoxyethyl acrylate (MEA). The similarity in the monomer structures provides a means to isolate the influence of H-bonding, which increases the incorporation of HEA into copolymer relative to that of butyl acrylate (BA) dependent on solvent choice. The copolymer-averaged propagation rate coefficient, k_p^{cop} , for HEA/BA is also increased over that of BA homopropagation, and is highly influenced by solvent choice. In contrast, MEA copolymerized with butyl acrylate (BA) and butyl methacrylate (BMA) in multiple solvents revealed classic behaviour, with no solvent effects exerted on k_p^{cop} or reactivity ratios other than the increase of k_p^{cop} in *n*-butanol (BuOH). The value of k_p^{MEA} was determined to be 35 000 L·mol⁻¹·s⁻¹ at 50 °C, 30% higher than the value for BA. In a simplified modelling approach, penultimate-unit parameters for BMA/BA were used to represent the evolution of k_p^{cop} for BMA/MEA in bulk.

Introduction

The determination and understanding of kinetic parameters of radical copolymerization (RP) is essential for the development of industrially relevant copolymerization models used to reduce cost and waste as well as to improve the process quality. Even small improvements can lead to significant benefits for high-throughput processes. Whereas many investigations have focused on the copolymerization of “classic” non-polar monomers of the methacrylate,¹ acrylate,² and styrenic³ families in bulk or organic media, a growing catalogue of kinetic parameters is now being developed for functional monomers that are more polar or undergo hydrogen-bonding.^{4–8} However, these studies also show that a certain level of complexity is introduced to RP systems, for example by the introduction of water as a “greener” solvent⁹ that provides a polar and dense H-bonding environment that has an immense effect on the RP kinetics of water-soluble monomers.^{7,10} Functional monomers are also gaining in importance as a means to introduce reactivity to polymer chains, as part of continued research to develop improved materials and reduce solvent content.^{6,11,12} Accordingly, analysis of these systems must consider kinetic effects not only derived from the nature of monomer but also the solvent, in contrast to the aforementioned non-polar systems.

A versatile tool to understand these functional systems and their propagation chain growth parameters is the IUPAC-recommended pulsed laser polymerization-size exclusion chromatography (PLP-

SEC) technique.¹³ Propagation rate coefficients, k_p , for homo- and copolymerization are easily determined with this method, which can also be adapted to study side reactions such as acrylate backbiting and its associated rate coefficients.^{14–16} Further modifications of the PLP technique allow for the determination of termination kinetics when combined with additional on-line measurements of monomer or radical concentrations.^{17,18}

Some general trends have emerged from these kinetic investigations, with family-like behaviour found for propagating radicals of the same nature; for example, the k_p values of alkyl methacrylates increase roughly by 50% with increasing length of the ester side chain from methyl to dodecyl, although the activation energy remains constant.^{1,19} Other factors causing reactivity differences within a particular monomer family include the isometric orientation of side chains (i.e., cyclic structures)²⁰ and the introduction of functional groups that lead to intermolecular interactions between monomer and solvent or with the polymer chains.^{11,12} We have been systematically studying the influence of the hydroxyl functionality on polymerization kinetics, generally introduced to systems through addition of 2-hydroxyethyl acrylate (HEA) or 2-hydroxyethyl methacrylate (HEMA) monomers, but also possibly through solvent choice. The interaction between the hydroxyl hydrogen and the carbonyl oxygen of the acrylic ester reduces the electron density at the double bond to increase its reactivity, as detected through infrared spectroscopy;^{21,22} thus, the k_p value for HEMA in bulk²³ is found to be higher than that of butyl methacrylate (BMA) by a factor of 2.5. Hydrogen-bonding also leads to concentration-dependent k_p in aqueous systems,²⁴ as well as a modified relative reactivity in copolymerization, as has been demonstrated for the most prominent systems involving hydroxyl-functional HEA or HEMA^{8,22} and carboxyl-functional acrylic acid or methacrylic acid (AA/MAA).^{4,5}

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

While H-bonding is known to lead to the formation of dimers of MAA,²⁵ it has been shown that this formation does not correlate with homopropagation k_p values.⁴ In an investigation of the solution copolymerization of styrene (ST) and MAA, however, it was hypothesized that interaction between MAA monomer and an incorporated MAA unit in the polymer backbone can channel MAA towards the propagating radical, leading to an increased incorporation into the copolymer, with the effect on MAA relative reactivity more pronounced under dilute conditions.²⁶

We have recently published results from a kinetic investigation of 2-hydroxyethyl acrylate (HEA), copolymerized with butyl methacrylate (BMA) in various organic solvents.²⁷ The presence of H-bonding introduced through the hydroxyl function of HEA affected the relative monomer reactivity, leading to an increased incorporation of HEA into the copolymer in a bulk system in comparison to butyl acrylate (BA) copolymerized with BMA. The HEA incorporation was found to be strongly solvent dependent, enhanced in the non-polar solvent toluene and reduced in the polar solvent dimethyl formamide (DMF). However, the effect of solvent on composition-averaged propagation rate coefficients, k_p^{cop} , was found to be lessened, with little difference between solution and bulk copolymerization except for the cases of DMF and *n*-butanol (BuOH). Surprisingly, the solution copolymerization behaviour, both composition and k_p^{cop} , could be fully represented by the terminal model for many solvents. With this work, we extend the investigation to the copolymerization of HEA and BA in order to directly examine the influence of H-bonding on reactivity in an acrylate-only system. Additionally, we investigate the copolymerization behaviour of 2-methoxyethyl acrylate (MEA), a monomer similar to HEA in polarity. MEA itself is an interesting monomer used to produce copolymers with a variety of applications,²⁸⁻³¹ some exhibiting LCST behaviour,³² and has been copolymerized with HEA.³³ Here we investigate it as a non H-bonding analogue of HEA, with a comparison of the systems providing a deeper understanding of the origin and magnitude of H-bonding effects on radical copolymerization kinetics.

Experimental

Monomers BA (99% purity, containing 10-60 ppm monomethyl ether hydroquinone as inhibitor), BMA (99% purity, containing 10 ppm monomethyl ether hydroquinone as inhibitor), HEA (96% purity, containing 200-650 ppm monomethyl ether hydroquinone as inhibitor), MEA (98% purity, containing 50-100 ppm monomethyl ether hydroquinone as inhibitor), and photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99% purity) were used as received from Sigma-Aldrich. Solvents including *n*-butanol (BuOH, 99.9% purity from Sigma-Aldrich), *N,N*-dimethylformamide (DMF, 99.8% purity from Sigma-Aldrich), methyl isobutyl ketone (MIBK, 98.5 % purity from Sigma-Aldrich), tetrahydrofuran (THF, 99% purity from ACP Chemicals Inc.), methanol (99.8% purity from ACP Chemicals Inc.), hexanes (98.8% purity from ACP Chemicals Inc.), diethyl ether (99% purity from ACP Chemicals Inc.), xylenes (99.9% purity from Fisher Scientific), chloroform-*d* (CDCl₃, 99.8% deuterated from Sigma-Aldrich) and dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, 99.9% deuterated

from Cambridge Isotope Laboratories, Inc.) were also used without any modification.

Polymers were synthesized in a pulsed laser photopolymerization setup consisting of a Coherent Excimer Laser Xantos XS (XeF mixture as the reactive gas) creating 5 ns pulse durations at a wavelength of 351 nm and energies ranging from 1-6 mJ/pulse. Polymerization was performed using 5 mmol·L⁻¹ DMPA photoinitiator in bulk and 50 vol% solvent in monomer mixtures. The sample mixture in a quartz cuvette was allowed to equilibrate at the desired temperature regulated by a thermostatted circulating oil bath before being exposed to laser radiation. Experiments were carried out between 30 and 80 °C, and controlled to ±0.5 °C during pulsing while maintaining conversion below 5% to achieve the desired PLP structure in the resulting molecular mass distributions (MMD) and minimize composition drift, as previously reported.²⁷ Further details of individual experiments can be found in the supporting information (SI). The polymer was isolated by evaporating solvent and unreacted monomer with air before precipitating in a liquid nitrogen cooled suitable solvent. BA/HEA samples were precipitated with a 50:50 mixture of diethyl ether and hexanes. BA/MEA and BMA/MEA samples were precipitated using a 50:50 and 80:20 mixture of deionized water and methanol, respectively. The precipitated polymer was dried under vacuum overnight at 60 °C.

The purified polymers were prepared for SEC analysis by dissolving in THF and filtering through 0.2 µm nylon filters. SEC analysis was performed with a Waters 2960 separation module and a Waters 410 differential refractometer (RI detector). The THF solution flows through four Styragel columns at 0.3 mL·min⁻¹ maintained at 35 °C. The RI detector was calibrated with polystyrene (PS) standards having narrow polydispersities and molecular weights between 870 and 875000 Da. The resulting MMD is transformed using known Kuhn-Mark-Houwink (KMH) parameters to obtain the absolute MMD, which was then differentiated to provide the first-derivative plots used to estimate k_p from the position of the first maximum. A Wyatt instruments Dawn EOS 690 nm laser photometer multi-angle light scattering (LS) detector was used to provide a second measure to validate the k_p estimates from the RI detector. The LS detector is calibrated with one PS standard as a reference, and requires the refractive indices (dn/dc) to provide an absolute MMD. Refractive indices and KMH parameters used in processing the MMD data are summarized in Table 1, noting that the values for the copolymer are calculated as a weighted average of the polymer composition, as previously performed and reported.²⁷ While the BA, BMA, and HEA values have been validated and used in our previous investigations, the values for MEA were taken from literature,³⁴ with the agreement between k_p estimates from the two detectors verifying their accuracy: inflection points determined from the two detectors (LS analysis using

Table 1 Parameters required for analysis of PLP-SEC results

Monomer	dn/dc (mL·g ⁻¹)	Mark-Houwink parameters in THF	
		K (dL·g ⁻¹)	a
BA ³⁵	0.064	0.000122	0.700
BMA ³⁶	0.083	0.000148	0.664
HEA ²²	0.066	0.000322	0.602
MEA ³⁴	0.060	0.000047	0.750
Styrene ³⁶	0.184	0.000114	0.716

dn/dc and the KMH-transformed RI-signal) were found to be in good agreement, with variation of less than 10 % for copolymers and less than 5 % in case of the MEA homopolymerizations.

Polymer composition was determined using proton NMR on a Bruker 400 MHz spectrometer. HEA containing polymers were analyzed using DMSO- d_6 solvent to obtain a peak from the hydroxyl proton as reported elsewhere,²⁷ while $CDCl_3$ was used for all other samples. The composition was calculated by taking a ratio of the peak areas of signals resulting from different monomer units, with peak assignments and calculations detailed in Fig. S1.

Results and discussion

BA/HEA Copolymerization Kinetics

A common starting point for the analysis of copolymerization kinetics is the copolymer composition. For the BA/HEA system 1H -NMR was performed to measure the compositions of copolymer produced via a series of low-conversion PLP experiments performed with known comonomer compositions. The resulting copolymer vs. comonomer composition data were used to estimate the terminal model reactivity ratios based on Eqn 1

$$F_1^{inst} = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad ; \quad (1)$$

$$r_1 = \frac{k_{p_{11}}}{k_{p_{12}}}, r_2 = \frac{k_{p_{22}}}{k_{p_{21}}}, f_1 = \frac{[M_1]}{[M_1] + [M_2]}, f_1 + f_2 = 1$$

using the non-linear parameter estimation capabilities of the modelling software PREDICI®, as described in our previous BMA/HEA study.²⁷ Experiments were performed at 50 °C covering the complete range of composition for the bulk system, as well as for copolymers produced with 50 vol% monomer in various solvents. Temperature can be assumed to have a negligible effect on copolymer composition, as found in previous studies,^{27,37} and verified by comparing compositions determined at 30 and 70 °C. A 1986 study by Catala et al.³⁸ found that HEA possessed an increased reactivity in comparison to a non-polar acrylate, similar to what was observed for the corresponding methacrylate relatives in our previous study;²⁷ no further values for BA/HEA reactivity ratios could be found. As shown in Fig. 1, the fraction of HEA incorporated into the copolymer is greater than its fraction in the monomer phase in the bulk system. The preferential incorporation of HEA into the copolymer is also reflected by the best-fit reactivity ratios, $r_{BA} = 0.35 \pm 0.06$ and $r_{HEA} = 1.64 \pm 0.34$. (While the small number of data points leads to the larger 95% confidence intervals reported in Table 2, the parameter estimation procedure indicates no significant correlation between the estimates of the two reactivity ratios.) These values are, within experimental error, the same as found for the equivalent bulk methacrylate system, BMA/HEMA.⁸ This important finding indicates that the influence of monomer induced H-bonding on copolymerization is of similar magnitude for acrylate and methacrylate only systems. However, it is not clear why the HEA (or HEMA) hydroxyl functionality does not also promote the reactivity of the BA (or BMA) in the bulk system; this behaviour may be related to hydrogen bonding between HEA

monomer and units incorporated in the chain, an idea put forth by Noguchi and Kuzuya²⁶ and currently under further investigation.

The previous methacrylate study also investigated the influence of solvent on the copolymerization parameters, finding that the additional H-bonding introduced through the addition of BuOH equalized the relative reactivity of HEMA and BMA such that the copolymer composition curve shifted to the diagonal.⁸ This result was explained by the role of BuOH in establishing H-bonds to both BMA and HEMA monomeric acrylate carbonyl groups. The same behaviour is seen in Fig. 1 for HEA/BA, with a clear shift to equal reactivity seen when copolymerized in BuOH; the data lie slightly above the diagonal, indicating that a minor preference for HEA incorporation (perhaps caused by marginally stronger H-bonding from HEA than from BuOH) is maintained. The effect of conducting the copolymerization in DMF is similar, with the copolymer composition equal to comonomer composition for BA/HEA (Fig. 1) as was also found for BMA/HEMA.⁸ However, the reason behind the behaviour is quite different than in BuOH, in that DMF disrupts the H-bonding in the system due to its strong H-bonding acceptor properties. Therefore, the two solvent-induced results for BuOH and DMF are identical, but are caused by different effects, namely substitution versus disruption.

In our previous study of HEA/BMA copolymerization, we also examined the influence of less-interacting solvents commonly used in industry, such as ketones and xylenes. These data turned out to be more difficult to interpret; with no functional groups to completely disrupt or induce H-bonding, the relative incorporation of HEA into the copolymer was found to be even greater than for the bulk system.²⁷ As presented in Fig. 1 and summarized in Table 2, use of the non-interacting solvents MIBK and xylenes leads to copolymer composition curves that are similar to that of the bulk BA/HEA system: i.e., still with significantly increased HEA incorporation over BA, as also found by Catala et al. in 2-methoxyethanol.³⁸ The effects of non-interacting solvents are of different magnitude for HEA copolymerized with BA (HEA compositions in xylenes/MIBK similar in bulk) than with BMA (HEA incorporation enhanced in

Fig. 1 Mole fraction of HEA incorporated into copolymer (F_{HEA}) as a function of HEA molar fraction in the monomer mixture (f_{HEA}) measured experimentally (points) and respective terminal model data fits (lines) for BA/HEA copolymerization in bulk (black), xylenes (green), MIBK (red), BuOH (blue) and DMF (orange). Solution experiments conducted with 50 vol% solvent. Best-fit reactivity ratios summarized in Table 2.

xylenes/MIBK compared to bulk), although both systems maintain the preferential incorporation of HEA. Further discussion is deferred until after presentation of the accompanying k_p^{cop} data and the comparison between HEA and MEA copolymerization systems.

To complement the copolymer composition data, the PLP-SEC technique has been used to determine how the copolymer-averaged propagation rate coefficient, k_p^{cop} , varies with HEA content in bulk as well as in solution. Unfortunately, the analysis was limited by the solubility of the formed copolymers in THF, found to be $f_{\text{HEA}} \approx 0.6$ for the particular MW range of PLP-generated acrylates. Results for the HEA/BA study are presented for the 50 °C experiments, with additional data exhibiting the same trends at 30 °C included as Fig. S2. The PLP-structured MMDs contain at least two inflection points clearly located on the first-derivative plots,¹³ as shown in Fig. 2 for copolymer produced from pulsing a 70/30 v/v BA/HEA mixture in 50 vol% DMF and an 80/20 BA/HEA mixture in 50 vol% xylenes, each at two different repetition rates. The value of k_p^{cop} is calculated according to Eqn 2, where MW_1 is the MW of the first inflection point, Φ_{mon} the volume fraction of the comonomer mixture in solution, ρ_{mon} the density of the comonomer mixture (calculated assuming volume additivity), and t_0 the time between pulses (i.e., the inverse of the pulse repetition rate):

$$k_p^{\text{cop}} = \frac{MW_1}{\Phi_{\text{mon}} \rho_{\text{mon}} t_0} \quad (2)$$

Pulse repetition rates were kept at a minimum of 400 Hz for bulk and 300 Hz for solution polymerizations of these acrylate mixtures to keep the MW in an easily measurable range, while also suppressing the influence of backbiting on the study of chain-end propagation kinetics.^{14–16,39} As seen in Fig. 2, the MMDs and positions of the first inflection points shift to higher MW values as the repetition rate is decreased, with the corresponding k_p^{cop} values showing good consistency within 10%.

The complete set of results are tabulated as Supporting Information (Table S4–S14), with the k_p^{cop} values plotted as a function of HEA mol fraction in Fig. 3. The BA homopolymer value from our studies, 26 500 L·mol^{−1}·s^{−1}, is in excellent agreement with the predicted value of 27 500 L·mol^{−1}·s^{−1} from the Arrhenius relation fit to the benchmark data set for bulk BA.⁴⁰ Starting with that value, a continuous increase in k_p^{cop} is observed with increasing HEA content in the BA/HEA mixture (Fig. 3a), as expected from the influence of hydroxyl functionality on propagation kinetics.^{41,42} A strong influence of H-bonding is seen even at low HEA monomer content, with the addition of 13 mol% HEA increasing k_p^{cop} by 17% above the bulk BA value. The increase continues in a linear fashion to $f_{\text{HEA}} = 0.5$, and then levels out for the last measured composition at 60 mol% HEA. The value of 41 000 L·mol^{−1}·s^{−1} at $f_{\text{HEA}} = 0.5$, however, is higher than the previously published HEA homopropagation value of 33 000 L·mol^{−1}·s^{−1} at 50 °C.²² This surprising result suggests that the HEA homopropagation kinetics should be reinvestigated: while k_p^{HEMA} ²³ was measured to be more than twice the value of k_p^{BMA} ,³⁶ the literature value of k_p^{HEA} is only 20% higher than the BA value.

The reason for the increase in k_p^{cop} with HEA content is hypothesized to be a combination of increased polarity and H-bonding, both effects increasing the reactivity through a

Fig. 2 a) Molar mass distributions of PLP generated copolymer samples generated at 50 °C from comonomer mixtures of 20/80 BA/HEA (v/v) in xylenes at 400 Hz (—) and 500 Hz (—), and of 30/70 BA/HEA (v/v) in DMF at 300 Hz (---) and 400 Hz (---); b) First derivative plots of respective distributions.

decreased electron density at the double bond.²¹ The results obtained in BuOH support this hypothesis, as the k_p^{cop} data are, within experimental uncertainty, the same as the bulk results at intermediate HEA levels (Fig. 3a). At lower HEA levels (including BA homopolymerization), the k_p^{cop} values measured in BuOH are higher than those in bulk due to the higher concentration of H-bonding species present. It is hypothesized that interactions with BuOH disrupt the HEA-HEA hydrogen bonding, increasing k_p^{cop} through interactions with carbonyl groups of both BA and HEA monomer units. This interpretation is supported by the composition data (Fig. 1), as the reactivity ratios for both monomers are close to unity in BuOH. The copolymerization of HEA and HEMA was found to follow a typical acrylate/methacrylate behaviour,⁴³ consistent with the idea that the H-bonding equally influenced the reactivity of both monomers. The postulated substitution and disruption mechanism is confirmed by the PLP-SEC experiments performed in DMF, also shown in Fig. 3a. The value of k_p^{cop} only slightly increases from the BA value with increasing HEA content, as the DMF decreases HEA reactivity by disruption of the H-bonding, a behaviour previously detected for 2-hydroxypropyl methacrylate in THF.⁴⁴ The increased polarity of HEA compared to BA still causes a slight increase in k_p^{cop} with increasing HEA content, a result mirrored by the MEA system described in the next section.

Fig. 3 Evolution of k_p^{cop} for BA/HEA as a function of HEA monomer mole fraction at 50 °C in (a) bulk (black), BuOH (red) and DMF (green), and (b) in bulk (black), MIBK (red) and xylenes (blue).

The influence of the non-interacting solvents xylenes and MIBK on BA/HEA k_p^{cop} is compared to bulk behaviour in Fig. 3b. While the incorporation of HEA into the copolymer in MIBK is slightly reduced compared to the bulk system (see Fig. 1 and Table 2), the evolution of k_p^{cop} in MIBK is quite similar to that in bulk, with the values in MIBK perhaps slightly lower. A similar result was obtained in our previous BMA/HEA study.²⁷ Since the influence of MIBK as a solvent on propagation kinetics is negligible for both copolymer systems, it can be concluded that the carbonyl function of the solvent is minimally interfering with the extent of HEA H-bonding.

Finally, we consider the results obtained in the non-polar xylenes. Although the copolymer composition produced in xylenes does not deviate greatly from the bulk system (Fig. 1), it Fig. 3b shows that the k_p^{cop} values increase with increasing HEA content in the comonomer mixture at a greater rate than seen in bulk, reaching a value of $48\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at $f_{\text{HEA}} = 0.35$, 20% higher than the corresponding value measured for bulk BA/HEA. Experiments at higher HEA compositions were performed but the polymer could not be analyzed by SEC analysis in THF, as the solutions could not be quantitatively filtered through $0.2 \mu\text{m}$ nylon filters. The reason behind the higher k_p^{cop} for BA/HEA in xylenes is unclear, as a similar increase (relative to bulk behaviour) was not seen for BMA/HEA.²⁷ As hypothesized by

Noguchi and Kuzuya,²⁶ perhaps the association between free polar monomer and recently polymerized units near the radical chain end leads to increased incorporation of the polar monomer, especially under diluted conditions in non-polar solvents, and thus the observed increase in k_p^{cop} in the acrylate only system. In contrast, k_p^{cop} in the methacrylate/acrylate system is largely controlled by the methacrylate (BMA) radical and thus is less affected by the H-bonding of the system.

BA/MEA Copolymerization Kinetics

A study of the copolymerization kinetics of BA/MEA has also been conducted to determine whether the effects of HEA on copolymerization kinetics can be attributed to increased reactivity caused by H-bonding or is simply a result of the increased polarity of the monomer relative to BA. The procedures and experimental conditions used for the BA/HEA study are repeated, but replacing the hydroxy functionality of HEA with the methoxy group of MEA. Copolymer composition was analyzed again through $^1\text{H-NMR}$ over the full range of feed compositions to determine system reactivity ratios, with details of peak assignments and complete experimental results presented in the SI. Copolymerization experiments were conducted in bulk and in BuOH and DMF solution, as these solvents had the most influence on HEA reactivity. As shown in Fig. 4, the copolymer composition measured for all three systems was identical and lay along the diagonal ($F_{\text{MEA}} = f_{\text{MEA}}$), indicating that the relative reactivity of MEA and BA are identical ($r_1 = r_2 = 1$) independent of solvent choice. Comparing this finding to the HEA/BA results (Fig. 1; with HEA/BA bulk results also shown in Fig. 4), it can be concluded that it is the hydroxyl function rather than the increased polarity that increases the relative reactivity of HEA. Despite its polar nature, MEA does not interact differently than BA upon the addition of a polar solvent such as BuOH. Indeed, MEA can be seen as a classic comonomer, with reactivity similar to any other alkyl acrylate: thus, for an acrylate-acrylate copolymerization $r_1 = r_2 = 1$, independent of solvent choice.

Fig. 4 Mole fraction of MEA or HEA incorporated into copolymer as a function of the mole fraction in the monomer mixture. Mayo-Lewis plot for BA/HEA copolymerization in bulk (—) and BA/MEA copolymerization in bulk (blue), in 50 vol% BuOH (black), and in 50 vol% DMF (red).

Table 2 Reactivity ratios (with 95% confidence intervals) acquired by fit of the terminal model to copolymer composition obtained by radical copolymerization

	HEA Bulk	HEA Xyl.	HEA MIBK	HEA DMF	HEA BuOH	MEA bulk, BuOH and DMF
$r_{\text{HEA/MEA}}$	1.64 ± 0.34	3.25 ± 0.37	1.87 ± 0.68	1	1.32 ± 0.96	1
r_{BA}	0.35 ± 0.06	0.93 ± 0.07	0.85 ± 0.19	1	0.88 ± 0.44	1

Fig. 5 Evolution of k_p^{cop} as a function of MEA monomer mole fraction (f_{MEA}) for BA/MEA in bulk (black) and BuOH (blue) at 30 (filled symbols) and 50 °C (hollow symbols)

To complete the study, k_p^{cop} values of BA with MEA were determined at 30 and 50 °C using the PLP-SEC method. As well as providing a comparison to the BA/HEA system, the data are examined for effects induced by the heteroatom in the side chain of MEA compared to BA, as the propagation kinetics of MEA have not yet been studied. As shown in Fig. 5, the presence of the methoxy group leads to an increased k_p value, 30% higher than the value for BA at 50 °C ($35\,000\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ in comparison to $26\,500\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$), with a similar increase observed at 30 °C. While this relative increase is higher than the 10% higher value reported for ethoxyethyl methacrylate in comparison to BMA,⁴⁵ similar effects have been found for nitrogen containing monomers, and were attributed to a change in polarity and electron density.^{46,47} Another useful comparison is glycidyl methacrylate (GMA) vs butyl methacrylate, as the O-containing glycidyl group is similar in size to MEA. At 50 °C the value of $1200\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for GMA⁴⁸ was found to be significantly higher, by 60%, than that of BMA ($750\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$).¹ The larger increase for GMA vs BMA compared to MEA vs BA may be related to the glycidyl ring, as other methacrylates with cyclic groups exhibited similar behaviour.²⁰

As shown in Fig. 5, the value of k_p^{cop} increases linearly with increasing MEA content between the two homopolymerization values both at 30 °C and 50 °C. This result is perhaps expected for a system with reactivity ratios of unity, and can be well-represented by the terminal model (see SI). This simple behaviour can be contrasted with the BA/HEA system (Fig. 3), for which a greater increase in k_p^{cop} is observed compared to the BA homopolymerization end point due to the H-bonding introduced with HEA as a comonomer. H-bonding effects can also be introduced to the BA/MEA system through the addition of BuOH as solvent. At both temperatures, the entire k_p^{cop} curve, including the two homopolymer endpoints, shifts higher by ~30

% upon the addition of BuOH: as reactivity ratios remain at unity for the BA/MEA in BuOH system, the increase is of similar magnitude over the complete composition range. Previous investigations have reported an increase of similar magnitude for the homopropagation kinetics of MMA in alcohols compared to bulk.^{41,49} Again, a contrast can be made with the more complex behaviour observed for BA/HEA copolymerized in BuOH (Fig. 3) for which the k_p^{cop} values converge to the bulk values as HEA fraction increases; as there is no monomer related H-bonding effect in the BA/MEA system, the hydroxyl group of BuOH interacts with both monomers to the same extent.

BMA/MEA Copolymerization Kinetics

To complete the investigation of the influence that substituting MEA for HEA has on copolymerization kinetics, we have conducted a series of experiments with BMA/MEA to compare to our previous BMA/HEA study.²⁷ When BMA was copolymerized with HEA, the net effect of both DMF (which disrupts HEA H-bonding) and BuOH (which induces H-bonding to BMA) was to decrease the HEA incorporation to a level almost equal to the BMA/BA case. Based on the comparison of BA/MEA with BA/HEA, it is expected that the increased polarity of MEA should not affect its copolymerization kinetics with BMA; i.e., that BMA/MEA behaviour should be similar to that of BMA/BA rather than BMA/HEA. The relation between copolymer and comonomer composition for these two limiting cases is plotted as curves in Fig. 6. With MEA replacing HEA as comonomer, it is seen that all three data sets – bulk and solution polymerizations in both DMF and BuOH – cannot be distinguished from each other within experimental error.

Fig. 6 Mole fraction of acrylate comonomer incorporated into copolymer as a function of the mole fraction in the monomer mixture. Mayo-Lewis curves for BMA/HEA²⁷ (—) and BMA/BA⁵⁰ (dotted) taken from literature compared to experimental data (points) for BMA/MEA in bulk (red), in 50 v% BuOH (blue), and 50 vol% DMF (green).

Fig. 7 Evolution of k_p^{cop} as a function of acrylate monomer mole fraction for BMA/MEA in bulk (red), BuOH (blue) and DMF (green) in comparison to previously published data for BMA/HEA in bulk²⁷ (black).

In addition, the copolymer compositions are similar to the BMA/BA, rather than the BMA/HEA (with its increased acrylate incorporation) bulk system. Thus, when copolymerized with both BA and with BMA, the polar functionality of MEA exerts no influence on copolymer composition in bulk or solution, in stark contrast to HEA.

We have also used the PLP-SEC technique to examine how solvent choice affects propagation kinetics when MEA is copolymerized with BMA. As shown in Fig. 7, the values of k_p^{cop} at 50 °C are reduced relative to the bulk BMA/HEA²⁷ system due to the absence of H-bonding capabilities in MEA. (The plot is truncated at an acrylate content of 75 mol%, due to the order of magnitude increase observed in k_p at high acrylate content, but is fully shown in Fig. S3.) Without any H-bonding in the system, the addition of DMF to BMA/MEA has very little effect on the averaged rate coefficient. However, the addition of BuOH as solvent promotes both the reactivity of BMA and MEA, such that the k_p^{cop} curve is increased throughout the composition range. Again, these effects are similar to those found for the BA/MEA system, and are in sharp contrast to the previously reported influence of solvent on BMA/HEA k_p^{cop} values.²⁷ Experiments performed at 80 °C, in the supplementary information, show identical trends.

With copolymer composition well-represented by the terminal model, it is interesting to consider whether the best-fit reactivity ratios can also adequately describe the composition-averaged propagation rate coefficient for BMA copolymerized with HEA and MEA, or whether the extra parameters contained in the implicit penultimate unit effect (IPUE) model are required. The terminal model, described by Eqn 3, provides a prediction of k_p^{cop} using only the reactivity ratios fit from the composition data and the two homopropagation rate coefficients ($k_{11}=k_{p1}$ and $k_{22}=k_{p2}$).

$$k_p^{\text{cop}} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\frac{r_1 f_1}{k_{11}} + \frac{r_2 f_2}{k_{22}}} \quad (3)$$

The IPUE model can be used if the terminal model does not adequately represent the data, introducing radical reactivity ratios (s_1

and s_2) that capture the influence that the chain-end penultimate unit exerts on reactivity according to:²⁷

$$k_{11} = \frac{k_{p1}(r_1 f_1 + f_2)}{r_1 f_1 + \frac{f_2}{s_1}} \quad k_{22} = \frac{k_{p2}(r_2 f_2 + f_1)}{r_2 f_2 + \frac{f_1}{s_2}} \quad (4)$$

The s values are usually estimated from fitting the variation in k_p^{cop} vs. monomer composition data. However, as the data set from this study is rather limited, we instead have used the values obtained from a previous study of MMA/BA, with $s_{\text{BMA}}=1.98$ and $s_{\text{BA}}=0.43$,⁵¹ to determine if the behaviour of BMA/MEA is typical of the classic methacrylate/acrylate system. As shown in Fig. 8a, while the terminal model does not provide a fit to the experimental data, the penultimate model predictions are quite reasonable. The same general conclusions can be made even for the BMA/HEA data taken from our previous study:²⁷ the terminal model underpredicts k_p^{cop} significantly, while the penultimate model prediction using MMA/BA radical reactivity

Fig. 8 Terminal model (—) and IPUE (--- and ...) model predictions of k_p^{cop} for BMA copolymerized with (a) MEA and (b) HEA in bulk at 50 °C. IPUE curves for MEA are calculated using s values taken from literature, with $s_{\text{methacrylate}} = 1.98$ and $s_{\text{acrylate}} = 0.43$.⁵⁰ The BMA/HEA data is taken from a previous study, showing the IPUE fit with the same s -values as used in a) (---) and the best-fit IPUE parameters $s_{\text{BMA}} = 3.03$ and $s_{\text{HEA}} = 1.0$ ²⁷ (---).

values is greatly improved (Fig. 8b). Using the BMA/HEA k_p^{cop} data set to estimate s values through least-squares fitting further improves the data representation, perhaps capturing the extra complexity introduced by the H-bonding in the system.

Conclusions

The copolymerization behaviour of HEA with both BMA and BA is compared to that of MEA, which has been studied using the PLP-SEC technique for the first time. The k_p value for MEA homopropagation is higher than that of BA by 30%, a result attributed to the heteroatom in the side chain. However, the analysis of both copolymer composition and k_p^{cop} data using the PLP-SEC technique showed no increase in MEA incorporation or solvent dependency compared to a “standard” acrylate monomer such as BA. Thus, the acrylate-acrylate copolymerization of BA/MEA is well described by the terminal model with reactivity ratios of unity in both bulk and solution, and an increase in k_p^{cop} found in BuOH due to H-bonding effects induced over the complete composition range. The polymerization behaviour is well understood and well-modeled using both monomer and radical reactivity ratios determined in previous studies of acrylate/methacrylate systems.

In contrast, both copolymer composition and k_p^{cop} are affected by solvent choice for the copolymerization of HEA with both BA and BMA due to the H-bonding induced by the HEA hydroxyl function. In a bulk system, the level of HEA incorporated into the copolymer as well as k_p^{cop} is significantly enhanced compared to that of an alkyl acrylate. Addition of BuOH, which introduces H-bonding in substitution to that of HEA, or DMF, which disrupts H-bonding, brings copolymer composition back to that seen for BA (or MEA) copolymerization. However, the k_p^{cop} curves for BA/HEA in BuOH solution remain complex due to the competing H-bonding between BuOH and HEA. It was found that the previously investigated BMA/HEA system was less influenced by solvent choice than BA/HEA, likely due to the controlling influence of the methacrylate monomer on radical fractions in the methacrylate/acrylate system. Work continues to generalize the representation of how the copolymerization behaviour of HEA, but also HEMA and other hydroxyl containing monomers, is influenced by hydrogen bonding.

Acknowledgement

The authors acknowledge the valuable input from Dr. David N. Nare, Dr. Mike Grady and coworkers at Axalta Coating Systems. This work was financially supported by Axalta Coating Systems (Wilmington, DE, US) and the Natural Sciences and Engineering Research Council of Canada.

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