PLP Labeling in ESR Spectroscopic Analysis of Secondary and Tertiary Acrylate Propagating Radicals

Michael Buback,* Pascal Hesse, Thomas Junkers,† Tatiana Sergeeva, and Thomas Theis‡

Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany

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Introduction. In addition to the general complexity of detailed analysis of individual kinetic steps in free-radical polymerization, e.g., of deducing chain-length and conversion-dependent rate coefficients, further difficulties are met in acrylate polymerizations where both secondary chain-end and tertiary midchain macroradicals, which show distinctively different propagation and termination behavior, may be present.[1−19] The group of midchain radicals (MCRs) may be further subdivided into radicals which are produced from secondary propagating radicals (SPR) undergoing an intramolecular 1,5-H shift or, via intermolecular transfer, from SPRs that abstract activated hydrogen atoms at arbitrary positions along the chain. The latter reaction encompasses intermolecular transfer as well as intramolecular transfer to remote positions on the same chain. The present contribution considers SPRs and MCRs produced by the intramolecular 1,5-H shift (backbiting) reaction, which is largely favored over intramolecular transfer to other positions along the backbone. The content of MCRs from intermolecular H transfer is considered to be rather low, as monomer conversion does not exceed 30% (at an initial monomer concentration of only 0.5 mol L^{-1}).[18]

The relevant reactions of SPR and MCR species are depicted in Scheme 1 together with the associated rate coefficients. Transfer to monomer, intermolecular transfer to polymer, and β-scission reactions of macroradicals are not included. SPRs formed by monomer (M) addition to primary initiator-derived radicals may propagate with the rate coefficient k_p^{SPR}, undergo backbiting with the rate coefficient k_{bb} (to produce an MCR), or terminate by reaction with an SPR (k_t^{SPR}) or with an MCR (k_t^{cross}). The MCRs may react back to SPRs by addition of a monomer molecule with the rate coefficient, k_p^{MCR}, or terminate with an SPR (k_t^{cross}) or an MCR (k_t^{MCR}). In case that radical termination is not too fast, backbiting in conjunction with propagation from a midchain radical may result in an equilibration of the SPR and MCR species, with the equilibrium concentrations depending on monomer content.

Electron spin resonance spectroscopy (ESR) is well suited for the analysis of different types of radicals. Because of band overlap, the ESR signals of SPRs and MCRs are, however, not easily separated,[3,4,12,14] and the associated concentrations are difficult to obtain. The band assignment may be facilitated by ESR analysis under pulsed laser polymerization (PLP) conditions. The ESR spectrum of SPRs should reflect laser pulsing to a larger extent, as the termination rate of SPRs is supposed to be much higher than the one of MCRs ($k_t^{SPR} \gg k_t^{cross}$, k_t^{MCR}).[17,19]

Within the present study, PLP-ESR experiments have been carried out on dodecyl acrylate (DA) in dilute solution (0.5 mol L^{-1}) of toluene at monomer-to-polymer conversions below 30%. Radical concentrations of about 10^{-6} mol L^{-1} are produced in the sample volume of 0.2 mL by photoinitiation. In addition to unambiguously assigning the SPR and MCR contributions to the ESR spectrum, our study is directed toward finding novel methods for obtaining insight into the kinetics of acrylate macroradicals.

Experimental Section. Dodecyl acrylate (Fluka, techn.), which actually is a mixture of DA (>55%) and tetradecyl acrylate, contains hydroquinone monomethyl ether as a stabilizer. The monomer was purified by passing through a column filled with "inhibitor−remover" (Aldrich, product no. 311332). 0.5 mol L^{-1} of the monomer in solvent (toluene, Fluka, p.a.) was degassed by several freeze−pump and thaw cycles. The photoinitiator, α-methyl-4-(methymercapto)-α-morpholinopropiophenone (MMMP, Aldrich, 98%), was used as received and was added to the monomer−solvent solution under an argon atmosphere. About 0.2 mL of the resulting mixture was filled into an ESR quartz tube of 5 mm o.d., 4 mm i.d., and 25 mm length. The sample tube was closed with a plastic cap and sealed with PARAFILM. The entire preparation of the sample tube was carried out in a glovebox under an argon atmosphere. Immediately after preparation, the sample tube was placed into the resonator cavity (equipped with a grid to allow for illumination) of a Bruker Elexsys E 500 CW-ESR spectrometer, operating in the X-band, where it was brought to the desired reaction temperature. The ESR spectra of the monomer−photoinitiator−toluene solutions were recorded either under laser pulsing at repetition rates of 10 or 20 Hz by a COMPex 102 excimer laser (Lambda Physik) or under continuous illumination by a 500 W mercury UV lamp (LAX 1450, Müller Elektronik). The ESR spectra were measured within the magnetic field range from either 330 to 340 mT or 329 to 341 mT by a single scan of 10.49 s duration, with a time constant of 0.01 ms and a conversion of time 10.24 ms, using 100 kHz field modulation (amplitude 0.1 mT) and a microwave power of 10 mW. The high microwave power was used for obtaining an ESR signal of sufficient intensity at the short scanning times. Absolute radical concentrations were obtained by calibration with a 10^{-5} M solution of TEMPO (Aldrich, 99%) in toluene containing 0.5 M dodecyl acrylate under otherwise identical experimental conditions.

Results and Discussion. ESR spectra during polymerization of 0.5 mol L^{-1} DA in toluene were recorded at several temperatures, between −40 and +60 °C. Shown in Figure 1 are ESR spectra for the two limiting temperatures measured at a laser pulse repetition rate of 20 Hz. The four-line spectrum (Figure 1a) was recorded at −40 °C. A four-line spectrum was also observed by Kajiwara for *tert*-butyl acrylate (*t*BA) polymerization in toluene at −30 °C and for a dimeric model radical of *t*BA at temperatures from −30 up to +150 °C.[20] The attractive aspect of studying the dimeric radical relates to the fact that this species cannot undergo a 1,5-H shift reaction to yield a midchain radical. The spectra presented by Kajiwara were convincingly assigned to SPR species, as were the low-temperature ESR spectra obtained in our preceding study into

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* Corresponding author: e-mail mbuback@gwdg.de, phone +49-551-393141, fax + 49-551-393144.

† Current address: School of Chemical Sciences and Engineering, University of New South Wales, Sydney, NSW 2052, Australia.

‡ Current address: Department of Chemistry, University of California, Berkeley, CA 94720-1460.

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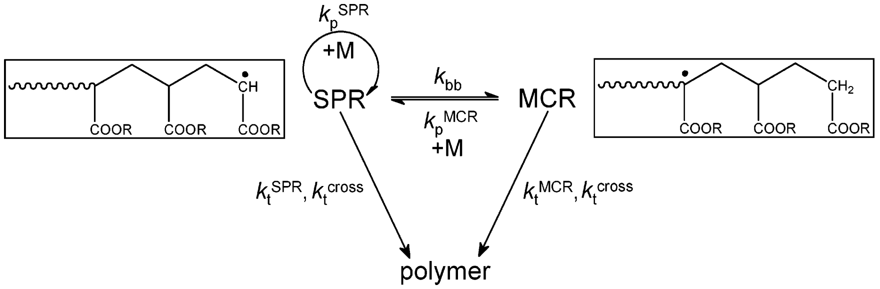
Scheme 1. Schematic View of the Relevant Propagation, Termination, and Transfer Reactions of Secondary Propagating Radicals (SPR) and Midchain Radicals (MCR) which Occur during Acrylate Polymerization



n-butyl acrylate (BA).[14] The splitting scheme of the SPR spectrum, which actually consists of a six-line spectrum that, due to line broadening, similarity of the coupling constants, and resulting partial overlap, reduces to a four-line contour may be adequately described by hyperfine coupling with the proton in the α-position and two equivalent protons in the β-position. The coupling constants, $\alpha_{H\alpha} = 2.26$ mT and $\alpha_{H\beta} = 2.12$ mT, deduced from the spectrum at low *T*, are very close to the associated literature data for BA and *t*BA, respectively.[14,20] Matsumoto and Giese reported narrow 16-line spectra for an acrylate type secondary radical with identical $\alpha_{H\alpha}$ and $\alpha_{H\beta}$ values in the range of 2.08 mT and a weak long-range coupling to the protons of the methyl ester moiety (∼0.14 mT).[21] Such a spectrum may reduce to a four-line contour similar to the one in Figure 1a in the case of pronounced broadening. Several effects may contribute to the experimentally observed line broadening. It has, however, been checked that, for the applied range of microwave power, line broadening is not caused by power saturation. The primary reason for band broadening with our system appears to be that the radicals are widely differing in size.[22]

The ESR spectrum recorded during DA polymerization at +60 °C (Figure 1b) differs from the one taken at −40 °C in that a seven-line spectrum is seen. The spectrum in Figure 1b is very similar to the one reported by Kajiwara[20] for photoinduced *t*BA polymerization in toluene solution at 60 °C and to the one recorded during PLP-induced polymerization of BA at 60 °C.[14] According to the earlier discussion,[14] the observed seven-line spectrum is due to the MCR species. The spectrum, which actually consists of nine lines, is understood as resulting from the hyperfine coupling of two pairs of protons at methylene moieties with the unpaired electron on the carbon atom in between. The hyperfine coupling constants, $\alpha_{H\beta1} = 1.07$ mT and $\alpha_{H\beta2} = 1.73$ mT, are close to the literature values for BA.[14]

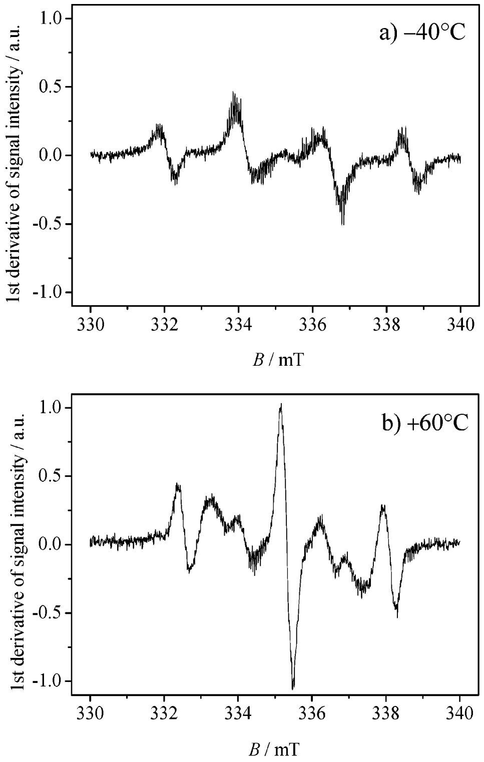


Figure 1. ESR spectra recorded under PLP conditions at a laser pulse repetition rate of 20 Hz for dodecyl acrylate in solution of toluene, $c_{DA} = 0.5$ mol L^{-1}, at −40 °C (a) and 60 °C (b).

The spectrum for 60 °C in Figure 1b appears to be essentially due to MCR species, whereas the four-line spectrum for polymerization at −40 °C primarily represents SPR radicals. It needs to be noted that the radical concentration associated with the spectrum in Figure 1a is by about a factor of 2 below the one for the spectrum in Figure 1b, although photoinitiator concentration, laser pulse intensity, and the parameters of the ESR instrument were identical for the −40 and +60 °C experiments in Figure 1. The difference suggests that the rate of termination for SPRs at −40 °C is even above the one for MCRs at a temperature as high as 60 °C.

A particularly interesting feature with the spectra in Figure 1a,b relates to the fact that, contrary to what one would expect, a stronger scattering seems to occur at the lower temperature. Closer inspection of the oscillations on the signal in Figure 1a, as will be illustrated in more detail further below, reveals that the seemingly scattered contour consists of individual lines separated by 0.048 mT. At a sweep time of 10.49 s for the entire magnetic field range from 330 to 340 mT, this spacing corresponds to the time interval of 0.05 s, which is the duration of the dark time between two successive laser pulses at a repetition rate of 20 Hz. The oscillations thus do not reflect poor signal-to-noise but represent the time dependence of SPR concentration, which sharply increases upon firing the laser pulse and decays during the subsequent dark-time period, before being enhanced again upon the arrival of the next pulse after 0.05 s.

Under pseudo-stationary conditions, which are reached after applying a few laser pulses, the decay of MCR concentration by either termination or propagation to yield SPRs, which may subsequently terminate, is too slow as to result in any pronounced decrease in MCR content during the short dark-time period. The production of MCRs by backbiting also seems to be not sufficiently fast as to induce a sharp increase of MCR concentration upon laser irradiation associated with a burst of new SPRs. As a consequence, the contour of the ESR spectrum in Figure 1b is rather smooth. Only in the field range where SPRs slightly contribute to the spectrum is some fluctuation seen. Scanning the ESR spectrum under periodic application of laser pulses thus allows for distinguishing spectral features due to SPRs and MCRs. In addition, ESR bands measured at different pulse repetition rates contain a wealth of kinetic

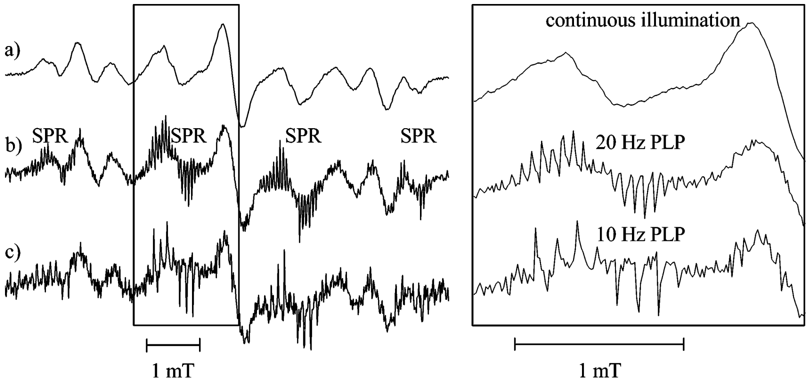


Figure 2. ESR spectra of 0.5 mol L^{-1} dodecyl acrylate in toluene, $c_{\mathrm{MMMP}} = 1.1 \times 10^{-2}$ mol L^{-1}; scanned at $T = 0$ °C under (a) continuous illumination and under PLP conditions at laser pulse repetition rates of 20 Hz (b) and 10 Hz (c). The positions of the ESR bands due to secondary propagating radicals are indicated by "SPR".

information that may be used for deducing rate coefficients associated with the two types of radicals.

At intermediate temperatures, contributions of both SPRs and MCRs should be clearly detectable in the ESR spectra. Shown in Figure 2 are three ESR spectra measured during DA polymerization in toluene solution at 0 °C with a sweep width of 12 mT and a sweep time of 10.49 s. The spectrum in Figure 2a, which was recorded under continuous irradiation with a UV lamp, exhibits lines for SPRs and MCRs. Interestingly, throughout the entire range, the signal-to-noise quality remains unchanged, which supports the view that the fluctuations in Figure 1 are due to laser-pulse-induced variations in SPR concentration rather than to noise. The spectrum recorded under laser pulsing with a repetition rate of 20 Hz (Figure 2b) corresponds to the overlay of the two types of spectra shown in Figure 1a,b with fluctuations occurring at the indicated SPR positions and with the contour being smooth at the MCR positions. Given on the rhs of Figure 2 is an enlarged section of the spectrum, which demonstrates an equidistant spacing, by 0.058 mT, of the SPR contour for the 20 Hz PLP-ESR experiment, whereas no fluctuations are seen on the MCR band.

The spectrum in Figure 2c has been recorded at 10 Hz, i.e., with a 0.1 s spacing between successive laser pulses, corresponding to a magnetic field difference of 0.116 mT at the particular scanning rate. The spacing between the fluctuations on the SPR contour is twice as large as with the 20 Hz PLP-ESR spectrum. As radical loss due to termination is stronger during the longer dark time period, the resulting spikes are more pronounced for 10 Hz than for 20 Hz. At the 10 Hz pulse repetition rate, also the ESR band of the MCR species shows some fluctuation (see the enlarged spectral section in Figure 2c).

The results of our novel PLP-ESR procedure show an immediate increase of SPR concentration after firing the laser pulse which reflects the fast monomer addition to initiator-derived radicals. The subsequent decrease of SPR concentration is caused by rapid termination together with some backbiting. The weaker fluctuations of MCR content are due to slower production, via backbiting, and to slower loss, via termination and via propagation from midchain radical positions. The difference in time evolution of SPR and MCR radicals during the dark-time period between two laser pulses suggests that, at the experimental conditions of 0 °C and 0.5 mol L^{-1} DA concentration, the interconversion between SPRs and MCRs via backbiting and propagation of MCRs, respectively, occurs at a significantly slower rate than does termination of SPRs. The ESR spectra indicate that k_t^{SPR} is significantly above k_t^{cross} and k_t^{MCR}. This result is in perfect agreement with evidence from recent PLP-SEC and chemically induced polymerization studies into BA under conditions where SPR and MCR species are present.[17,19] It is a matter of priority to further improve the quality of PLP-ESR experiments and to fully exploit the kinetic information contained in the ESR spectra scanned during pulsed laser initiation using a wide range of repetition rates.

Conclusion. Initiation by pulsed lasers in conjunction with ESR spectroscopic detection allows for the unambiguous assignment of contributions to the resulting ESR spectrum associated with chain-end and midchain radicals. PLP-ESR experiments on dodecyl acrylate in toluene solution at 0 °C reveal that, under these reaction conditions, backbiting of SPRs and propagation from MCRs are slow processes as compared to termination of secondary radicals which latter process is also significantly faster than termination of tertiary radicals.

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