Article

Acidic Aqueous-Phase Copolymerization of AA and HPEG Macromonomer: Influence of Monomer Concentration on Reactivity Ratios

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ABSTRACT: Poly(acrylic acid-*co*-polyethylene glycol 2-methyl-2-propenyl ether) copolymers are comb-like water-soluble copolymers produced by the copolymerization of acrylic acid (AA) and polyethylene glycol 2-methyl-2-propenyl ether (HPEG). The main application of these copolymers is as superplasticizers for cementitious materials, also known as polycarboxylate ethers (PCE's). The kinetics of the water-soluble monomers is substantially more complex than that of non-water-soluble monomers as their kinetics depend on various parameters such as monomer concentration, pH, and ionic strength. In this work, aqueous in situ ^{1}H NMR copolymerizations of AA and HPEG at different initial overall monomer weight fractions and comonomer molar ratios under acidic media were carried out. The gathered kinetic data were

used for the estimation of the reactivity ratios of AA-HPEG. A nonlinear least-squares (NLLSQ) method based on the Mayo−Lewis composition equation was used to estimate the reactivity ratios by fitting the cumulative copolymer composition or free monomer molar fraction as a function of overall monomer conversion. The estimation indicates that the reactivity ratio of acrylic acid is higher than that of the HPEG monomer, which is estimated as close to zero. In addition, the reactivity ratio of AA depends on the overall monomer weight fraction; the higher the initial overall monomer concentration, the higher the reactivity ratio is. An empirical expression is derived that describes the dependency of the reactivity ratio of AA on the overall monomer mass fraction ($r_{AA} = 1.76$ (± 0.062) $+ 0.0275$ ($\pm 4.37 \times 10^{-3}$) w_M (%); $r_{HPEG} = 2.3 \times 10^{-14}$ ($\pm 6.02 \times 10^{-3}$)).
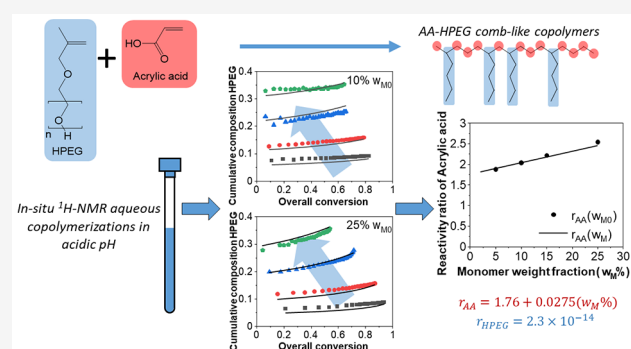
1. INTRODUCTION

Concrete is the single most widely used building material in the world due to its remarkably good mechanical properties and durability. In 2021, 9.42 billion cubic meters (Bcm) of concrete was produced globally, 49% (4.58 Bcm) of which was produced in 10 countries, China being the top producer holding 35% of the total volume. Derived from its high volume of production, an important carbon footprint contributes to global CO_2 emissions. It is estimated that for each ton of cement produced, 800 kg of CO_2 is released, and these high amounts of emissions represent 5−8% of annual anthropogenic global CO_2 production.[1] In order to overcome the challenge of reducing the environmental impact, energy and water consumption in construction industry, as well as the amount of cement used to build, stronger, lighter and less water-demanding concrete should be optimized. During decades, additives such as concrete admixtures have been used to improve the properties of concrete during its preparation, pouring, and casting, enhancing the manageability, hydration time, and air entrainment, among other properties. Concrete admixtures refer to the components of concrete that are added

immediately before or during the mixing process, except for cement, water, and aggregates. Producers use admixtures primarily to reduce the cost and also to modify the properties of hardened concrete to ensure the quality of concrete during mixing, transporting, placing, and curing. Among the different admixtures, air entrainment agents, accelerators, delayers, corrosion inhibitors, superplasticizers, and foam controllers can be found. By the end of 2020, concrete admixtures contributed about 30% of the global market of construction chemicals, followed by adhesives and sealants with 22%, reflecting their importance in the construction field.

Polycarboxylate superplasticizers, also called polycarboxylic ethers or PCEs, have become an essential admixture for the

concrete industry since their invention in the early 1980s,[2,3] with the global production volume that exceeded 10 million tons per year.[2] PCEs exhibit a particular comb- or brushlike structure, as shown in Figure 1. Two main synthesis routes are
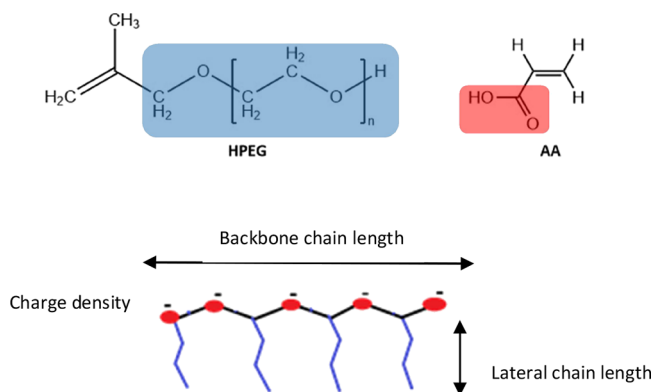

Figure 1. Chemical structure of HPEG and acrylic acid (top) and illustration of a typical comb-like PCE copolymer (bottom).

used for producing PCEs. One is the free-radical copolymerization (FRP) of a monomer bearing carboxylic groups and a monomer bearing the nonionic side chain.[4−6] This route is the most common, especially in industry, due to its simplicity and cost-effectiveness. Moreover, radical copolymerization is ideal for the incorporation of different kinds of monomers into the main chain and for the control of the copolymer composition by appropriately adjusting the monomer feeding rates. The other approach is polymer esterification of a preformed backbone bearing carboxylic groups with monofunctional PEG.[7] This procedure can lead to PCEs with a lower dispersity, provided that the backbone is produced by controlled polymerization different from free-radical polymerization. However, since this process is performed in batch, no control of side-chain distribution is achieved. In addition to this, the process is high-energy-demanding.

The main raw materials for synthesizing PCEs are water-soluble monomers such as unsaturated polyether macromonomers and (meth)acrylic acid. At present, the most commonly used macromonomers in industry are polyethylene glycol 3-methyl-3-butenyl ether (IPEG), methoxy polyethylene glycol (MPEG), polyethylene glycol monoallyl ether (APEG), and polyethylene glycol 2-methyl-2-propenyl ether (HPEG).[8] The structure of the HPEG macromonomer is shown in Figure 1.

Water-soluble monomers are widely used in the production of polymeric materials via free-radical homo- and copolymerizations in aqueous medium for different applications such as flocculants, textiles, super-absorbers, coatings, cosmetics, and water treatment.[9,10] When polymerizing in aqueous medium, water-soluble monomers exhibit differences in their reactivity when compared to polymerization in organic solvents because of the interactions between the growing radicals, monomers, polymers, and transition-state compounds with water molecules through hydrogen bonding which affect the activation energy and the barrier to the internal rotation of the transition state.[11,12] During the past few decades, an extensive study on the effect of these variables on the propagation kinetics of the most common water-soluble monomers has been conducted. These monomers include acrylic acid,[13−15] methacrylic acid,[16−19] acrylamide,[20,21] N-

vinylpyrrolidone,[22] N-vinyl formamide,[23,24] and N-isopropylacrylamide,[25] among others.[26] Researchers found that propagation and termination rate coefficients not only depend on temperature but also on the characteristics of the aqueous solution such as the concentration of the monomer, ionization degree, and ionic strength of the aqueous medium.[26−28] Accurate values of k_p measured by pulsed-laser polymerization (PLP) in combination with size-exclusion chromatography (SEC), near-infrared (NIR) spectroscopy, and electron spin resonance (EPR) techniques have been obtained, PLP-SEC being the benchmark technique recommended by the IUPAC Working Party for k_p measurement.

A common behavior among these monomers is the decrease of the propagation rate coefficient, k_p, with the monomer concentration, which was attributed to the large effects of strong hydrogen bonding between the species present in the system.[14,26] According to Deglmann et al., this solvent effect can entirely be explained by the degree of thermodynamic nonideality of the system, the relative variation of k_p with the monomer weight fraction in aqueous solution being the result of the influence of the solvent on the activity coefficients of the species involved in the propagation reaction transition state.[11,29] Regarding the ionization degree, α, a significant lowering of k_p at high ionization values was attributed to the repulsion between negatively charged species.[15,30]

(Methyl-) allyl polyether macromonomers are the other type of water-soluble monomers with a similar structure to PEGylated methacrylates; however, the main difference resides in the nature of the bond between the vinyl double bond and PEG units, which is an ether instead of an ester bond. This makes these macromonomers notably less reactive, being kinetically more similar to vinyl ethers.[31] In copolymerization reactions with acrylic acid and methacrylic acid, a major difference in reactivity ratios has been observed, making it difficult to produce homogeneous copolymer chains.[8,32−34]

Due to the nature of the comonomers that are used to produce this type of PCE polymer, i.e., complex kinetics of the (meth)acrylic acid monomer and low reactivity ratio of the macromonomer, obtaining the target microstructure can be challenging. It is well known that the difference in reactivity ratios between the comonomers will lead to a copolymer composition drift during the reaction.[35,36] Therefore, it is extremely important to be able to find proper strategies to control this polymer characteristic. To develop such control strategies for different polymer characteristics, such as copolymer composition, chemical composition distribution (CCD), and molar mass distribution (MMD), a predictive mathematical model of the copolymerization is needed. A knowledge of the reactivity ratios of macromonomers and AA is essential for developing the mathematical model of the copolymerization.

Open literature about the reactivity ratios of these types of macromonomers is very scarce. In fact, the results are limited to a couple of sources available.[32,37,38] So far, three of these macromonomers have been studied together with acrylic acid. These are polyethylene glycol monovinyl ether (EPEG), polyethylene glycol 3-methyl-3-butenyl ether (IPEG), and polyethylene glycol 2-methyl-2-propenyl ether (HPEG). Their reactivity ratios were estimated by following low conversion kinetics in copolymerization experiments by means of SEC, and HPLC. Considering that at very low monomer conversions, cumulative copolymer composition can be approximated to the instantaneous one, F, data were fitted

using classic linear methods such as Fineman−Ross (FR), Yezrelieve−Brokhina−Roskin (YBR), and Kellen−Tüdos (KT), as well as NLLSQ. The estimated values of these macromonomers are in the order of 10^{-1}, while that of acrylic acid is about 2 orders of magnitude higher. In the case of the AA−HPEG copolymerization system, the experiments were conducted in acidic conditions at 10 different molar ratios, at monomer concentrations of 40%, and the cumulative copolymer composition was determined for samples at low conversions (between 4 and 15%). Data were fitted by the KT method, and the resulting values for the reactivity ratios of acrylic acid and HPEG were 1.70 and 0.017, respectively.

Alternatively, ^{1}H NMR in situ experiments can be used to study the kinetics in copolymerization reactions and for the estimation of the reactivity ratios.[39,40] In situ ^{1}H NMR experiments consist of small-scale batch copolymerization experiments conducted in NMR tubes in which the progress of the reaction can be tracked by generating a series of spectra during the whole copolymerization reaction. The advantage of the in situ NMR method is that monomer consumption can be tracked almost instantaneously. In addition, the cumulative copolymer composition as well as the overall monomer conversion can be calculated from the monomer conversion data. Preusser and Hutchinson[41] used ^{1}H NMR in situ experiments to study the copolymerization kinetics of acrylamide (AM) and nonionized acrylic acid (AA) in aqueous solution, varying the initial monomer content between 5 and 40 wt % and estimated their reactivity ratios. These same authors[42] studied the influence of monomer concentration and ionization degree on the kinetics of this system to finally estimate the reactivity ratios and derive a set of equations that described their dependence on the ionization degree and weight fraction of the monomer. Using this methodology, Emaldi et al.[36] studied the influence of monomer concentration and PEGMA chain length on the aqueous-phase copolymerization kinetics of methacrylic acid (MAA) and PEGMA macromonomer, observing that for short PEGMA, the reactivity ratios r_{MAA} and r_{PEGMA} increased with the solid content. Interestingly, this trend was not maintained for the longer PEGMA's, whose reactivity ($r_{PEGMA23}$) decreased with the solid content, whereas the reactivity ratio of MAA remained roughly constant with the longer PEGMA.

In this work, aqueous in situ ^{1}H NMR copolymerization experiments at different initial overall monomer weight fractions and AA-HPEG comonomer molar ratios are carried out to generate kinetic data to be used for the estimation of the reactivity ratios of AA-HPEG under acidic media. Two NLLSQ methods[43,44] were used to estimate the reactivity ratios using the Mayo−Lewis equation as the copolymerization model, assuming terminal model kinetics.[45] One fits the cumulative copolymer composition as a function of the overall monomer conversion,[43] and the second fits the mole fraction of the unreacted monomer as a function of the overall monomer conversion.[44]

2. EXPERIMENTAL SECTION

2.1. Materials. Acrylic acid (AA) 99%, with 200 ppm hydroquinone monomethyl ether (MEHQ) as an inhibitor, and poly(acrylic acid) (M_w = 250,000 g/mol) were purchased from Sigma-Aldrich and used as received. Polyethylene glycol 2-methyl-2-propenyl ether, HPEG 2400 (M_n = 2400 g/mol), was kindly supplied by CHRYSO. Potassium persulfate (KPS > 99%) and the chain transfer agent sodium hypophosphite

monohydrate (NaPO$_2$H$_2$ H$_2$O ≥ 99% purity) were also purchased from Sigma-Aldrich and used as received. Deuterium oxide (D$_2$O > 99.9%) was purchased from Eurisotop and used as a cosolvent for ^{1}H NMR and ^{13}C NMR experiments.

AA monomer used for this series of experiments yielded an important amount of diacrylic acid (DAA) during storage. Thus, the content of DAA in AA used in this series of experiments was measured by ^{13}C NMR analysis. A ^{13}C NMR spectrum of AA in deuterium oxide is presented in the Supporting Information (Figure S1). The amount of DAA was calculated by the integration of the peaks A and B (δ, 129−127 ppm), corresponding to the carbons in the double bonds of AA and DAA, respectively. The content of DAA was around 15%.

To assess that the double bond of the dimer (DAA) reacts equal to the double bond of AA, a series of copolymerization experiments at different HPEG ratios and 10 wt % monomer concentration were carried out with AA that contained less than 1% of DAA. Figure S3 (in the Supporting Information) shows that the cumulative compositions of HPEG measured from the unreacted monomer concentrations of both series of experiments overlap. Therefore, it can be concluded that the double bonds of DAA and AA have very close reactivities, and hence the experiments carried out with AA that contained 15% of DAA were used to estimate the reactivity ratios of AA and HPEG.

2.2. In Situ ^{1}H NMR Copolymerization Reactions. Before the kinetic study was conducted, T1 relaxation experiments were conducted in order to assess the relaxation times of the protons in the system. Details are presented in the Supporting Information Section S2. As expected, the relaxation experiments showed that the protons, which take longer times to relax, were those of acrylic acid, since smaller molecules have less energy dissipation points than larger molecules such as the HPEG macromonomer. The average of the estimated relaxation times of the protons of the double bonds in the HPEG macromonomer and acrylic acid was 1.9 and 3.3 s, respectively.

Based on the T1 relaxation results, the following pulse sequence (Figure 2) was used to ensure a quantitative analysis:
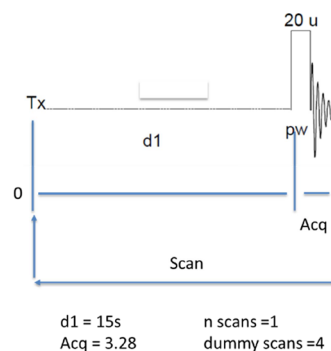

Figure 2. Pulse sequence applied during in situ ^{1}H NMR copolymerization experiments.

a single scan with an acquisition time of 3.28 s and a relaxation delay of 60 s. In the Supporting Information (Figure S6), we show that this sequence recovers very well the nominal ratios of AA/HPEG mixtures.

Stock solutions containing the comonomers, the chain transfer agent, and D$_2$O were prepared on a mass basis at 50%
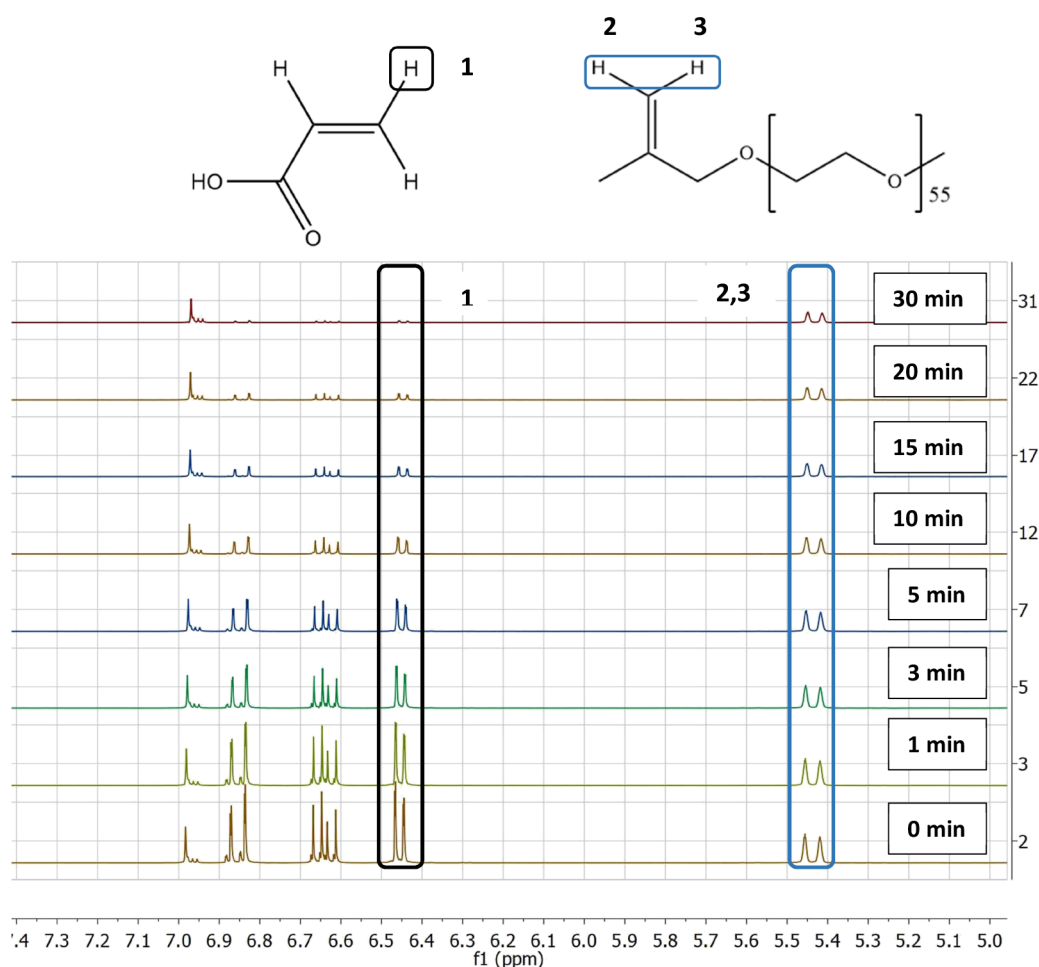
Figure 3. Evolution of the proton nuclear magnetic resonance (^{1}H NMR) spectra of the aqueous solution copolymerization of acrylic acid and HPEG macromonomer carried out at 70 °C, at a molar ratio (HPEG:AA) of 20:80, and 25% of the initial overall monomer weight fraction.

initial overall monomer weight fraction, w_{M0}, with different nominal monomer molar ratios: (HPEG:AA) 10:90, 20:80, 40:60, and 60:40. NaPO$_2$H$_2$ was used as a chain transfer agent to control the molar mass and thus the viscosity of the system. The given pH values of the solutions were measured by means of a HACH sensION+ PH3 pH meter (Germany) prior to copolymerization.

Aqueous-phase (D$_2$O) free-radical copolymerization reactions of acrylic acid and HPEG were carried out in NMR tubes in acidic pH (between 2.4 and 4.4 for the mixture of reactants). All reactions were initiated by the KPS initiator, adjusting its concentration to 1 wt % based on the monomer, which means that increasing w_{M0} increases the overall initiator concentration used in the experiments. Tables S1−S4 of the Supporting Information summarize the formulations of experiments in acidic pH conducted at the initial overall monomer weight fractions between 5 and 25% w_{M0} and four HPEG:AA molar ratios (10,90, 20:80, 40:60, and 60:40). Note that the monomer molar ratios expressed here are the nominal values; the actual monomer molar ratios were calculated from the vinyl proton signal peak areas of the comonomers before starting the reaction (t_0 in the NMR tube; see Section S3 of Supporting Information for more details).

Comonomer mixture solutions were prepared in 2 mL glass vials at different initial overall monomer weight fractions (w_{M0} = 5−25%) by dilution of a measured quantity of each stock solution with D$_2$O and homogenized using a vortex stirrer.

Then, the contents of each vial were transferred to the NMR tubes. The NMR probe was heated to the required temperature for about half an hour before the sample insertion. After insertion, the sample temperature was equilibrated for 5 min, and shimming of the magnetic field was performed before starting measurements. Before the reaction was initiated, a first spectrum was acquired to calculate the initial molar ratio of comonomers (considered as t_0 in the NMR tube). Once the target temperature was reached, the NMR tube was taken out, and 30 μL of the KPS initiator solution was added, and the sample was mixed. The tube was reinserted into the NMR probe, and the temperature was equilibrated for 2 min before starting the spectral acquisitions (this point was considered as the beginning of the reaction). The reactions at acidic pH were conducted at 343 K using ^{1}H spectra with the suppression of the solvent using the WATERGATE sequence.[46−48] The spectra were recorded every minute, using one scan, acquisition time of 3.28 s, and a relaxation delay of 60 s. The first 30 minutes of reaction were recorded. Data were processed with Mnova 14.0.4 (Mestrelab Research, S.L.).

Conversions of AA and HPEG were calculated using the evolution of the area of the peaks corresponding to the two vinyl protons of HPEG (δ, 5.4−5.5 ppm) and one vinyl proton of AA (δ, 6.4 and 6.5 ppm), as illustrated in Figure 3 In this case, no internal reference was used. The individual conversion data from the copolymerization experiments are included in Tables S8−S11 in the Supporting Information Section S4.
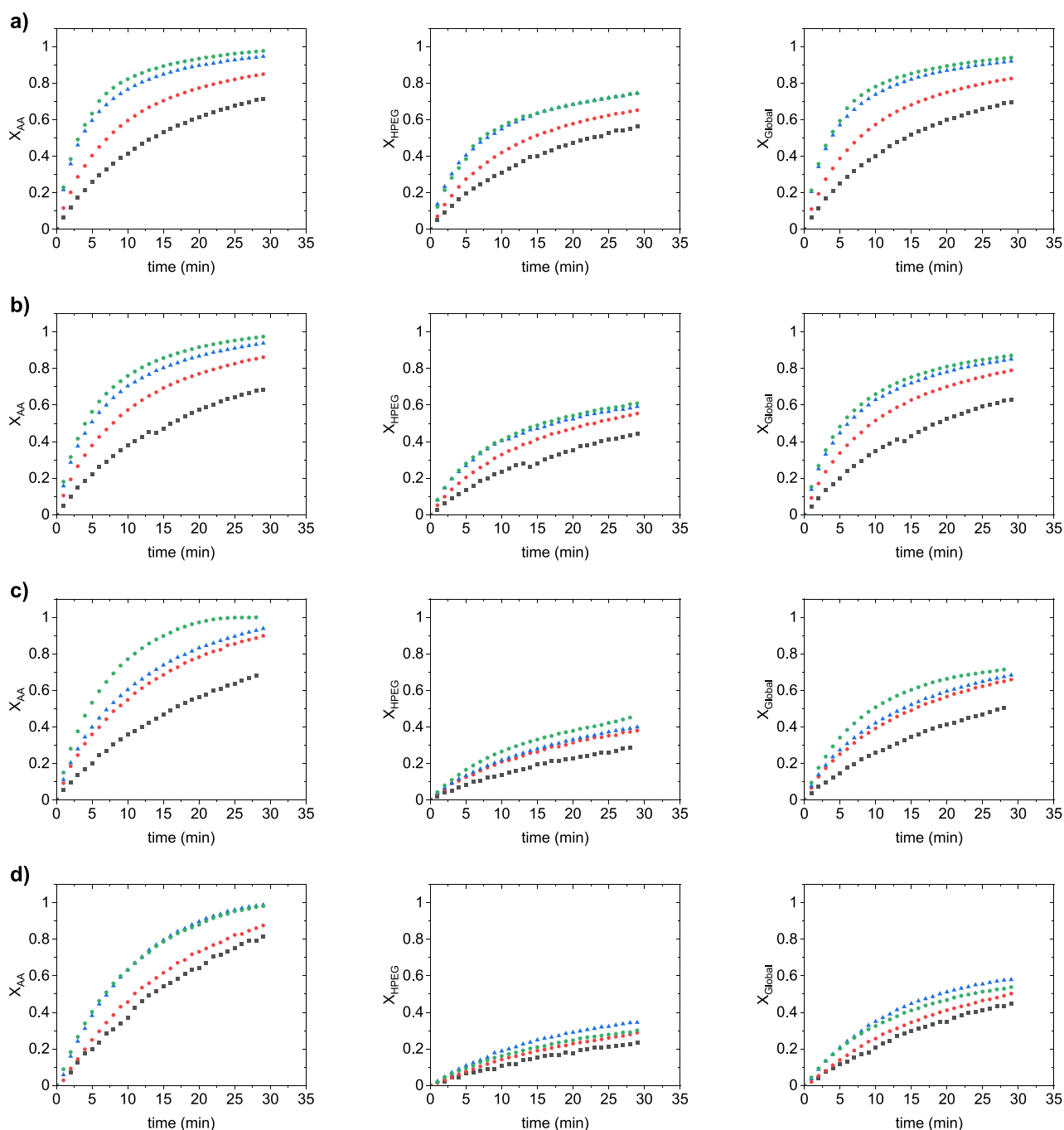
Figure 4. Evolution of individual and global conversions at four different initial overall monomer weight fractions (w_{M0}) (5% (black square), 10% (red circle), 15% (blue triangle), and 25% (green pentagon)), and four HPEG molar ratios ((a) 10%; (b) 20%; (c) 40%; and (d) 60%).

3. ESTIMATION OF REACTIVITY RATIOS BY NLLSQ

The reactivity ratios were estimated based on two methods: the first one uses the data of the evolution of individual conversions, X_A, over the overall conversion, X_T, minimizing the predicted and experimental conversion evolution of the cumulative copolymer composition, F_A, based on the method developed by De la Cal et al.[43] and recently used by Emaldi et al.[36] to study the kinetics of aqueous copolymerization of MAA and PEGMA macromonomer. The second method fits the mole fraction of the unreacted monomer, f_A, as a function of the overall monomer conversion, X_T, as proposed by Penlidis and co-workers.[44]

The estimation methods from De la Cal et al.[43] and Penlidis and co-workers[44] are described in detail in the Supporting Information Section S5. Herein, the methods are described briefly.

The reactivity ratios r_A and r_B are estimated using a parameter estimation algorithm that minimizes the objective functions of eqs 1 and 2, where F_{Aexp} and f_{Aexp} are the experimentally measured cumulative copolymer composition and mole fraction of the unreacted monomer, respectively, referred to HPEG determined by in situ ^{1}H NMR. F_{Acal} and f_{Acal} are the theoretically determined cumulative copolymer composition and mole fraction of the unreacted monomer, respectively. $w_{i,j}$ is the weighting factor equal to $^1/_{\sigma_{i,j}^2}$ that
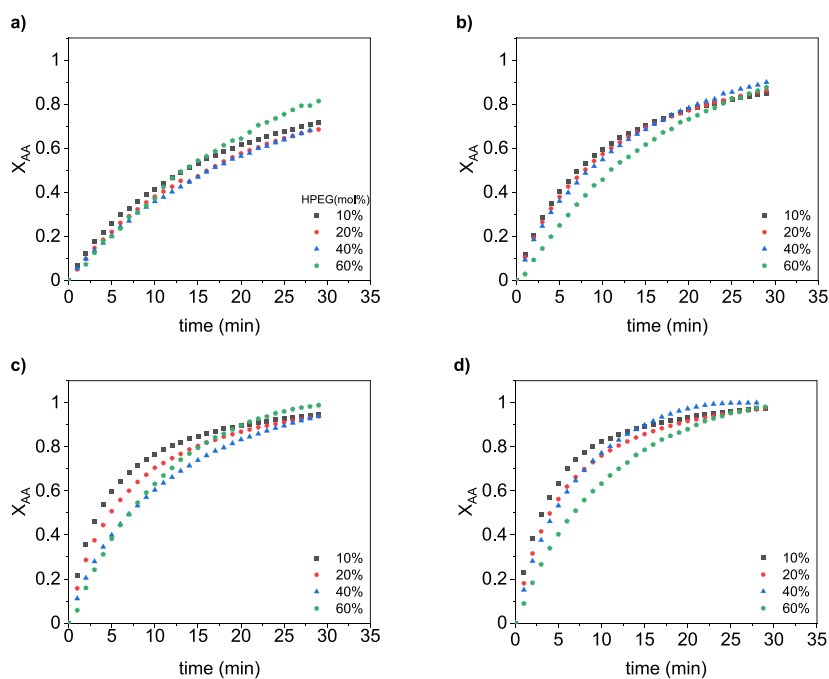
Figure 5. Evolution of individual conversion of AA at four different initial overall monomer weight fractions (w_{M0}) ((a) 5%; (b) 10%; (c) 15%; and (d) 25%) and four HPEG molar ratios (10% (black square), 20% (red circle), 40% (blue triangle), and 60% (green pentagon)).
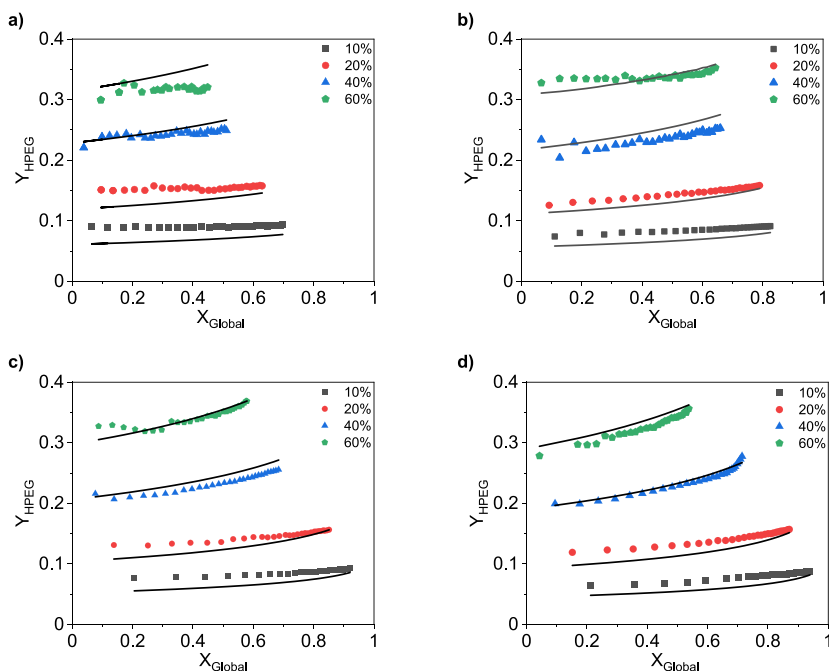

Figure 6. Cumulative copolymer composition of HPEG in in situ ^{1}H NMR experiments at four different initial overall monomer weight fractions (w_{M0}) ((a) 5%; (b) 10%; (c) 15%; and (d) 25%) and four different HPEG molar ratios (10% (black square), 20% (red circle), 40% (blue triangle), and 60% (green pentagon)). Lines: model predictions using the estimated reactivity ratios of Section 4.1.3.

considers the error for each measurement and has been assumed to be constant over the range of measurements ($w_{i,j} = 1$). An error assessment for an experimental data set considering variable weighting factors can be found in the Supporting Information. The subscript i makes reference to the experiment and subscript j to the sample number of each of the experiments used in the estimation procedure. The only parameters of the model are the reactivity ratios.

$$J = \left[\sum_{i=1}^{N} \sum_{j=1}^{Pi} w_{i,j} \left(F_{\text{Aexp}i,j} - F_{\text{Acal}i,j} \right)^2 \right] \quad (1)$$

$$J = \left[\sum_{i=1}^{N} \sum_{j=1}^{Pi} w_{i,j} \left(f_{\text{Aexp}i,j} - f_{\text{Acal}i,j} \right)^2 \right] \quad (2)$$

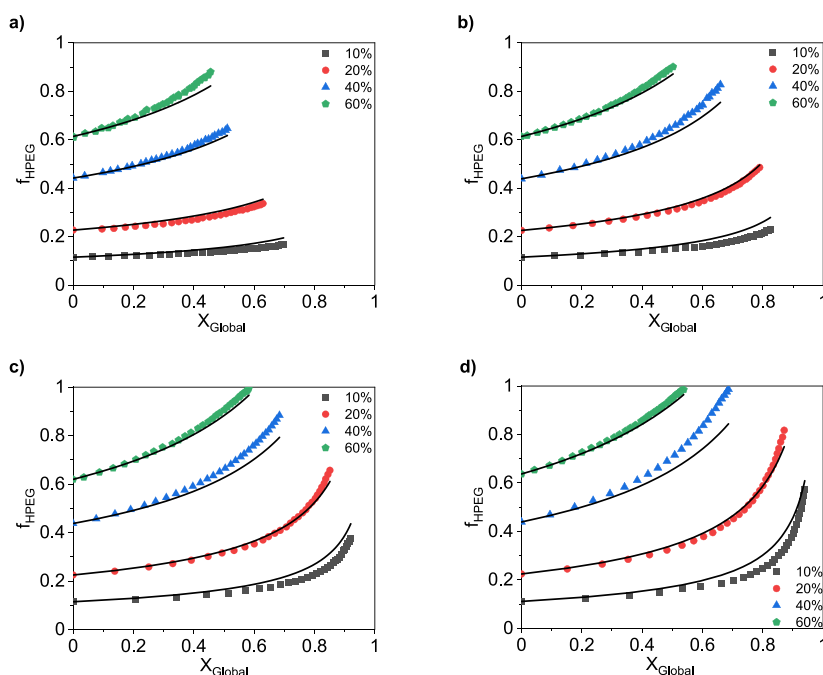The model algorithm was built in Matlab using the ODE45 solver for ordinary differential equations and LSQNONLIN for

Figure 7. Mole fractions of unreacted HPEG in in situ ^{1}H NMR experiments at four different initial overall monomer weight fractions (w_{M0}) ((a) 5%; (b) 10%; (c) 15% and (d) 25%) and four different HPEG molar ratios (10% (black square), 20% (red circle), 40% (blue triangle), and 60% (green pentagon)). Lines: model predictions.

nonlinear data fitting. 95% confidence intervals were calculated using the nonlinear regression parameter confidence interval function (NLPARCI).

4. RESULTS AND DISCUSSION

4.1. In Situ ^{1}H NMR Copolymerization Experiments in Acidic pH.
4.1.1. Global and Individual Conversions. Figure 4 shows the evolution of global and individual conversions of HPEG and AA during copolymerization reactions with different initial monomer ratios at different initial overall monomer weight fractions.

The instantaneous conversions of AA are higher than those of HPEG in all the experiments, and increasing the initial weight fraction of the monomer increases the individual and overall polymerization rates. The first observation clearly indicates that the reactivity ratio of AA is higher than that of HPEG. The second observation can be explained by the simultaneous increase in the monomer concentration and initiator concentration (which is proportional to the monomer in the formulation) when increasing the initial overall weight fraction of the monomer. An exception to this trend is observed in the experiments carried out with a comonomer ratio of HPEG/AA = 60/40 (see Figure 4 d), where the increase of the initial overall monomer fraction does not follow this trend for the highest initial overall monomer fraction (i.e., 25 wt %). The other noticeable observation is that the overall conversion decreases with the increasing HPEG content in the formulation at any initial monomer fraction. This decrease is due to the low propagation rate of HPEG.[31] A similar behavior was observed by Bevington et al.[49] from the copolymerizations of allyl ethers with methyl methacrylate (MMA), styrene (STY), and acrylonitrile (ACN), where allyl ethers showed a retarding effect, decreasing the rate of polymerization, acting as degradative transfer agents. On the other hand, the effect of HPEG content on the acrylic acid conversion does not seem to

be as clear as in the case of HPEG conversion (see Figure 5). It can be seen that the effect of HPEG content on AA conversion is less pronounced at a lower initial overall monomer fraction.

4.1.2. Cumulative Copolymer Composition. Figure 6 shows the evolution of the cumulative copolymer composition of HPEG over the global conversion. The set of data shows a clear composition drift in copolymer chains through the reaction. The cumulative copolymer composition of HPEG starts from values much lower than the initial feed ratio, namely, the copolymer chains are richer in AA. In none of the cases, polymerization reaches full overall conversion of monomers in the analyzed time (30 min). Furthermore, the maximum conversion achieved in each series (different initial overall monomer concentration) decreases by increasing the molar ratio of HPEG in the copolymerization reaction.

4.1.3. Estimation of Reactivity Ratios in Acidic pH. The NLLSQ methods based on the Mayo−Lewis equation described in Section S5 in the Supporting Information were used to estimate the reactivity ratios using the experimental data of cumulative copolymer composition (method of De la Cal et al.) and the mole fractions of the unreacted monomer (method of Penlidis et al.) over global conversion from experiments in acidic pH. Here, all of the reactions were used in the parameter estimation algorithm.

Figures 6 and 7 show the comparison of the predicted and experimental cumulative copolymer compositions and the predicted and experimental mole fractions of the unreacted monomer obtained by the methods of De la Cal et al. and Penlidis et al., respectively. It can be seen that the fittings are reasonably good.

Figures 8 and 9 show the estimated reactivity ratios at different w_{M0} values together with the approximated 95% confidence interval ellipses using both methods of estimation. These values are summarized in Tables 1 and 2. The estimated reactivity ratio of the HPEG at all solids content converges to zero, and the reactivity ratio of AA at different initial monomer
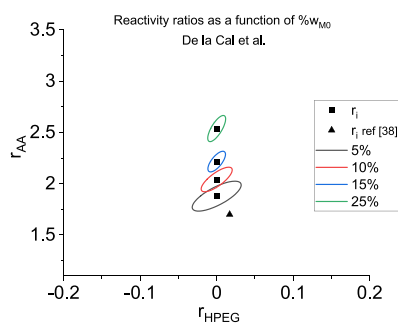
Figure 8. Reactivity ratios of AA and the HPEG macromonomer and the corresponding approximated 95% confidence interval ellipses, estimated from the experimental data at different $\%w_{M0}$ and HPEG molar ratios using the method of De la Cal et al. (Estimated reactivity ratios (black square); estimated reactivity ratios at 40% w_{M0} from ref 38 (black triangle); colored ellipses (5% w_{M0} (black); 10% w_{M0} (red); 15% w_{M0} (blue); and 25% w_{M0} (green)).
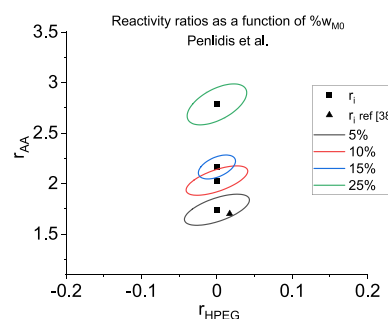

Figure 9. Reactivity ratios of AA and HPEG macromonomer and the corresponding approximated 95% confidence interval ellipses, estimated from the experimental data at different $\%w_{M0}$ and HPEG molar ratios using the method of Penlidis et al. (Estimated reactivity ratios (black square); estimated reactivity ratios at 40% w_{M0} from ref 38 (black triangle); colored ellipses (5% w_{M0} (black); 10% w_{M0} (red); 15% w_{M0} (blue) and 25% w_{M0} (green)).

contents shows values between 1.87 and 2.54 for the method proposed by De la Cal et al. It has to be clarified that the estimated values of the reactivity ratio of HPEG converge to zero due to the boundary restrictions in the estimation algorithm, which restricts the solution to be a positive value due to the lack of physical meaning of a negative reactivity ratio. Although there is a small overlap in the approximated 95% confidence interval ellipses of 5 and 10% monomer weight fractions, the data clearly show the dependence of the reactivity ratio of AA on w_{M0}. In addition, the values of confidence intervals of the reactivity ratio of AA are considerably lower than the estimated values, assuring that the accuracy reached for these estimations is sufficient. The values obtained with the alternative method used by Penlidis et al. are very similar, although the approximated confidence interval ellipses are slightly broader. The influence of the

monomer content can also be better distinguished when the estimation method of De la Cal et al. is used. Despite these differences, it can be concluded that both methods give similar results within the expected error with small confidence intervals. The reactivity ratios estimated by Wang et al.[38] for this comonomer system using a linear method for $w_{M0} = 0.4$ were $r_{HPEG} = 0.017$ and $r_{AA} = 1.7$. According to Figure 8, these values should correspond to a substantially lower initial monomer fraction than that reported by Wang et al.[38] (40%). This discrepancy might easily come from the notably lower amount of data used by these authors, the quality of the instantaneous copolymer compositions (that were inferred from cumulative copolymer compositions calculated from low conversion samples), and the inherent errors of the linear regression method used in the estimation.

From this point on, the discussion will be focused on the results obtained from the estimation method of De la Cal et al.[43]. The estimated values of the reactivity ratios of AA are plotted against the initial overall weight fraction of monomers in Figure 10, which shows a linear dependency of the reactivity ratio of AA on the initial w_{M0} (%). eq 5 shows an empirical expression calculated by fitting the dependence of the reactivity ratio of AA to the initial overall monomer weight fraction (w_{M0} (%)).

$$r_{AA}(w_{M0}\%) = 1.71 + 0.0331(w_{M0}\%) \tag{5}$$

It should be noted that the reactivity ratios were estimated at different initial overall wt % of monomers, assuming that the reactivity ratios do not vary during the reaction. However, it is shown above that there is a meaningful dependency of the reactivity ratios of acrylic acid on the total weight fraction of the monomer, which varies during the reaction. To shed light on the reliability of the estimated reactivity ratios in the whole range of polymerization, the instantaneous copolymer composition was calculated from the individual time evolution of the conversion of each monomer and using eq 6. These experimental instantaneous compositions were compared with those calculated using the Mayo−Lewis equation[45] and the estimated reactivity ratios.

$$Y_A^{inst} = \frac{[A]_0 \frac{dX_A}{dt}}{[A]_0 \frac{dX_A}{dt} + [B]_0 \frac{dX_B}{dt}} \tag{6}$$

Figure 11 displays the comparison between the experimentally calculated and Mayo−Lewis equation-predicted instantaneous copolymer composition as a function of the fraction of HPEG in the reaction. There are four predicted instantaneous copolymer composition lines (one per each set of reactivity ratios obtained at each initial overall monomer concentration). Although the differences in the predicted HPEG compositions are small, it is clear that by increasing the initial overall monomer concentration, the composition of HPEG slightly decreases. On the other hand, the exper-

Table 1. Reactivity Ratios of AA and HPEG Macromonomer and the Corresponding 95% Confidence Intervals, Estimated from the Experimental Data at Different Initial Overall Monomer Fractions ($\%w_{M0}$) and HPEG Molar Ratios Using the Method of De la Cal et al.

w_{M0} (%)	5		10		15		25	
monomer	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)
HPEG	0.000	0.026	0.000	0.016	0.000	9.2×10^{-3}	0.000	9.4×10^{-3}
AA	1.878	0.118	2.041	0.097	2.216	0.081	2.538	0.103

Table 2. Reactivity Ratios of AA and HPEG Macromonomer and the Corresponding 95% Confidence Intervals, Estimated from the Experimental Data at Different Initial Overall Monomer Fractions (%w_{M0}) and HPEG Molar Ratios Using the Method of Penlidis et al.

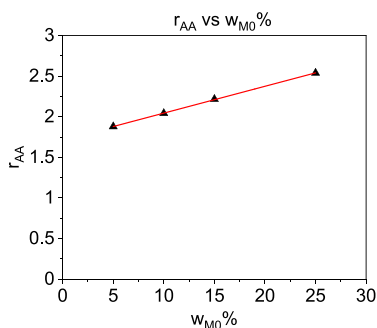| w_{M0} (%)	5		10		15		25	
monomer	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)	r_i	C.I. ($\pm$)
HPEG	0.000	0.035	0.000	0.033	0.000	0.020	0.000	0.032
AA	1.740	0.124	2.029	0.118	2.164	0.096	2.783	0.164

Figure 10. Reactivity ratio of AA at different values of the initial overall weight fraction of monomers. Black triangles: experimental data; red line: fitting with eq 5.
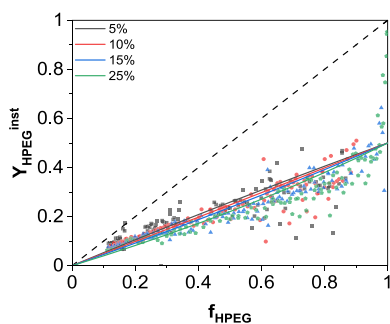

Figure 11. Comparison between the instantaneous HPEG copolymer composition from the Mayo−Lewis equation based on constant reactivity ratios and experimental data. Experimentally calculated cumulative copolymer composition (5% w_{M0} (black square); 10% w_{M0} (red circle), 15% w_{M0} (blue triangle), and 25% w_{M0} (green pentagon)); instantaneous composition based on the Mayo−Lewis equation (5% w_{M0} (black line), 10% w_{M0} (red line), 15% w_{M0} (blue line), and 25% w_{M0} (green line)). Dotted line: instantaneous copolymer composition in ideal copolymerization.

imentally determined instantaneous copolymer compositions cover the whole range of fractions of HPEG. It can be seen that, up to HPEG molar fractions below 0.5, the experimental data (within the error associated with the derivative calculation of dX_A/dt and dX_B/dt) overlap with the predicted instantaneous copolymer compositions. Above $f_{HPEG} > 0.5$, the predicted instantaneous copolymer composition overestimates the incorporation of HPEG into the copolymer chains.

As discussed above, we found that the reactivity ratio of AA was strongly dependent on the initial overall concentration of the monomer. The dependency is given in eq 5. We explored the possibility of upgrading the estimation of the reactivity ratios by not assuming r_{AA} is constant but considering it as a function of the fraction of the total monomer in the reaction medium, as shown in eq 7. Therefore, in the upgraded estimation algorithm, three parameters were estimated: α and β for the reactivity ratio of AA, and r_{HPEG}, which was considered not affected by the initial monomer concentration

$$r_{AA} = \alpha + \beta(w_M\%) \tag{7}$$

where α and β are parameters, and w_M is the total mass fraction of the monomer on a polymer-free basis (i.e., considering only water and both monomers in the system). Table 3 displays the

Table 3. Estimated Parameters from the NLLSQ Fitting of Experimental Data from In Situ Copolymerization Experiments under Acidic Conditions

parameter	estimated value	CI ($\pm$)
r_{HPEG}	2.27×10^{-14}	6.02×10^{-3}
α	1.76	6.2×10^{-2}
β	0.0275	4.37×10^{-3}

estimated parameters α, β, and r_{HPEG}. Figure S8 in the Supporting Information presents the comparison between the experimental HPEG cumulative copolymer composition and the prediction of the model using the estimated parameters of Table 3.

Notably, the parameters estimated for the dependence of the reactivity ratio of AA on $w_M\%$ (Table 3) are very similar to the dependency found in eq 5 (when estimating r_{AA} at each initial monomer weight fraction).

5. CONCLUSIONS

Aqueous in situ ^{1}H NMR copolymerization experiments of AA-HPEG at different initial overall monomer weight fractions and comonomer molar ratios were carried out. The evolution of the cumulative copolymer composition over global conversion showed a clear effect of the initial monomer weight fraction on the reactivity ratios.

The kinetic data gathered from the in situ ^{1}H NMR experiments were used to estimate the reactivity ratios of acrylic acid and HPEG macromonomer in the aqueous copolymerization system at acidic pH using two NLLSQ methods. In the De la Cal method, the conversion evolution of the cumulative composition was used in the objective function, while in the Penlidis method, the conversion evolution of free monomer molar fraction was used. In both cases, the estimated reactivity ratios for AA showed a clear dependency on the initial overall monomer content of the system, and the reactivity ratio of the HPEG macromonomer converged to zero in all cases. The values obtained with both methods showed similarities, while the approximated confidence interval ellipses are slightly broader using the method of Penlidis et al.

An empirical expression was derived that describes the dependency of the reactivity ratio of AA over the initial mass fraction. A global estimation of the reactivity ratio of AA was also done using the whole set of data points that describes the dependency of the reactivity ratio of AA on the actual mass fraction of both monomers through the reaction. Both approaches yielded similar expression for the dependency of r_{AA} on the overall monomer fraction.

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Notes

The authors declare no competing financial interest.

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