PLP−ESR Monitoring of Midchain Radicals in *n*-Butyl Acrylate Polymerization

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ABSTRACT: The percentage of two types of free radicals occurring within *n*-butyl acrylate pulsed laser polymerization (PLP) has been measured via ESR spectroscopy. Polymerization in solution of toluene, at monomer concentrations between 0.50 and 2.53 mol L^{-1} and temperatures between −50 and 70 °C, was induced by 351 nm excimer laser pulses applied at a repetition rate of 20 Hz. The ESR spectra obtained at low degrees of monomer conversion may be adequately represented by superimposing a six-component four-line spectrum assigned to secondary propagating radicals (SPRs) and a nine-line spectrum assigned to tertiary midchain radicals produced by backbiting (MCR1s). The percentage contribution to total radical concentration of the latter species, which is produced from an SPR by a 1,5-H shift backbiting reaction, is negligible at −50 °C and is close to 80% at 70 °C. The transition of an SPR to a MCR1 species invalidates the linear correlation of time *t* after applying a laser pulse with the size of the growing radical. The observed high concentration of MCR1 species explains the known severe limitations met in acrylate PLP−SEC experiments directed toward measuring the propagation rate of acrylate radicals with chain-end functionality.

Introduction

The precise knowledge of kinetic parameters is of paramount importance for the detailed mechanistic understanding of free-radical polymerization. In the 1980s, the introduction of pulsed laser polymerization (PLP) gave rise to a new era in this field. PLP in conjunction with size-exclusion chromatography (SEC) has provided access to accurate propagation rate coefficients (k_p). The PLP−SEC method has been applied to a large group of monomer systems since its recommendation as the method of choice by the IUPAC Subcommittee Modeling of Polymerization Kinetics and Processes.[1−3] A series of papers have been published with benchmarked k_p values based on independent PLP−SEC studies carried out in different laboratories.[4−8] The most recent paper of this series is on *n*-butyl acrylate.[8]

The PLP−SEC method comprises the periodic generation of radicals by dissociation of a photoinitiator with laser light of a pulse width of about 10 ns. Radicals originating from the same laser pulse have approximately the same chain length; i.e., they exhibit a narrow chain-length distribution. The time of growth for a polymer chain is controlled by the time between two pulses. Laser pulsing leads to preferential termination which is associated with a structure on the molecular weight distribution of the resulting polymer. Termination in the dark-time period between applying laser pulses produces the so-called background polymer material. The degree of polymerization for polymer chains initiated and terminated by laser pulsing is given by the simple relation[9]

$$L_{0,i} = ik_p c_M t_p \tag{1}$$

where $L_{0,i}$ is the characteristic chain length of a macroradical formed by propagation during the time interval between two laser pulses, c_M is monomer concentration, t_p is the time between two successive laser pulses, and $i = 1, 2, 3, ...$ Higher-order characteristic chain lengths $L_{0,2}$, $L_{0,3}$, $L_{0,4}$ for ($i = 2, 3, 4, ...$) may occur in case that macromolecular growth that has been initiated by a laser pulse is not terminated by primary radicals produced within the next laser pulse.

Application of PLP−SEC to acrylates suffers from significant difficulties as outlined by van Herk[10] and within a recent IUPAC paper on *n*-butyl acrylate.[8] Above 20 °C, the polymer molecular weight distributions lose their characteristic PLP structure as a consequence of intramolecular and/or intermolecular chain transfer to polymer. Failure of the PLP−SEC experiment as a consequence of chain transfer to monomer is not overly likely, as this would require unrealistically high transfer coefficients.[11] Chain transfer to polymer has received considerable attention by the group of Lovell.[12−15] Under the low conversion conditions of the PLP−SEC experiments, that is at low polymer contents, intramolecular chain transfer to polymer is particularly important. The occurrence of midchain radicals, produced by transfer-to-polymer processes, has been confirmed by electron spin resonance (ESR) spectroscopy under stationary free-radical polymerization conditions chiefly carried out by Yamada and colleagues[16−18] and by Kajiwara and Kamachi[19] and by the observation of quaternary carbon atoms with ^{13}C NMR[20] under PLP conditions. Quantitative studies into midchain radical concentrations under PLP conditions have not been reported so far. The present paper addresses PLP experiments performed in conjunction with ESR detection of terminal and midchain radical concentrations at temperatures between −50 and 70 °C.

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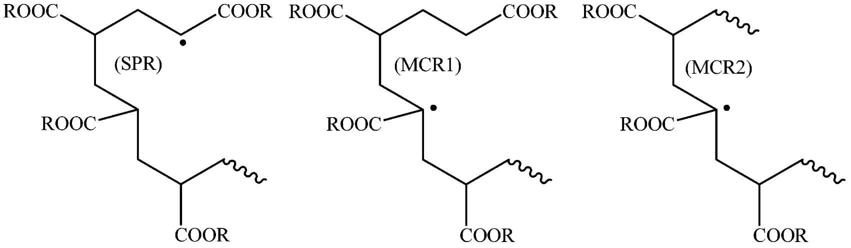

Figure 1. Chemical structure of the secondary propagating radical (SPR) and of two types of tertiary radicals which are formed either by backbiting (MCR1) or by intramolecular transfer to more remote positions on the backbone and by intermolecular chain transfer reactions (MCR2).

Experimental Section

ESR spectra were recorded on a Bruker Elexsys E 500 series CW-EPR spectrometer. The sample solution was contained in a quartz tube of 5 mm o.d. and 4 mm i.d. The tube was fitted into a cavity equipped with a grid. The sample was irradiated through the grid with a COMPex 102 excimer laser (Lambda Physik) operated on the XeF line at 351 nm with a repetition rate of 20 Hz. The laser energy per pulse was around 50 mJ. Laser irradiation occurs at right angle to the cylindrical axis of the sample tube. To improve signal-to-noise, between two and five individual ESR spectra were coadded to yield the spectrum which is subjected to quantitative analysis of terminal and midchain radical concentrations. The software Xepr v1.0 (Bruker), which also controls the spectrometer settings, was used for primary data acquisition. The software Simfonia v.1.25 (Bruker) was used to simulate ESR spectra.

The photoinitiator α-methyl-4-(methylmercapto)-α-morpholinopropiophenone (MMMP, 98%, Aldrich Chemie) was used as supplied at initial concentrations of about 1×10^{-2} mol L^{-1}. Butyl acrylate (>99%, stabilized with 0.005 wt % hydroquinone monomethyl ether, Fluka Chemie) was purified by distillation under reduced pressure in the presence of K_2CO_3. Toluene (Fluka Chemie, >99.7%) was used as supplied.

Solutions of BA in toluene were prepared and treated by three freeze−pump−thaw cycles to remove oxygen. Under an argon atmosphere, MMMP was added to the solution which was then filled into an ESR sample tube. Only spectra measured at low degrees of monomer conversion, up to about 10%, were analyzed. The time required for recording a single ESR spectrum was close to 5 s. The fraction of midchain radicals (in percent of the total radical concentration) was determined rather than absolute radical concentration. PLP parameters were selected to be close to the ones of typical PLP−SEC experiments where pulse-induced radical concentration is of the order of 1×10^{-5} mol L^{-1}.[21,22]

The percentage of midchain radicals is determined by assuming that the measured ESR spectrum is composed of a linear combination of the spectrum for terminal secondary radicals and the spectrum for tertiary midchain radicals. A least-squares method was used to fit the simulated ESR spectra of these two species to the experimental spectra (after noise reduction by Fourier transformation). Within the fitting procedure, a triangular weighting function with maximum sensitivity at the central position of the ESR spectrum has been used. The experimental spectra shown in the following section are the measured ones without any data treatment.

Results and Discussion

Intramolecular and intermolecular chain transfer to polymer processes play an important role in free-radical polymerization of acrylates.[12−15,20,23,24] Via these reactions, secondary propagating radicals (SPRs) are transferred into tertiary midchain radicals (MCR) (see Figure 1). In addition to propagation and termination, SPRs can undergo hydrogen-transfer reactions associated with shifting the radical functionality to a carbon atom on the same polymer chain (intramolecular transfer), preferably by the so-called backbiting process[25] which produces a midchain radical MCR1 (Figure 1), or to the carbon atom of another polymer molecule (intermolecular transfer) which results in an MCR2 species (Figure 1). Both types of transfer reactions primarily occur by hydrogen abstraction from carbon atoms which are activated by the ester moiety. Backbiting which occurs as a 1,5-H shift reaction via a six-membered transition structure is a particularly rapid process with acrylates. Because of the high propagation rate of acrylates,[8] primary radical species from photoinitiator decomposition, small-size radicals from the initial propagation period, and small radicals produced by chain transfer to monomer molecules are not easily seen in the ESR spectrum at typical polymerization conditions because of the very rapid addition of monomer molecules to these species. The radical species which are contributing to the ESR spectrum are shown in Figure 1.

Intermolecular chain transfer may be neglected under PLP−SEC conditions, where monomer conversion and thus the amount of polymer are low. As backbiting is favored over intramolecular hydrogen transfer from arbitrary positions along the backbone of the macroradical other than the one which affords for 1,5-H shift via the six-membered transition structure, MCR1 will be the preferred MCR species under PLP conditions. That SPR and MCR1 species dominate the PLP−ESR spectrum is for different reasons: (i) Rapid addition to acrylate monomer of SPRs does not diminish the concentration of this type of radicals as this process transforms one SPR species into another. (ii) The MCR1 radical is relatively stable with a significant steric hindrance contributing to the low addition rate to monomer of this species.

MCR1 radicals may undergo β-scission,[26] which process, however, occurs with a significant rate only at temperatures above 80 °C. The propagation rate from MCR1 has been estimated via the kinetics of the sterically hindered butyl acrylate dimer[27] and the methyl acrylate dimer.[28] Because of the low speed of this reaction, formation of MCR1 via backbiting is associated with macroradical chain length being no longer linearly related to the time t after applying the laser pulse at $t = 0$. Under polymerization conditions where only a small fraction of SPRs has not be converted into long-lived MCR1 (or MCR2) species in the time period between two successive laser pulses, the quality of k_p measurements via PLP−SEC may be intolerably reduced.

Electron spin resonance (ESR) spectroscopy can provide information on both the structure and the concentration of propagating radicals.[29,30] The interpretation of ESR spectra recorded during free-radical polymerization of acrylates is however far from trivial. Different types of ESR assignments have been made for SPRs in acrylate polymerizations.[16,17,31−34] Also, for midchain radicals no final understanding of the ESR spectra has been reached so far.[16,17,19,35] A major reason behind the discrepancies is seen in polymerization conditions and polymer properties being dissimilar. The differences affect the dynamics of molecular reorientation processes and thus can modify hyperfine splitting.

Yamada et al. confirmed the occurrence of midchain radicals for cyclohexyl acrylate,[17] phenyl acrylate,[16] *tert*-butyl acrylate, and 2-ethylhexyl acrylate.[18] These authors assigned the ESR spectra measured during acrylate solution polymerization in benzene at 60 °C to the overlap of an SPR seven-line spectrum (with hyperfine splitting constants, e.g., for cyclohexyl acrylate, of $\alpha_{H\alpha} = 1.77$ mT, $\alpha_{H\beta 1} = 1.07$ mT, and $\alpha_{H\beta 2} = 2.95$ mT) and a MCR three-line spectrum (with $\alpha_{H\beta} = 2.75$ mT). For the midchain radicals, Yamada and others[16,17] assumed that only two out of the four β-hydrogen atoms can couple with the unpaired electron. To support their assignments, Yamada et al. referred to earlier work on acrylate systems.[32–34,36] In a recent paper by Tanaka et al.,[37] ESR spectra measured during cyclohexyl acrylate were analyzed adopting the same assignment. Interestingly, the early work on midchain radicals was carried out on cross-linked systems where the low mobility of the polymer chains may be responsible for the coupling of only two out of the four β-hydrogen atoms with the unpaired electron. Kim et al., however, demonstrated for midchain radicals in a butyl acrylate film that increasing temperature enhances the number of lines in the MCR ESR spectrum. The authors attributed this effect to the coupling of the radical functionality with two sets of slightly nonequivalent protons.[38] Kajiwara and Kamachi[19] reported on changes of the ESR spectra in the solution polymerization of *tert*-butyl acrylate at temperatures between −30 and 60 °C. In the initial stage of the polymerization at −30 °C, a six-line spectrum was observed. This spectrum is assigned to the SPR with the radical functionality coupling with the α-proton ($\alpha_{H\alpha} = 2.28$ mT) and with two β-methylene protons ($\alpha_{H\beta} = 2.06$ mT). The spectrum changes into the long-lived seven-line spectrum at 60 °C, which looks very similar to the one reported by Azukizawa et al.[16] The interpretation of the ESR spectrum of the propagating SPRs provided by Kajiwara and Kamachi thus is slightly different from the one given by Azukizawa et al.[16] Kajiwara and Kamachi[19] leave a question mark on the interpretation of the spectra at elevated temperatures.

Shown in Figure 2 is the ESR spectrum measured during the initial period of a pulsed laser *n*-butyl acrylate polymerization in toluene solution at −50 °C with laser pulsing being applied at a repetition rate of 20 Hz. A spectrum with four broad lines is seen which is very similar to the one reported by Kajiwara and Kamachi for *tert*-butyl acrylate polymerization at −30 °C. The four-line spectrum actually consists of six components with two pairs of components being overlapping, as is indicated by the assignment bars in the lower part of Figure 2. The spectrum is due to the SPR species in which the radical functionality couples with the α-proton and with two equivalent β-methylene protons. The hyperfine coupling constants, $\alpha_{H\alpha} = 2.35$ mT and $\alpha_{H\beta} = 2.04$ mT, are in close agreement with data reported by Kajiwara and Kamachi for *tert*-butyl acrylate.[19,39]

The ESR spectrum obtained in the initial period of *n*-butyl acrylate solution PLP at 60 °C, shown in Figure 3, is significantly different from the ESR spectrum recorded at −50 °C (Figure 2). Visual inspection tells that the spectrum consists of more than 10 components. Linear combination of the four-line spectrum for the SPR species with a three-line spectrum (as used for representing the ESR contour of the MCR so far[16,17,37]) thus will not afford for an adequate fit of the entire ESR spectrum. On the other hand, no reason is seen why, for *n*-butyl acrylate polymerization at 60 °C with pulsed laser initiation being used for controlling polymer size, the dynamics of MCRs should not be sufficiently large to provide identical coupling situations of the radical functionality with each of the two protons of the two adjacent methylene moieties. In MCR1, which is the by far dominant midchain radical species under PLP−SEC polymerization conditions, these two CH_2 moieties are slightly different (see Figure 1), as MCR1 has a short-armed and a long-armed branch. As a consequence, it appears reasonable, if not mandatory, to consider a nine-line spectrum for representation of MCR1. The simulated ESR contour in Figure 3 which results from a linear combination of a nine-line spectrum for MCR1

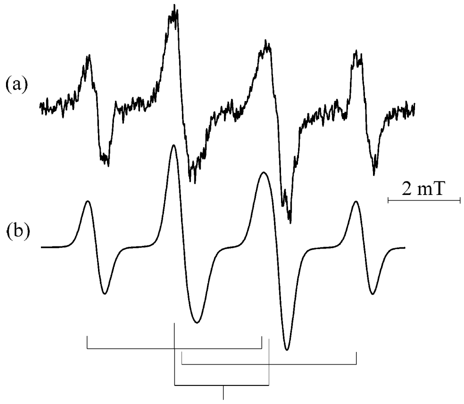

Figure 2. ESR spectrum for *n*-butyl acrylate polymerization: (a) experimental curve recorded during the initial period of a quasi-stationary solution (in toluene) polymerization at −50 °C initiated with 351 nm excimer laser pulses applied at a repetition rate of 20 Hz, $c_{BA} = 1.52$ mol L^{-1}, $c_{MMMP} = 9.0 \times 10^{-3}$ mol L^{-1}; (b) simulated spectrum using hyperfine coupling constants of $\alpha_{H\alpha} = 2.35$ mT and $\alpha_{H\beta} = 2.04$ mT.

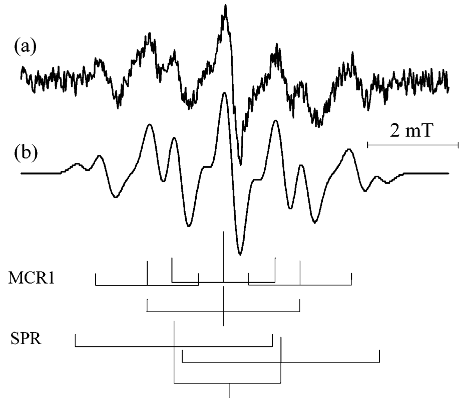

Figure 3. ESR spectrum for *n*-butyl acrylate polymerization: (a) experimental curve recorded during the initial period of a quasi-stationary solution (in toluene) polymerization at 60 °C initiated with 351 nm excimer laser pulses applied at a repetition rate of 20 Hz, $c_{BA} = 1.52$ mol L^{-1}, $c_{MMMP} = 9.0 \times 10^{-3}$ mol L^{-1}; (b) simulated spectrum using hyperfine coupling constants of $\alpha_{H\beta 1} = 1.09$ mT and $\alpha_{H\beta 2} = 1.64$ mT for fitting the nine-line spectrum of MCR1 and using $\alpha_{H\alpha} = 2.35$ mT and $\alpha_{H\beta} = 2.04$ mT (as in Figure 2) for fitting the SPR signal. The contribution of the MCR1 spectrum to the entire ESR signal corresponds to a fraction of 84% MCR1 species being present.

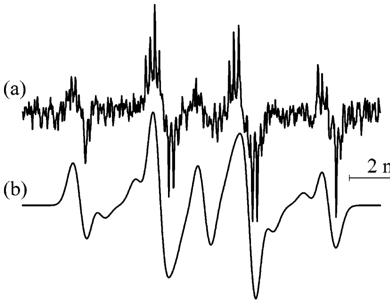

Figure 4. ESR spectrum for *n*-butyl acrylate polymerization: (a) experimental curve recorded during the initial period of a quasi-stationary solution (in toluene) polymerization at −20 °C initiated with 351 nm excimer laser pulses applied at a repetition rate of 20 Hz, $c_{BA} = 1.52$ mol L^{-1}, $c_{MMMP} = 9.0 \times 10^{-3}$ mol L^{-1}; (b) simulated spectrum using the hyperfine coupling constants as in Figure 3. The contribution of the MCR1 spectrum to the entire ESR signal corresponds to a fraction of 36% MCR1 species.

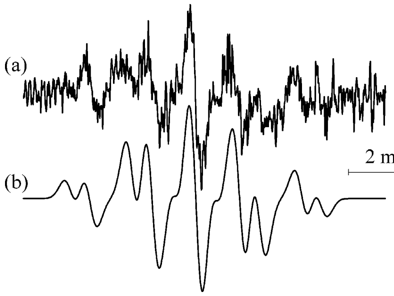

Figure 5. ESR spectrum for *n*-butyl acrylate polymerization: (a) experimental curve recorded during the initial period of a quasi-stationary solution (in toluene) polymerization at 30 °C initiated with 351 nm excimer laser pulses applied at a repetition rate of 20 Hz, $c_{BA} = 1.52$ mol L^{-1}, $c_{MMMP} = 9.0 \times 10^{-3}$ mol L^{-1}; (b) simulated spectrum using the hyperfine coupling constants as in Figure 3. The contribution of the MCR1 spectrum to the entire ESR signal corresponds to a fraction of 76% MCR1 species.

with an SPR spectrum (with the coupling constants as used for the fit in Figure 2) indeed shows nice agreement with the measured ESR spectrum. The hyperfine coupling constants for the two types of slightly dissimilar methylene protons are $\alpha_{H\beta1} = 1.09$ mT and $\alpha_{H\beta2} = 1.64$ mT. In view of these coupling constants, it is noteworthy to add the results of a study by Harbron et al.,[40] who investigated the occurrence of radicals in acrylate and methacrylate polymers created after side chain cleavage by photolysis. In the case of poly(methyl methacrylate), cleavage of the ester side chain results in a radical structure rather similar to species MCR1 or MCR2 with coupling constants in the range of $\alpha_{H\beta1} = 1.13{-}1.17$ mT and $\alpha_{H\beta2} = 1.62{-}1.64$ mT, depending on the stereochemistry of the polymer.

As is demonstrated by Figure 4 and Figure 5, also at intermediate polymerization temperatures of −20 and 30 °C, respectively, the overall contour of the ESR spectrum is adequately fitted by assuming an overlap of a four-line SPR spectrum with a nine-line spectrum for MCR1.

The spectra in Figures 4 and 5 are of poorer signal-to-noise quality than are the ESR spectra taken at both lower and higher temperature. That lower *T* improves the quality of ESR spectra is well-known. The improvement toward higher temperature, in the particular situation of acrylate free-radical polymerization, is due to the fact that at higher *T* the majority of the radicals are long-lived MCR1 species.

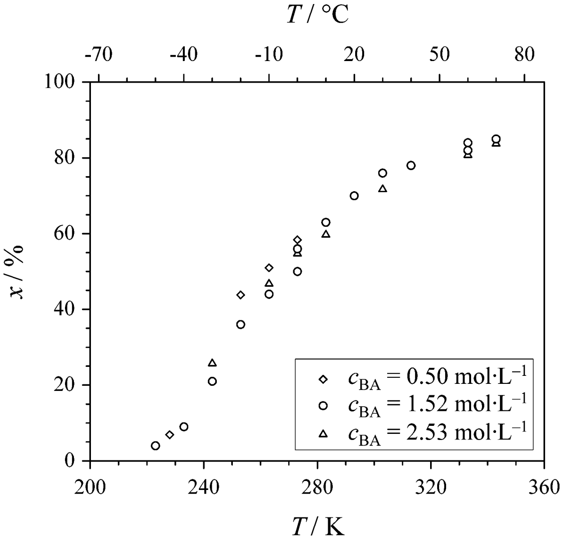

Figure 6. Percentage of midchain radicals, *x*, plotted as a function of polymerization temperature, *T*, for quasi-stationary *n*-butyl acrylate solution polymerizations induced by 351 nm excimer laser pulses applied at a repetition rate of 20 Hz. The data refers to the low-conversion regime of polymerizations with different initial *n*-butyl acrylate concentrations, c_{BA}.

Whereas the low-temperature ESR spectra of this work are close to the literature ones, the ESR spectra measured during polymerization at high temperature are less similar. The reason behind this discrepancy is seen in differences of polymerization conditions other than temperature. Thus, the studies by Yamada and colleagues[16−18] and by Kajiwara and Kamachi[19] have been carried out at higher degrees of monomer conversion, which may lead to the occurrence of both MCR1 and MCR2 species. High conversion may also affect the reorientation dynamics of macroradicals which in turn may be reflected in the shape of the ESR spectrum as, e.g., two methylene protons being equivalent or non-equivalent influences hyperfine splitting. In addition to coil dynamics, also the kinetics of interconversion of different types of radicals may be largely affected by the polymerization conditions. Sato et al.[18] pointed out that the rate of interconversion between terminal and midchain radicals may occur with a complex kinetic scheme that includes backbiting and intermolecular hydrogen transfer with both processes being followed by addition to monomer and/or fragmentation by *β*-scission. Our PLP−ESR studies into *n*-butyl acrylate polymerization appear to deal with a simplified system, one in which, at low degrees of monomer conversion, intermolecular hydrogen transfer plays no major role and where temperature is not sufficiently high to induce a large extent of *β*-scission after backbiting.

Presented in Figure 6 are the results of the deconvolution of the measured ESR spectra into a four-line component assigned to SPR and into a nine-line component assigned to MCR1. The contribution of these individual components to the overall ESR shape yields the fraction of the two types of radicals. Plotted in Figure 6 is *x*, the percentage of midchain radicals MCR1, as a function of polymerization temperature at three initial *n*-butyl acrylate concentrations, c_{BA}.

At the lowest temperature, the amount of midchain radicals is almost negligible, and polymerization essentially occurs via SPR species. With increasing temperature, the fraction of MCRs largely increases and becomes as large as 75% at 30 °C. This observation

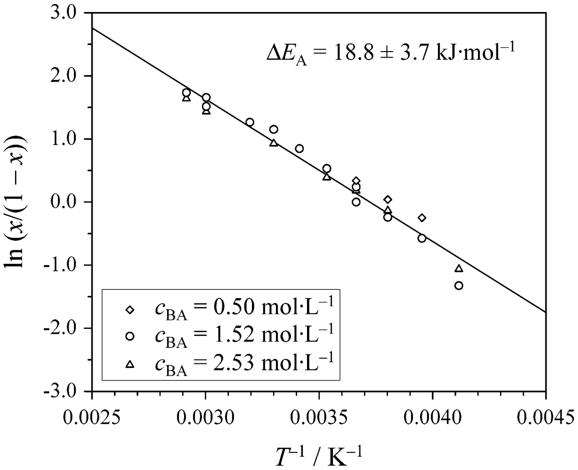

Figure 7. Plot of ln(x/(1 − x)) vs T^{-1} for pulsed laser polymerizations of n-butyl acrylate (see text).

explains the enormous difficulties seen with PLP−SEC experiments on acrylates at temperatures above 30 °C. The large fraction of midchain radicals scrambles the narrow size distribution of propagating radicals and gives rise to broad structureless SEC curves for the PLP-produced polymeric products. This finding is in full agreement with Monte Carlo simulations by Arzamendi et al.[24] It should be noted that a remarkably high fraction of midchain radicals has also been observed by the Yamada group[18] within the ESR studies into UV-induced EHA polymerization. These authors report a midchain radical concentration of 70% for 25 °C which value is in close agreement with the one observed for PLP polymerization of n-butyl acrylate (Figure 6).

The data in Figure 6 for n-butyl acrylate concentrations between 0.50 and 2.53 mol L^{-1} suggest no clear effect of monomer concentration on the percentage of midchain radicals. This result may be understood as being due to the enormous difference in monomer and radical concentrations. Thus, each radical is surrounded by a sufficiently large number of monomer molecules, and the radical−monomer reaction will not be significantly affected by varying n-butyl acrylate content. Assuming that the stationary fraction of midchain radicals under PLP−SEC conditions is given by the difference in the rates of backbiting of an SPR species, which produces midchain radicals MCR1, and of monomer-addition reaction within the resulting monomer-complexed MCR1 species, referred to as MCR1*, yields the following expression:

$$c_{\mathrm{SPR}}/c_{\mathrm{MCR1^*}} = k_p{}^*/k_{\mathrm{bb}} \tag{2}$$

where k_{bb} is the backbiting rate coefficient of SPRs and $k_p{}^*$ is the propagation rate coefficient of MCR1* in the monomer-complexed MCR1* species. Equation 2 may be rearranged into an expression in terms of x, the percentage of MCR1 species.

$$x/(1 - x) = k_{\mathrm{bb}}/k_p{}^* \tag{3}$$

In Figure 7, the logarithm of the right-hand side (rhs) of eq 3 is plotted vs T^{-1} for the n-butyl acrylate. According to the rhs of eq 3, the linear slope of the Arrhenius-type plot of $k_{\mathrm{bb}}/k_p{}^*$ should yield the difference between the activation energies of backbiting of an SPR species, $E_A(k_{\mathrm{bb}})$, and of the propagation reaction from an MCR1* species, $E_A(k_p{}^*)$. The data in Figure 7, which are the ones for conditions where the concentration ratio of MCR1 to SPR radicals is in the range 0.1 and 10, closely fit to a straight line. The difference of activation energies turns out to be $\Delta E_A = E_A(k_{\mathrm{bb}}) - E_A(k_p{}^*) = 18.8 \pm 3.7$ kJ mol^{-1}. With independent information becoming available for $k_p{}^*$, absolute numbers for k_{bb} may be estimated from the ESR spectroscopically measured percentages of midchain radicals. The simplifying assumptions underlying eqs 2 and 3 have to be kept in mind. It seems, however, that they are valid under the PLP−SEC conditions used in the present study. It appears to be a matter of priority to extend such studies to pulsed laser-induced polymerization at higher conversion, where MCR2 species significantly come into play. The difficulties in interpreting ESR spectra at such higher degrees of monomer conversion, which are due to having a mixture of different types of midchain radicals and to effects of chain dynamics on hyperfine coupling constants, may perhaps be overcome by such experiments with pulsed laser initiation.

The large fraction of MCR1 midchain radicals which is associated with a small number of SPR species that do not undergo backbiting in the time period between two successive laser pulses adequately explains the difficulties of applying the PLP−SEC methodology toward k_p analysis of acrylates at temperatures of 30 °C and above. Within a forthcoming study, the percentages of midchain radicals will be determined for acrylates with ester alkyl groups of quite different size.

Conclusions

ESR experiments were carried out during n-butyl acrylate homopolymerization in solution of toluene between −50 and 70 °C. Polymerization was induced by 351 nm excimer laser pulses applied at a repetition rate of 20 Hz. The ESR spectra obtained under pulsed laser polymerization conditions at low degrees of monomer conversion may be adequately represented by the superposition of a four-line spectrum assigned to secondary propagating radicals (SPRs) and a nine-line spectrum assigned to tertiary midchain radicals (MCR1s), which latter radical results from backbiting of SPR species via a 1,5-H shift reaction. The percentage of MCR1 species is negligible at the lowest experimental temperature but increases significantly with temperature. At ambient temperature, about 60% of the stationary radical concentration are MCR1 species. This observation explains the limitations for PLP−SEC experiments on n-butyl acrylate at temperatures of and above 30 °C. The fraction of midchain radicals is highly relevant for modeling overall propagation but also for understanding termination and transfer behavior in acrylate free-radical polymerizations. Within forthcoming studies, midchain radical concentrations will be determined for acrylates differing in both type and size of alkyl ester group. Part of these studies is already underway.

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