The influence of hydrogen bonding on radical chain-growth parameters for butyl methacrylate/2-hydroxyethyl acrylate solution copolymerization

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2-Hydroxyethyl acrylate (HEA), commonly introduced to control resin properties and introduce crosslinking sites, affects radical copolymerization kinetics through hydrogen-bonding, with the extent of the influence dependent upon solvent choice. The pulsed-laser polymerization technique has been applied to systematically investigate the influence of solvent choice on composition-averaged propagation rate coefficients (k_p^{cop}) and copolymer composition for HEA copolymerized with butyl methacrylate (BMA) in xylenes, dimethyl formamide (DMF), n-butanol (BuOH), methyl isobutyl ketone (MIBK) and butyl propionate. It is found that copolymer composition (as measured by proton NMR) has a greater dependency on solvent choice than propagation kinetics. HEA is incorporated into the BMA copolymer at higher relative rates than butyl acrylate (BA) in bulk, with the introduction of DMF and BuOH both reducing HEA incorporation rates. In contrast, the other solvents increase the relative reactivity of HEA, with reactivity ratios for the highest HEA incorporating case of BMA/HEA in xylenes found to be $r_{\text{BMA}} = 0.96 \pm 0.05$ and $r_{\text{HEA}} = 1.35 \pm 0.14$. Surprisingly, k_p^{cop} could be represented by the terminal model for polymerization in xylenes, MIBK and butyl propionate, but not for the bulk system.

Introduction

Free radical copolymerization allows for the robust production of materials with tailored properties by simply varying the type and relative amounts of monomers,¹ and is widely used in industry for acrylic coatings and resin production. By adding functionality such as hydroxyl groups to the polymer, a wider range of application can be accomplished by allowing post-modifications such as crosslinking,^{2,3} as commonly used for automotive coatings. While Liang et al. systematically investigated the kinetics of 2-hydroxyethyl methacrylate (HEMA) copolymerization systems,⁴⁻⁶ similar studies are lacking for 2-hydroxyethyl acrylate (HEA). Besides the coatings industry, HEA has a wide range of applications as a component in hydrogels,⁷ as it is known to form a stable polymer backbone under varying pH and temperature conditions.⁸ With a suitable adsorbing comonomer, promising aqueous gels for heavy metal removal can be synthesized.⁹ In aqueous solution, HEA also exhibits lower critical solution temperature behavior that can be controlled by copolymer composition, as investigated by Hoogenboom et al. for HEA/methoxyethyl acrylate copolymers under various conditions.^{10,11} To effectively tailor the copolymer and its

properties of these and other possible applications, reliable kinetic parameters are needed. In particular, the propagation kinetics in a copolymerization system control composition, with the mole fraction of monomer incorporated into the copolymer (F_1^{inst}) expressed by the well-known Mayo-Lewis equation:

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

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

In addition, an averaged rate coefficient for propagation k_p^{cop} can be expressed as

$$k_p^{\text{cop}} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\left(\frac{r_1 f_1}{k_{p_{11}}}\right) + \left(\frac{r_2 f_2}{k_{p_{22}}}\right)} \quad (\text{Eq. 2})$$

Both equations are derived assuming the terminal model, with $k_{p_{ij}}$ the rate of addition of monomer j to chain-end radical species i . The overall rate of polymerization and the associated heat generation is directly related to the value of k_p^{cop} .

Today the widely accepted and IUPAC recommended technique to determine k_p^{cop} and $k_{p_{ij}}$ propagation coefficients is pulsed laser polymerization-size exclusion chromatography (PLP-SEC).^{12,13} The combination of efficient photopolymerization and simple chromatography allows a direct measurement of k_p under controlled conditions to minimize side reactions.¹⁴ Determination of copolymer

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composition is used to estimate comonomer reactivity ratios.^{4,13} Due to the development of high frequency lasers it is now easier to investigate faster reacting systems such as acrylates.^{15–18} Versatile extensions are also possible by adding electron spin resonance (ESR) detectors to obtain further parameters for termination or backbiting.¹⁹

In general acrylic non-aqueous solution (and bulk) polymerizations are not significantly dependent on solvent choice.^{20,21} Small deviations from bulk propagation behavior can be explained in terms of differences in solvent and monomer molar volumes,^{20,22} and the “fish in water” argumentation applied to weak interactions: solvent molecules replacing monomer molecules allow for a higher rotational freedom of the monomer, including intermolecular interactions based on changing dipole moments of the solvent.²³ For these types of systems, copolymerization reactivity ratios are generally independent of solvent choice, as no strong interactions are present.⁶ An exception to these generalities is if the reacting system undergoes hydrogen bonding, which significantly affects propagation kinetics for hydroxyl functional monomer or solvent containing systems.^{4,5,23} These influences were examined in a study that correlated methacrylate k_p values with the solvatochromatic properties of various solvents (including ionic liquids), expressed as a function of polar donor and acceptor capabilities and hydrogen bonding in the system.^{24,25} H-bonding is classically known from water as an electrostatic force and has a large impact, for example, on self-assembly of DNA.²⁶ In terms of polymerization kinetics this force can be introduced by either solvents or monomers.^{5,27} In aqueous acrylamide/ acrylic acid systems, for example, influences on polymerization rates were found to be strongly concentration dependent,²⁸ whereas reactivity ratios change with the degree of ionization of acrylic acid.²⁹ On the organic side, alcohols as solvents promote (meth)acrylate reactivity through H-bonding, causing significant increases in k_p , up to 40 %.²⁷ Similar increases were also detected for hydroxyl-containing monomers such as 2-hydroxypropyl methacrylate compared to alkyl methacrylates.³⁰ The influence of H-bonding (i.e., solvent and monomer choice) on reactivity also affects copolymerization systems.^{4,6,31} In this work we study the copolymerization kinetics of HEA with butyl methacrylate (BMA) in a range of solvents, in order to systematically investigate the influence of H-bonding on copolymerization kinetics.

Experimental

Monomers HEA (96 % purity, containing 200–650 ppm monomethyl ether hydroquinone as inhibitor), BMA (99 % purity, containing 10 ppm monomethyl ether hydroquinone as inhibitor) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99% purity) were received from Sigma-Aldrich and used without further purification. The solvents *n*-butanol (BuOH, 99% purity), dimethylformamide (DMF, 99.8 % purity), methyl isobutyl ketone (MIBK, 98.5 % purity), butyl propionate (BPI, 98% purity) and anhydrous

dimethyl sulfoxide d-6 (DMSO-d₆, containing 99.9% D) were also used as received from Sigma-Aldrich.

Low conversion pulsed laser photopolymerizations were performed using 5 mmol·L^{−1} DMPA photoinitiator in monomer mixtures, following earlier established procedures.^{4,5} All solution polymerizations were prepared using 50 vol% of solvent. Sample mixtures in a quartz cuvette were placed into a temperature-controlled unit and exposed to laser radiation of 351 nm wavelength. A Coherent Excimer Laser Xantos XS (XeF mixture as the reactive gas) was used as the radiation source, creating pulses of 5 ns duration with energy between 1–6 mJ/pulse. Temperatures were controlled to keep variations less than 0.5 °C during pulsing whilst maintaining conversions lower than 5% to maintain PLP structure in the resulting molar mass distributions (MMDs), as well as instantaneous composition conditions. The polymer formed was isolated by evaporating a majority of the supernatant solution under air before precipitation in a suitable ice-cold solvent. BMA homopolymers were precipitated in methanol whereas copolymers were precipitated in a 50/50 mixture of diethyl ether and hexanes. The polymer obtained was then dried under vacuum at 60 °C overnight.

Polymers were dissolved in THF at 3 g·L^{−1} and filtered through 0.2 µm nylon filters for SEC analysis. The SEC setup consists of a Waters 2960 separation module connected to a Waters 410 differential refractometer (DRI) and a Wyatt Instruments Dawn EOS 690 nm laser photometer multi-angle light scattering (LS) detector. The eluent THF was used at flow rates of 0.3 mL·min^{−1} through four Styragel columns maintained at 35 °C. The DRI detector was calibrated by polystyrene standards with narrow polydispersities over the range of 870–875000 Da. The LS detector was calibrated with a single polystyrene (PS) standard as a reference. Based on PS-calibration, absolute molar mass distributions from DRI can be obtained via a suitable transformation using the known Mark-Houwink parameters. Table 1 provides the necessary parameters for the system examined. It is assumed that copolymerization values can be calculated based on the weight-averaged polymer composition, as shown to be valid in previous studies.^{5,32} Results were verified by comparing the output from LS detection which determines absolute molar mass distributions using known refractive indices (dn/dc values), a necessary check as the analysis via composition-averaged Mark-Houwink parameters may not be valid for all copolymerization systems.

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
HEA ³²	0.066	0.000322	0.602
BMA ³³	0.083	0.000148	0.664
Styrene ³³	0.184	0.000114	0.716

Results and discussion

Copolymer composition is measured in this work by NMR spectroscopy using the side chain peak patterns of BMA and HEA (Figure 1). The BMA CH₂ group adjacent to the ester is found at 3.9 ppm, with two CH₂ side chain peaks from HEA at 3.5 ppm and 4.0 ppm surrounding this signal. Additionally, the HEA OH-peak is detected in DMSO-d₆ at 4.7 ppm, giving two reliable possibilities to calculate the HEA content in the copolymer. The estimates from equation 3 and 4 were in good agreement, with the reported compositions taken as an average.

Fig. 1 Expanded ¹H-NMR spectrum showing peak assignments for determination of BMA/HEA copolymer composition in d₆-DMSO; sample produced with *f*_{HEA} = 0.58 in DMF at 50 °C by PLP-SEC.

$$F_{\text{HEA}} = \frac{2 \int \text{OH}(4.7 \text{ ppm})}{(\int \text{CH}_2(3.9 \text{ ppm}) + \int \text{CH}_2(4.0 \text{ ppm}))} \quad (\text{Eq. 3})$$

$$F_{\text{HEA}} = \frac{\int \text{CH}_2(3.5 \text{ ppm})}{(\int \text{CH}_2(3.9 \text{ ppm}) + \int \text{CH}_2(4.0 \text{ ppm}))} \quad (\text{Eq. 4})$$

Given a set of samples over the whole feed composition range, a Mayo-Lewis plot can be established. Reactivity ratios were fit from Equation 1 using non-linear parameter estimation tools in the modelling software PREDICI®. This model for instantaneous copolymer composition, commonly known as the terminal model,³⁴ has been proven to be valid for a wide range of systems. The BMA/HEA composition data in this study was obtained at 30 °C and 50 °C in bulk and in a variety of solvents with 50 vol%. A few 80 °C samples were checked to ensure that the influence of temperature on *r*-values is negligible, as also found in other studies.^{35,36}

In the previous investigations with HEMA,^{4,6} we found that H-bonding increased the activity of the hydroxyfunctional monomer relative to nonpolar BMA, but that the extent of this influence is affected by solvent choice. There is also an increased relative reactivity of HEA in HEA/BMA bulk copolymerization in comparison to BA in the non-polar BA/BMA system: as shown in Figure 2a, the HEA incorporation is increased over that of BA when copolymerizing with BMA. A similar influence of H-bonding has been seen before for HEMA copolymerizations^{4,5,37} and HEA copolymerized with ST.³² The best fit reactivity ratios in

bulk are *r*_{HEA} = 0.37 ± 0.06 and *r*_{BMA} = 0.98 ± 0.06, compared to *r*_{BA} = 0.40 and *r*_{BMA} = 2.28 for the BA/BMA system.³⁸ To the best of our knowledge, these are the first reported values for this system. Only limited data is available for the related acrylate only BA/HEA system,³¹ which also reported increased incorporation rates for HEA into the copolymer, in good agreement with our findings. The significant difference in the *r*_{BMA} value for HEA compared to BA copolymerization is due to the reduction in electron density, and hence increased reactivity, at the HEA double bond. Note that the *r*_{BMA} value is very close to unity, with *F*_{HEA} ≈ *f*_{HEA} for BMA-rich conditions (*f*_{HEA} < 0.2).

Fig. 2 Mole fraction hydroxyethyl acrylate (HEA) in HEA/BMA copolymers as a function of HEA composition in the monomer mixture. Experimental results are given as symbols and terminal model fits as lines: a) bulk (black) and solution polymerization in DMF (50 vol%, purple) and BuOH (50 vol%, red), compared to bulk BMA/BA results from literature³⁸ (dark grey); b) BMA/HEA solution polymerization in MIBK (50 vol%, grey), butyl propionate (50 vol%, green) and xylenes (50 vol%, blue) in comparison to bulk BMA/HEA (black).

We next investigate how this behavior changes with addition of solvent to the copolymerization system. DMF and BuOH both have a large influence on the relative reactivity in the system: as shown in Figure 2a these “high interacting” solvents lead to Mayo-Lewis plots that almost reproduce the bulk BA/BMA

curve. The two solvents exert this influence by different mechanisms;^{4,6,24} whereas BuOH promotes the BMA reactivity relative to HEA by providing hydrogen bonds, DMF, a polar aprotic acceptor that due to its mesomeric structures can be considered as partially charged, disrupts the HEA-HEA H-

bonding and reduces its reactivity relative to the bulk case. As summarized in Table 2, both effects result in the increase of the r_{BMA} value.

Table 2 Reactivity ratios (with 95% confidence intervals) for BMA/HEA copolymerizations in different solvents (50 vol%), as fit to the data sets plotted in Figure 2.

	Bulk	MIBK	BPI	Xyl.	DMF	BuOH
r_{HEA}	0.37 ± 0.09	0.49 ± 0.09	0.55 ± 0.07	1.35 ± 0.14	0.31 ± 0.08	0.35 ± 0.04
r_{BMA}	0.98 ± 0.13	0.72 ± 0.10	0.80 ± 0.09	0.96 ± 0.05	1.83 ± 0.14	1.66 ± 0.06

A series of solvents commonly used in resin production for coatings applications have also been studied. When changing to these lower interacting ketone (MIBK) and ester (BPI) solvents, HEA is incorporated at slightly higher levels than seen in bulk, as shown in Figure 2b. These results suggest that whereas the carbonyl function should disrupt H-bonding, its effect is minimized or shielded through the significantly larger non-interacting aliphatic side chains. The logical follow-up can be observed when using xylenes, with no functional group. Accordingly, the reactivity of HEA increases. This trend has been seen before for HEMA copolymerization with styrene in toluene.⁶ For HEA copolymerized with BMA, it leads to the unusual result that the acrylate component is incorporated at a greater rate into the copolymer than the methacrylate over the complete HEA composition range in xylenes. There have been several hypothesis put forward to explain the strength of hydrogen bonding in diluted systems such as bootstrap effects or other polar-polar interactions which result in the formation of local concentration gradients, promoting the reactivity of one monomer;³⁹ however, this explanation is inconsistent with the k_p^{cop} results presented below.

A generalized trend can be seen in the reactivity ratios summarized in Table 2, which shows that solvent effects manifest themselves in changing the relative reactivity of monomer addition to the BMA radical for the strongly interacting solvents. The influence of other solvents is seen by small changes in both values that push the system closer towards the diagonal. Similar effects have been observed before for the HEMA systems.^{4,6} The effect of xylene remains the only exception, with a strong promotion of HEA incorporation.

Determination and representation of k_p^{cop}

k_p^{cop} was determined over a range of BMA/HEA compositions in bulk and solution following the IUPAC recommended procedure of PLP-SEC. Once SEC curves for the PLP-generated polymer samples were obtained, the first derivative was taken to determine the inflection points used to calculate k_p^{cop} according to Equation 5, in which MW_n represents the polymer molar mass at the n^{th} inflection point, Φ_{mon} is the volume ratio of the comonomer mixture in solution, ρ_{sol} the mixture density and t_0 the time between pulses, the inverse of the laser frequency.

$$k_p = \frac{MW_n}{n \Phi_{\text{mon}} \rho_{\text{sol}} t_0} \quad (\text{Eq. 5})$$

Figure 3a is an example of the MMDs obtained for HEA/BMA samples of two different compositions (10 and 30 vol% HEA in comonomer mixture) prepared in 50 vol% BuOH at 50°C and two different repetition rates. One can see typical PLP structure with the specific shape of several maxima, representing polymer created after n laser bursts. The magnitude as well as the position of the first and second maxima on the first derivative plot vary with frequency; the second maxima is slightly more pronounced at the higher frequencies (here 100 Hz), as a greater fraction of polymer radicals survive the first terminating burst. As shown in Figure 3b, up to four inflection points can be seen under some conditions.

The first peak in the MMD remains the largest maxima, indicating that proper frequencies were chosen for the system to obtain high quality results.⁴⁰ The position of the maxima shifts proportionally to the frequency, with positions of inflection points doubling when frequency is halved from 100 to 50 Hz. (Note that the position of the first inflection point of each 50 Hz sample is roughly at the same position of the second inflection point of the respective 100 Hz sample.) The influence of HEA content on k_p can also be seen in Figure 3, as MMDs shift to higher M at increased HEA content. The quality of the PLP-SEC traces shows that side reactions such as backbiting are not affecting the determination of chain-end k_p^{cop} at higher acrylate fractions; the influence of side reactions must be taken into consideration for acrylate only systems, as reported elsewhere.¹⁸

The complete set of experimental results (PLP/SEC conditions and resulting MW analysis) are tabulated as Supporting Information, which also documents the good agreement between inflection point position determined by the two (RI and LS) detectors. Throughout the entire set of data, it was found that the reproducibility of k_p at a given temperature and composition stayed within the expected typical error of roughly 15%;²³ in most cases agreement was within 10%. Values of k_p^{cop} could only be measured to $f_{\text{HEA}} = 0.8$, as copolymers with greater HEA fraction are insufficiently soluble in THF for SEC analysis. Similar to as shown in Figure 3, the IUPAC consistence criterion for all experiments used to estimate k_p^{cop} were fulfilled, with all samples having a ratio of two between the first and second inflection points.

Fig. 3 Polymer MMDs (a) and corresponding first derivative plots (b) from SEC analysis of PLP-generated BMA/HEA copolymers prepared in 50 vol% BuOH at 50 °C for BMA/HEA volume ratios of 90/10 at 50 Hz (grey) and 100 Hz (black), and BMA/HEA volume ratios of 70/30 at 50 Hz (purple) and 100 Hz (red).

Bulk homopolymerization k_p values are known at 50 °C to be 753 L·mol⁻¹·s⁻¹ for BMA⁴⁰ and 33000 L·mol⁻¹·s⁻¹ for HEA,³² differing by a factor of over 40. As shown in Figure 4, the k_p^{cop} values determined by PLP-SEC do not dramatically increase from the BMA value with increasing HEA content: with $f_{\text{HEA}} = 0.77$, k_p^{cop} at 50 °C is 3815 L·mol⁻¹·s⁻¹, five times higher than $k_{p\text{BMA}}$ and at 80 °C the relative increase is very similar. For a better understanding of this behavior, a consideration of the radical fractions is helpful. Under the assumption of the terminal model the radical fraction is dependent on crosspropagation rate coefficients and monomer composition.

$$\frac{[P_1]}{[P_2] + [P_1]} = \frac{k_{p_{21}} f_1}{k_{p_{12}} f_2 + k_{p_{21}} f_1} \quad (\text{Eq. 6})$$

where $[P_i]$ is the concentration of chain-end radical i . Setting species 1 as BMA, and with known homopropagation k_p and r values, it can be calculated that $k_{p_{21}}$ is significantly larger than $k_{p_{12}}$, favoring the crosspolymerization such that most radicals end in a methacrylate moiety. Thus BMA-HEA behaves as a standard methacrylate acrylate system,^{4,41} with a dominant fraction of BMA radicals controlling the reaction kinetics.

Figure 4 also contains k_p^{cop} values measured in the presence of the non-interacting solvents MIBK, BPi, and xylenes. The data coincide closely with the bulk data over the entire range of composition at both temperatures studied. The slight increase in $k_{p\text{BMA}}$ at 80 °C from 1550 L·mol⁻¹·s⁻¹ in bulk to 1650 L·mol⁻¹·s⁻¹ in ketones and esters and 1700 L·mol⁻¹·s⁻¹ in xylenes is consistent with arguments regarding the influence of relative molar volumes of solvent and monomer,^{20,22} but is within experimental uncertainty. The negligible solvent effect on k_p^{cop} for this class of solvents is perhaps surprising, given the influence of solvent on copolymer composition (Figure 2b). The same result (identical k_p^{cop} but varying composition in bulk vs toluene) was also observed for the HEMA/ST system.⁶

Fig. 4 k_p^{cop} for BMA/HEA copolymerization as a function of HEA composition (f_{HEA}), as measured by PLP/SEC for bulk (black) and solution polymerization in MIBK (grey), xylenes (blue) and butyl propionate (green) at 50 and 80 °C.

In contrast to the low interacting solvents, BuOH and DMF affect both copolymer composition and k_p^{cop} . Although their influence on the H-bonding mechanism are opposite (BuOH promotes BMA reactivity, DMF decreases HEA reactivity), the resulting k_p^{cop} trends are similar; as shown in Figure 5, the k_p^{cop} values are reduced relative to the bulk values for both solvents. This decrease is consistent with the increased values of r_{BMA} (Table 2) that lead to an increased BMA incorporation and a higher BMA radical fraction due to the reduced $k_{p_{12}}$ value (Equation 6).

A more detailed examination is necessary to understand why DMF and BuOH have a comparable effect on k_p^{cop} , starting with the homopolymerization of BMA. The value of $k_{p\text{BMA}}$ in BuOH is 2200 L·mol⁻¹·s⁻¹ at 80 °C, roughly 35% higher than in bulk due to the introduction of H-bonding. Meanwhile DMF has a negligible effect on $k_{p\text{BMA}}$, as no H-bonding is present. As soon as HEA is introduced to the system k_p^{cop} decreases relative to the bulk system for both solvents. DMF continuously disrupts the H-bonding of HEA so that its reactivity is reduced to that of an alkyl acrylate. However, BuOH continues to promote BMA reactivity, reducing the HEA radical fraction in the system, thus reducing k_p^{cop} relative to bulk. For the latter system, this decrease is counteracted by the positive solvent effect of BuOH on BMA, but as f_{BMA} decreases

the net effect is a decreased k_p^{cop} relative to bulk at 80 °C. This influence of BuOH on k_p^{cop} may have some temperature dependency, however, as at 50 °C the k_p^{cop} values remain higher for bulk values even at higher HEA. Similar trends have been reported and attributed to the influence of temperature on H-bonding.²⁷ At high temperatures it is hypothesized that the increased kinetic energy disrupts more H-bonds than at lower temperatures due to increased molecular movement. Similar effects are also known from polymerizations in high H-bond concentration systems, e.g. aqueous solution.⁴² A further approach to explain these results can be found in the Supporting Information, which contains room temperature IR measurements that demonstrate the influence of H-bonding on the carbonyl stretching even at low HEA content.

Fig. 5 k_p^{cop} for BMA/HEA copolymerization as a function of HEA composition (f_{HEA}), as measured by PLP/SEC for bulk (black) and solution polymerization in BuOH (red) and DMF (purple) at 50 and 80 °C.

Often the implicit penultimate unit model (IPUE), presented in equation 7-8, is required to represent k_p^{cop} data.

$$k_p^{\text{cop}} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\left(\frac{r_1 f_1}{\bar{k}_{11}}\right) + \left(\frac{r_2 f_2}{\bar{k}_{22}}\right)} \quad (\text{Eq. 7})$$

$$\bar{k}_{11} = \frac{k_{p_{111}}(r_1 f_1 + f_2)}{r_1 f_1 + \left(\frac{f_2}{s_1}\right)}; \bar{k}_{22} = \frac{k_{p_{222}}(r_2 f_2 + f_1)}{r_2 f_2 + \left(\frac{f_1}{s_2}\right)} \quad (\text{Eq. 8})$$

$$\text{with } s_1 = \frac{k_{p_{211}}}{k_{p_{111}}} \text{ and } s_2 = \frac{k_{p_{122}}}{k_{p_{222}}}$$

The polymer radical selectivity parameters s_1 and s_2 account for the influence of the penultimate unit next to the propagating radical on monomer addition.^{6,32} However, the relative rates of monomer addition are not influenced by the penultimate unit, such that r -values can be fit according to the terminal model. To complete our study, we examine whether the terminal model (Equation 2) is sufficient to represent the k_p^{cop} data, or whether

the extra parameters introduced by the IPUE are required to fit the data. Figure 6 compares experimental results for the bulk system to the terminal model prediction. As observed for other acrylate/methacrylate^{4,43,44} systems and also ST/HEA,³² the predictions of k_p^{cop} are lower than the experimental data. Then, the IPUE model was fit to the data, again using the non-linear parameter estimation of PREDICI®. While the IPUE can be used to successfully represent the data (see Figure 6), there is high uncertainty in the s estimates, especially s_{HEA} which controls the slope of the curve at higher HEA content. However, regardless of temperature the fits still allow for a good representation of experimental data. More data for HEA-rich systems, including homopolymerizations, is required to reduce the uncertainty in the parameters. As shown in the Supporting Information, the IPUE is also required to fit the data obtained in BuOH and DMF, as the TM also underpredicts the experimental data.

Fig. 6 Experimental results for k_p^{cop} as a function of f_{HEA} for bulk BMA/HEA copolymerizations at 50 (open symbols) and 80 °C (filled symbols) in comparison to TM predictions (dotted line at 50 °C, dashed line at 80 °C) and IPUE fits (dot-dashed line at 50 °C, solid line at 80 °C) with $s_{\text{BMA}} = 3.03 \pm 0.36$ and $s_{\text{HEA}} = 1.0 \pm 10$

For the low interacting solvents MIBK, BPi and xylenes it was found experimentally that the variation of k_p^{cop} with HEA content was similar to that of bulk (see Figure 4), although composition data indicate a higher incorporation of HEA into the copolymer in these solvents relative to the bulk system (see Figure 2b). Surprisingly, as shown in Figure 7, the TM predictions for these three solvents calculated using the reactivity ratios summarized in Table 2 provide an excellent representation of the experimental data, despite the model's inability to represent the bulk system. The fact that k_p^{cop} is well represented by TM predictions will facilitate the modelling of BMA/HEA copolymerization in these common solvents.

Polymer Chemistry

ARTICLE

Fig. 7 Experimental results for k_p^{cop} as a function of f_{HEA} by PLP/SEC for BMA/HEA solution copolymerization at 50 (open symbols) and 80 °C (filled symbols) in MIBK (a), BPI (b) and xylenes (c) in comparison to the TM predictions (lines) calculated using reactivity ratios from Table 2.

Conclusions

The combined results from PLP-SEC and H-NMR composition analysis show a strong dependency of propagation kinetics on solvent choice during BMA/HEA copolymerization. The use of DMF and BuOH as solvents influence both composition and k_p^{cop} strongly, due to their influence on H-bonding in the system. While both solvents tend to push the system towards behavior expected for BA/BMA, the origin of the behavior is quite different, as DMF disrupts the effect of HEA intermolecular H-bonding while BuOH promotes BMA reactivity by introducing H-bonding. For these systems, as well as for bulk BMA/HEA, the IPUE model is required to fit the variation in k_p^{cop} with monomer composition. Copolymer composition was also found to be highly solvent dependent in the low interacting solvents like ketones, esters and xylenes, with increased HEA incorporation observed compared to bulk. However, these solvents did not cause any changes in k_p^{cop} compared to bulk, and the terminal model provides an excellent representation of k_p^{cop} in these industrially relevant solvents. Further investigations shall be extended to BA/HEA to explore the effects of H-bonding in acrylate-only systems. Of particular interest will be the influence of HEA content and H-bonding on the backbiting mechanism, and thus level of branching observed.⁴⁵

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Notes and references

- 1 B. B. Noble, M. L. Coote, *Int. Rev. Phys. Chem.*, 2000, **32**, 3523.
- 2 Y. Baek, N. S. Kwak, T. S. Hwang, *Polymer Korea* 2011, **35**, 586-592.
- 3 D. Mertz, C. J. Ochs, Z. Y. Zhu, L. Lee, S. N. Guntari, G. K. Such, T. K. Goh, L. A. Connal, A. Blencowe, G. G. Qiao, F. Caruso, *Chem. Commun.* 2011, **47**, 12601-12603.
- 4 K. Liang, T. R. Rooney, R. A. Hutchinson, *Ind. Eng. Chem. Res.* 2014, **53**, 7296-7304.
- 5 K. Liang, M. Dossi, D. Moscatelli, R. A. Hutchinson, *Macromolecules* 2009, **42**, 7736-7744.
- 6 K. Liang, R. A. Hutchinson, *Macromolecules* 2010, **43**, 6311-6320.
- 7 S. A. Dergunov, G. A. Mun, M. A. Dergunov, I. E. Suleimenov, E. Pinkhassik, *React. Funct. Polym.* 2011, **71**, 1129-1136.
- 8 K. M. Antic, M. M. Babic, J. J. J. Vukovic, D. G. Vasiljevic-Radovic, A. E. Onjia, J. M. Filipovic, S. L. Tomic, *Appl. Surf. Sci.* 2015, **338**, 178-189.
- 9 Z. Li, Y. M. Wang, N. M. Wu, Q. C. Chen, K. Wu, *Environ. Sci. Pollut. Res.* 2013, **20**, 1511-1525.
- 10 W. Steinhauer, R. Hoogenboom, H. Keul, M. Moeller, *Macromolecules* 2010, **43**, 7041-7047.
- 11 R. Hoogenboom, A. M. Zorn, H. Keul, C. Barner-Kowollik, M. Moeller, *Polym. Chem.* 2012, **3**, 335-342.
- 12 M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumperman, F. D. Kuchta, B. G. Manders, K. F. O'Driscoll, G. T. Russell, J. Schweer, *Macromol. Chem. Phys.* 1995, **196**, 3267-3280.
- 13 S. Beuermann, M. Buback, *Prog. Polym. Sci.* 2002, **27**, 191-254.
- 14 O. F. Olaj, G. Zifferer, F. Hinkelmann, *Makromol. Chem. – Macromol. Chem. & Phys.* 1987, **188**, 1689-1702.

- 15 C. Barner-Kowollik, F. Gunzler, T. Junkers, *Macromolecules* 2008, **41**, 8971-8973.
- 16 B. Dervaux, T. Junkers, M. Schneider-Baumann, F. E. Du Prez, C. Barner-Kowollik, *J. Polym. Sci. Part A: Polym. Chem.* 2009, **47**, 6641-6654.
- 17 C. Barner-Kowollik, S. Beuerman, M. Buback, P. Castignolles, B. Charleux, M. L. Coote, R. A. Hutchinson, T. Junkers, I. Lacík, G. T. Russell, M. Stach, A. M. van Herk, *Polym. Chem.* 2014, **5**, 204-212.
- 18 B. Wenn, T. Junkers, *Macromol. Rapid Commun.* 2016, **37**, 781-787.
- 19 H. Kattner, M. Buback, *Macromol. Symp.* 2013, **333**, 11-23.
- 20 S. Beuermann, *Macromol. Rapid Commun.* 2009, **30**, 1066-1088.
- 21 A. P. Haehnel, B. Wenn, K. Kockler, T. Bantle, A. M. Misseke, F. Fleischhaker, T. Junkers, C. Barner-Kowollik, *Macromol. Rapid Commun.* 2014, **35**, 2029-2037.
- 22 S. Beuermann, N. Garcia, *Macromolecules* 2004, **37**, 3018-3025.
- 23 L. Uhelská, D. Chorvat, R. A. Hutchinson, S. Santanakrishnan, M. Buback, I. Lacík, *Macromol. Chem. Phys.* 2014, **215**, 2327-2336.
- 24 A. Jelacic, F. Köhler, A. Winter, S. Beuermann, *J. Polym. Sci. Part A: Polym. Chem.* 2010, **48**, 3188-3199.
- 25 A. Zgrzeba, E. Andrzejewska, A. Marcinkowska, *RSC Advances* 2015, **5**, 100354-100361.
- 26 L. Pauling, R. B. Corey, *Arch. Biochem. & Biophys* 1956, **65**, 164-181.
- 27 S. Beuermann, *Macromolecules* 2004, **37**, 1037-1041.
- 28 C. Preusser, R. A. Hutchinson, *Macromol. Symp.* 2013, **333**, 122-137.
- 29 M. Riahinezhad, N. McManus, A. Penlidis, *Macromol. React. Eng.* 2015, **9**, 100-113.
- 30 R. A. Hutchinson, S. Beuermann, D. A. Paquet, J. H. McMinn, C. Jackson, *Macromolecules* 1998, **31**, 1542-1547.
- 31 J. M. Catala, A. Nonn, J. M. Pujol, J. Brossas, *Polym. Bull.* 1986, **15**, 311-315.
- 32 E. Mavroudakakis, K. Liang, D. Moscatelli, R. A. Hutchinson, *Macromol. Chem. Phys.* 2012, **213**, 1706-1716.
- 33 R. A. Hutchinson, S. Beuermann, D. A. Paquet, J. H. McMinn, *Macromolecules* 1997, **30**, 3490-3493.
- 34 F. R. Mayo, F. M. Lewis, *JACS* 1944, **66**, 9-1594-1601.
- 35 D. Li, N. Li, R. A. Hutchinson, *Macromolecules* 2006, **39**, 4366-4373.
- 36 M. L. Coote, L. P. M. Johnston, T. P. Davis, *Macromolecules* 1997, **30**, 8191-8204.
- 37 D. J. T. Hill, N. G. Moss, P. J. Pomery, A. K. Whittaker, *Polymer* 2000, **41**, 1287-1296.
- 38 A. M. Aerdts, A. L. German, G. P. M. van der Velden, *Mag. Res. Chem.* 1994, **32**, 80-88.
- 39 M. L. Coote, T. P. Davis, B. Klumperman, M. J. Monteiro, *J. M. S.-Rev. Macromol. Chem. Phys.* 1998, **C38**, 567-593.
- 40 S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwarra, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* 2000, **201**, 1355-1364.
- 41 M. Buback, E. Muller, *Macromol. Chem. Phys.* 2007, **208**, 581-593.
- 42 J. Schrooten, I. Lacík, M. Stach, P. Hesse, M. Buback, *Macromol. Chem. Phys.* 2013, **214**, 2293-2294.
- 43 M. Buback, A. Feldermann, C. Barner-Kowollik, I. Lacík, *Macromolecules* 2001, **34**, 5439-5448.
- 44 R. A. Hutchinson, J. H. McMinn, D. A. Paquet, Jr., S. Beuermann, C. Jackson, *Ind. Eng. Chem. Res.* 1997, **36**, 1103-1113.
- 45 K. Liang, R. A. Hutchinson, J. Barth, S. Samrock, M. Buback, *Macromolecules* 2011, **44**, 5843-5845.