Analyzing the discrepancies in the activation energies of the backbiting and β-scission reactions in the radical polymerization of n-butyl acrylate

S. Hamzehlou,[a] N. Ballard,[a] Y. Reyes,[b] A. Aguirre,[a] J. M. Asua[a] and J. R. Leiza*[a]

The formation of midchain radicals (MCRs) and their subsequent fate heavily influences the radical polymerization of acrylic monomers. This article aims to shed light on the discrepancies in the activation energies of the formation of MCRs by backbiting and their reaction by beta-scission in the radical polymerization of n-BA determined by both experimental and theoretical methods. For this purpose, bulk and solution batch polymerizations of n-BA at different solids contents and over a wide range of nominal temperatures of 60, 100 and 140 °C initiated by a thermal initiator were carried out and the kinetics, branching density and average molar masses as well as the macromonomer density were measured by means of ^{13}C NMR, ^{1}H NMR and size-exclusion chromatography with multi-angle light scattering (SEC/MALS). A detailed model was used to predict the experimental data and to estimate the activation energies for the backbiting and β-scission reactions. The estimated values for the backbiting activation energy are closer to the upper range of values previously reported and, on the other hand, the estimation shows that in the whole range of temperatures, the β-scission rate coefficient should be higher than the accepted values reported in the literature which failed to predict the properties in the wide range of temperatures used in this work.

Introduction

Acrylic (co)polymers are widely used in many commercial pro-ducts and applications such as coatings, films, latex paints, adhesives and drug delivery systems.[1-5]Radical polymerization of acrylic monomers is unique as compared with other vinyl monomers because, in addition to chain-end radicals, a sub-stantial portion of the radicals in the system exist as so-called mid chain radicals (MCRs), which can be formed by either intra- or inter-molecular chain transfer to polymer reactions.[6–8] Upon further propagation, MCRs lead to the formation of short and long chain branches (SCBs and LCBs), respectively. The intra-molecular mode of chain transfer to polymers, also known as a backbiting reaction, has been shown to be much more prevalent than the inter-molecular one and accounts for essentially all of the branching points.[6,9–12] In addition to propagation, the MCRs can undergo β-scission reactions pro-ducing shorter chains with terminal double bonds (so-called macromonomers),[13,14] which have found technological application in automotive coatings.[15,16] These mechanistic complex-ities strongly shape the architecture of acrylic polymers because in addition to the SCBs and LCBs, intermolecular chain transfer to polymers followed by termination by combi-nation can produce crosslinking reactions that lead to polymer network formation and gel polymers, which can be of para-mount importance to achieve the desired performance of polymer latexes used in adhesives and coatings. The presence of the MCRs also affects the kinetics because the higher stability of these radicals substantially reduces the polymerization rate.[6]

The importance of the MCR reactions has stimulated investigation in this field, and plenty of research has been conducted to determine the kinetic parameters of the reac-tions of propagation, backbiting, β-scission and propagation to terminal double bonds.[17–20] Two basic approaches have been employed to determine the kinetic parameters: (a) fitting the experimental data gathered under different experimental con-ditions with the mathematical models that account for these reaction mechanisms, and (b) using quantum mechanical approaches. Table 1 summarizes the Arrhenius parameters of the kinetic rate coefficients for the propagation, backbiting and β-scission reactions for n-butyl acrylate (n-BA) determined either by fitting the experimental data or by means of quantum mechanical calculations.

It can be seen from Table 1 that with the exception of the activation energy for the propagation reaction, widely different

[a]POLYMAT and Kimika Apl katua saila, Kim ka Zientzien Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia-San Sebastián, Spain. E-mail: jrleiza@ehu.eus

[b]Departamento de Recursos de la Tierra, Universidad Autónoma Metropolitana Unidad Lerma (UAM-L), Av. Hidalgo 46, Col. La Estación, CP 52006 Lerma de Villada, México

values are provided by the two approaches. The differences observed in the pre-exponential factors are somewhat expected, because the accuracy of quantum mechanics to predict this value is lower than for the activation energy, likely because the reactions are simulated under vacuum and experimentally are carried out in bulk or in solution. However, the differences in the activation energies of backbiting and β-scission are remark-able. It has to be pointed out that there are experiments in the literature which similarly suggest a higher activation energy for the backbiting reaction (E_{bb}). For example, Willemse et al.[28] used electron spin resonance (ESR) to monitor the relative con-centrations of tertiary and secondary radicals during pulsed laser polymerization (PLP) of n-BA as a function of temperature, concluding that the difference between the energy of activation of the backbiting reaction and that of the propagation of MCRs was 18.8 kJ mol^{-1}, which, considering that the reported value for the energy of activation of the propagation of MCR is 28.9 kJ mol^{-1} (ref. 24), leads to a value of E_{bb} = 47.7 kJ mol^{-1}.

It is worth mentioning that the discrepancy between the experimental β-scission activation energies and those calcu-lated by quantum mechanics is even higher for midchain radi-cals of a similar structure generated during reversible addition–fragmentation chain transfer (RAFT) polymerization using thiocarbonylthio compounds as the RAFT agent. These RAFT MCRs show mechanistic and kinetic similarities to the MCRs produced during conventional free radical polymeriz-ation, and the rate at which they undergo fragmentation is the subject of an ongoing discussion in the literature.[17,33,34]

Gaborieau et al.[18] studied the branching density of n-BA bulk polymerization in a wide range of temperatures with and without chain transfer agents. Fig. 1 shows the branching density at 3 different nominal temperatures. According to their experiments the branching density increased significantly at high temperatures. However the authors did not provide any information on the kinetics and thermal exotherm that are typical in the bulk polymerization of n-BA.

The experiments were repeated in this work and the temp-erature was monitored (details are provided in the Experi-mental part). The bulk polymerizations of n-BA were highly exothermic (Fig. 2) and, due to the rapid onset of the gel effect, monitoring of the kinetics and polymer microstructure throughout the reaction proved a difficult task. Modeling the exothermicity for batch RAFT polymerization of acrylates was also found to be critical for the prediction of the kinetics.[36]

The measured branching densities of these experiments are also shown in Fig. 1. It should be commented that as the actual temperature in the reactor in batch bulk polymerization went higher than the monomer boiling point, the effective monomer concentration could be less than the expected one. This can lead to higher branching density. In addition the lack of mixing in the reactor could lead to the formation of a non-homogeneous polymer. However, it can clearly be seen in Fig. 1 that the model prediction with the values of pre-exponential factors and activation energies of backbiting and β-scission from ref. 27, 30 (considering the exotherm of the reaction) are significantly lower than the experimental results of independent experiments in the batch bulk polymerization of n-BA, especially at higher temperatures. It is worth mention-ing that in addition to the poor prediction of the degree of branching shown in Fig. 1, the final weight average molar masses were also measured and no good agreement was found between model prediction and experimental data.

Thus, both experiments conducted over a broad range of temperatures in bulk and estimates of the activation energy of backbiting and β-scission from quantum mechanical calcu-lations suggest a higher impact of MCRs at high temperatures. This article aims at shedding light on this issue by studying the effect of temperature on the degree of branching and molar masses as well as macromonomer content in the polymerization of n-BA. The impact of higher activation ener-gies for backbiting and β-scission reactions on the polymeriz-ation of n-BA should be clearly manifested in the branching, molar mass distribution and macromonomer content of poly-mers synthesized at widely different temperatures. For this purpose, in this work, due to the difficulties mentioned above in the bulk polymerization, solution batch polymerizations of n-BA at different solids contents at the nominal temperatures of 60, 100 and 140 °C initiated by a thermal initiator were carried out and the branching density and average molar masses were measured by means of ^{13}C NMR and SEC/MALS. In addition, a detailed model implemented in Predici®[37] was used to predict the experimental data and to shed light on the discrepancies reported in the literature (see Table 1) for the backbiting and β-scission kinetic rate coefficients using a wide range of temperatures that has not previously been used for estimating these parameters.

Experimental

Materials

n-Butyl acrylate (Quimidroga, technical grade) was purified by distillation and was kept at −20 °C until use. The initiators, 2,2′-azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) and 1,1′-azobis(cyclohexanecarbonitrile) (ACHN, Aldrich, 98%), and the solvent, p-xylene (99%, Aldrich), were used as received. All other solvents were purchased from Scharlab, were of tech-nical grade, and were used without purification.

Synthetic procedures

Batch bulk polymerization. Batch bulk polymerizations of n-BA were carried out at three nominal temperatures, 60, 100 and 140 °C. In a typical experiment, 1.79 g of n-BA and 0.0016 g of AIBN (for the experiments at 60 and 100 °C) and 0.0024 g of ACHN, for the reaction at 140 °C, (both from Aldrich) were added to a Head Space GC glass vial of 20 mL, and then the vials were sealed. A thermocouple was inserted through a small pinhole to directly measure the temperature

within the reaction mixture. A silicon oil bath was used to run the polymerizations. The set-point temperatures of the silicone oil bath were 60, 100 and 140 °C. The vial (containing the monomer and initiator) was completely immersed in the silicon oil bath. The reaction time for a set point temperature of 60 °C was 216 000 s (2.5 days), for 100 °C it was 1635 s and for 140 °C it was 305 s. At the end of the reaction the vial was placed in an ice bath. Finally, the residual monomer was evap-orated in a vacuum oven at room temperature up to constant weight. The final monomer conversions (determined by gravi-metric measurements) were 0.90, 0.78 and 0.80 for 60, 100 and 140 °C nominal temperatures, respectively.

Batch solution polymerization. The reactions were carried out in a commercial calorimetric reactor (RTCal™, Mettler-Toledo). The reactor consists of a 1 L glass jacket reactor vessel, an anchor impeller, a platinum resistance thermo-meter, a nitrogen inlet and a sampling tube. n-BA (80–120 g) and p-xylene (318–278 g) were loaded into the reactor, purged with nitrogen over the course of 30 minutes, and heated to the reaction temperature under constant agitation of 200 rpm. After equilibration of the temperature, the initiator (either AIBN (0.12 g) for the reactions conducted at 60 and 100 °C or ACHN (0.15 g) for the reactions conducted at 140 °C) dissolved in 2 g p-xylene was added in a single shot. Samples were taken periodically and short stopped with benzoquinone. Conversion was measured by gravimetry and the dried polymer samples were used for a subsequent analysis of molar mass and NMR measurements.

Characterization

NMR spectra were recorded at 25 °C in $CDCl_3$ at a concen-tration of 300 mg ml^{-1} on a Bruker AVANCE 400 MHz spectro-meter equipped with a z-gradient double resonance probe. 1D ^{1}H spectra were acquired by the use of 16k data points which were zero-filled to 64k data points prior to Fourier transform-ation. 1D ^{13}C spectra were recorded at a ^{13}C Larmor frequency of 100.61 MHz. The spectra were recorded using 5000 transi-ents. Quantitative ^{13}C spectra were recorded using single pulse excitation, using a 5.5 μs 90° pulse, inverse gated Waltz16 decoupling to avoid NOE effects and a relaxation delay of 10 s. Apodization was achieved using an exponential window func-tion equivalent to a linewidth of 5 Hz. Experiments with longer relaxation delay were performed to ensure complete relaxation of the chains between pulses and did not result in any quantitative difference in the integrals of the signals used in this work. The branching densities of the polymers were calculated from the quantitative ^{13}C spectra from the ratio of the integral of the quaternary carbon peak (45–49 ppm) and the methyl group of the butyl ester (11–14 pm). The amount of macromonomer was calculated by ^{1}H NMR from the ratio of the sum of the integral from hydrogens from the macromono-mer at shifts of 5.52 and 6.15 ppm to the OCH_2 peak. The rela-tive error in the branching density was calculated from the inverse of the signal to noise ratio of the quaternary carbon peak. This approach was considered valid given that the inte-gral areas of the peaks are substantially smaller than the peaks

against which they are compared.[38] The signal to noise ratio was estimated to be 2.5 times the ratio of the peak to the peak-to-peak noise of the baseline.

The average molar mass was analyzed by SEC/MALS. The equipment was composed of a LC20 pump (Shimadzu) coupled to a miniDAWN Treos multi-angle (3 angles) light scat-tering laser photometer equipped with an He–Ne laser (λ = 658 nm), and an Optilab Rex differential refractometer (λ = 658 nm) (all from Wyatt Technology Corp., USA). Separation was carried out using three columns (Styragel HR2, HR4 and HR6 with a pore size of 10^2–10^6 Å). Filtered toluene (HPLC-grade from Sigma-Aldrich) was used for the calibration of the 90° angle scattering intensity. The detectors at angles other than 90° in the MALS instrument were normalized to the 90°detector using a standard (PS 28 770 g mol^{-1}, Polymer Labs), which is small enough to produce isotropic scattering. In addition, the same standard and conditions were used to perform the alignment (interdetector delay volume) between concentration and light scattering detectors and the band broadening correction for the sample dilution between detectors.

The analysis was performed at 35 °C and THF was used as the mobile phase at a flow rate of 1 mL min^{-1}. The dried polymer was diluted in HPLC grade THF at concentrations of about 4 mg mL^{-1} and was then injected into the equipment. The dn dc^{-1} used for the molar mass calculation was the one corresponding to pBA (dn dc^{-1} = 0.064 mL g^{-1}). The SEC/MALS data were analyzed by using the ASTRA software version 6.0.6 (Wyatt Technology, USA). The absolute molar mass was calcu-lated from the MALS/RI data using the Debye plot (with 1st order Zimm formalism).

Modeling

A full kinetic model for the polymerization of n-BA was implemented in the commercial software Predici.[37] The model includes the reactions that are specific to acrylates, such as backbiting, intermolecular chain transfer to polymers, β-scis-sion and propagation to macromonomers. The kinetic scheme considered in the model is shown in Scheme 1. As the experi-ments had been performed also at high temperature, self-initiation was also included in the reaction mechanism accord-ing to the mechanism and parameters reported by Rantow et al.,[15] although this reaction is less important in low solids content solution polymerization compared to the bulk polymerization.

The kinetic parameters taken from the literature are pre-sented in Table 2. Note that the dependence of propagation and termination coefficients on conversion was not considered in this work because its impact on the solution polymerization (30 and 20 wt% solids content) of BA was considered to be neg-ligible. The activation energy of the propagation rate coeffi-cient of the macromonomer was considered to be equal to that of the propagation rate coefficient of the chain end radicals according to the reported studies in the literature.[30,39] It is worth mentioning that the migration of the midchain radical along the backbone of the polymer chains was not considered in the model as the occurrence of this reaction has only been proved in the absence of the monomer, but not in solution polymerization.40,41

Results and discussion

The above model was used to estimate the kinetic parameters by fitting the experimental data obtained at different tempera-tures and under different conditions.

Solution polymerizations of n-BA at 30 and 20 wt% solids content were performed at three different nominal tempera-tures, 60, 100 and 140 °C. The temperature was monitored during the reaction and only in the case of 30 wt% solids content at temperatures 100 and 140 was any significant exo-therm observed. In the rest of the experiments the increase of temperature was less than 2 °C and therefore these experi-ments were considered isothermal. Fig. 3 shows the tempera-ture profiles for the cases in which a significant exotherm was observed.

For these two non-isothermal reactions the experimentally obtained temperature profile was used in the simulation to properly account for the variation in temperature. Branching density and macromonomer density were measured by 13C and 1H NMR spectroscopy respectively.

Fig. 4 and 5 show the measured branching density and the macromonomer density as well as the weight average molar mass of polymerizations at different temperatures and solids contents.

The branching density increases during the reaction and it can be seen that it is highly dependent on the temperature of the reaction. The same trend has been seen for the macro-monomer density. No measurable amount of macromonomer was found at 60 °C.

The weight-average molar mass shows a decreasing ten-dency as a function of conversion. The experimental weight average molar mass also decreased with increasing tempera-ture, and at high temperatures, a highly branched low molar mass polymer is formed.

Fig. 4 and 5 show that decreasing the solids content increases significantly the macromonomer density. This high-lights the effect of a β-scission reaction, which is especially important at high temperatures and low monomer concen-trations. Although MCR radicals also undergo termination and transfer reactions, they overwhelmingly tend to undergo either propagation (leading to a branch point) or β-scission (leading to the formation of macromonomer species). Thus, the sum of branching density and macromonomer can be reasonably assumed to be equal to the density of backbiting reactions compared to propagation. The density of backbiting clearly shows a higher number of backbiting reactions at lower monomer concentrations at a constant temperature (Fig. 6).

The model was used to fit the experimental data with kinetic coefficients obtained from the literature. Fig. 7 shows the prediction of the model with backbiting and β-scission rate coefficients presented in Table 2. It can be seen that experi-ments show higher temperature dependency on the density of backbiting compared to the model results. It is worth mention-ing that the kinetic rate coefficients of backbiting and β-scis-sion were estimated at high temperatures but using a narrow range of temperatures. Therefore, the measured density of backbiting together with the weight average molar mass and conversion were used to estimate these parameters using the parameter estimation algorithm of the Predici package. The parameters in Table 3 were estimated simultaneously by fitting all three experimental data sets. In this algorithm, the relative total residual is

$$ r_{rel} = \frac{1}{\sqrt{N}} \sqrt{ss_E} $$

where N is the total number of data and SSE is the weighted residual sum of squares. Together with backbiting and β-scission the chain transfer to the solvent and termination rate coefficients were estimated to fit both the kinetics and microstructure properties of the polymer. The sensitivity analysis has been performed on other uncertain parameters, e.g. propagation rate coefficients of the macromonomer, and their effect on the final results was not significant. It is worth mentioning that the values of k_β and k_{mac} are strongly correlated. The concentration of the macro-monomer is proportional to $2k/k_{mac}$, so k_β and k_{mac} could not be estimated separately using the macromonomer concen-tration.[30] Therefore the value of k_{mac} was fixed at $k_p \times 0.5$ according to the previous findings in the literature.[39,44,45]

Table 3 presents the estimated backbiting and β-scission coefficients. In low solids content solution polymerizations, the molar masses are mostly controlled by transfer to solvent reaction, so the chain transfer to the solvent and termination coefficients were also estimated to fit the kinetics and the molar masses of the polymers. Fig. 8 and 9 show the compari-son of experimental results and the simulation results using the estimated parameters at different initial monomer concentrations.

The estimated parameters fit reasonably well the experi-mental data over a wide range of temperatures and different solids contents. The estimated activation energy of backbiting is substantially higher than the value reported in ref. 7, 23–26 but very close to the values estimated by quantum calculations and not far from that obtained from the Willemse et al.28 data and represents well the high temperature dependency of back-biting reactions. It is worth mentioning that the 2 sets of para-meters of backbiting (Tables 2 and 3) give almost the same rate coefficient of backbiting at around 120 °C. This is within the range of temperatures that was used in ref. 30 to fit the experimental data. In the mentioned reference, a better fit of the experimental degree of branching was obtained at 110 °C than those obtained at higher temperatures (140 °C and 170 °C). On the other hand, the estimated activation energy of the β-scission of the MCRs was lower than the values reported before, which makes this reaction more relevant in the whole range of temperatures. It is worth mentioning that although the activation energy of the β-scission is not much higher than that of the backbiting reaction, the β-scission reaction of MCRs is observed at higher temperatures. This is due to the fact that for a β-scission reaction to occur, a backbiting reac-tion should have occurred previously. Therefore, the prob-ability for a β-scission reaction is the product of the

probabilities for a backbiting reaction and for a β-scission reac-tion of a MCR. There are reports in the literature that suggest higher rates of β-scission reactions at high temperature reac-tions for acrylates, which is in agreement with the estimated values in this work.[14,44,46] While the β-scission rate coefficient is 12 s^{-1} at 140 °C using the values of ref. 30, Junkers et al.[14] suggest a value of 78 s^{-1}, which is closer to the estimated value in this work (140 s^{-1}).

Finally, it should be noted that the activation energy reported herein is seemingly in good agreement with the measured MCR fraction across a range of temperatures as measured by Willemse et al. by the PLP-ESR method. Assum ing that the long chain hypothesis holds in their experiments, they calculated a difference in the activation energy between backbiting and propagation of the tertiary radical of 18.8 kJ mol−1, which leads to an activation energy for back-biting of 47.7 kJ mol−1. Where much lower activation energies are used such that $E_{bb} \approx E_{kp3}$ the MCR fraction is insensitive to temperature and even at low temperatures relatively high MCR fractions are expected, which is not the case experimentally.

Conclusions

Solution batch polymerizations of n-BA at different solids con-tents and nominal temperatures of 60, 100 and 140 °C initiated by a thermal initiator were carried out and the kine-tics, branching density and average molar masses as well as the macromonomer density were measured by means of 13C NMR, 1H NMR and SEC/MALS. A detailed model was used to explain the batch polymerizations.

It was found that the effect of the temperature on the density of backbiting and molar masses could not be described by using the currently accepted set of parameters for backbiting and β-scission in the polymerization of n-BA. A sub-stantially better fitting for the density of backbiting and Mw could be obtained with activation energies (52.3 and 55.4 kJ mol−1 for backbiting and β-scission, respectively). The higher activation energy of the backbiting reaction leads to stronger thermal dependency of this reaction and is in better agreement with the values calculated by quantum chemistry and experimental values reported by Willemse et al. On the other hand the density of the macromonomer showed that the β-scission reaction should be stronger in the whole range of temperatures.

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