Pushing the Limit: Pulsed Laser Polymerization of *n*-Butyl Acrylate at 500 Hz

Christopher Barner-Kowollik,* Fabian Günzler, and Thomas Junkers*

Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Universität Karlsruhe (TH)/Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany

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Introduction. Pulsed laser polymerization (PLP) coupled with size exclusion chromatography (SEC)[1−3] is the standard technique to measure propagation rate coefficients for radical polymerization.[4] In this procedure, the polymerization is initiated by laser pulses at a constant repetition rate. With each laser pulse, chain growth is not only started but also largely terminated as the initiator-derived radical fragments (as well as short propagating radicals) quench most of the propagating chains. Therefore, and unless conventional termination is not dominating over the chain-stopping action of the laser pulses, the resulting polymer material is of the characteristic chain length that corresponds to the dark time between two consecutive laser pulses, t_0, as well as the propagation rate coefficient, k_p (and monomer concentration, c_M). As a set of active chains survives the quenching by newly generated radicals, not only polymer with the length corresponding to one dark time period is found but also "overtones" corresponding to two or more multiples of t_0 are formed, which results in a very specific molecular weight distribution, often referred to as the PLP distribution or PLP structuring. The characteristic chain lengths L_i are given by the simple relation of

$$L_i = k_p c_M i t_0 \qquad \text{where } i = 1, 2, 3, ... \tag{1}$$

Because of its relative precision, reliability, and simplicity, the PLP−SEC technique is the IUPAC-recommended technique[5] to determine k_p, and a series of papers have been dedicated to produce benchmark values for the most important monomers.[5−10] For acrylates (one of the most important type of monomers), however, no satisfactory data could be obtained for temperatures above ambient values, a difficulty that was addressed in 2005 in a joint publication by the IUPAC working party "modeling of polymerization kinetics and processes", which identified the extensive occurrence of transfer to polymer reactions, namely the so-called backbiting reaction,[11,12] to be responsible for the loss of PLP structuring of samples obtained at technically relevant temperatures.[13−16] Via transfer to polymer, the propagating radicals are converted into a relatively stable intermediate species, so-called midchain radicals (MCR), that can either undergo scission, termination, or monomer addition reactions.[11] Although monomer addition leads to retrieving a secondary propagating radical chain end, the much slower rate at which those radicals initially propagate[17] causes severe blurring of the chain length distribution and thus the loss of a clear PLP distribution.[18] Although attempts have been made to overcome these problems,[14] no completely reliable data were obtained so far, and only extrapolations for k_p from low-temperature data are in use up to date. A determination of k_p at higher temperatures (for reasons detailed below) does only yield the rate coefficient for secondary propagating radicals (SPRs) and not the effective propagation rate of the polymerizing system, which number is probably of higher practical interest. However, effective propagation rates can be calculated when all relevant rate parameters are known,[9,19] which demands highly accurate data for the individual reaction steps. It is thus mandatory to determine k_p of acrylate monomers in a wide temperature range with high accuracy.

We herein report the determination of *n*-butyl acrylate (BA) k_p from PLP at 500 Hz repetition rate up to 70 °C, a temperature range that has not been accessible before. High energy output lasers with comparable frequencies have only recently become available, and to the best of our knowledge we are the first to report successful PLP at such high laser repetition rates.

Experimental Section. Bulk monomer solutions of BA containing 5×10^{-3} mol L^{-1} initiator (2,2-dimethoxyacetophenone, DMPA) were transferred into sample vials (containing about 0.2 mL of reaction solution each) and sealed with rubber septa. Oxygen was removed by purging the samples with nitrogen for about 2 min. The sample vial was then placed into a stainless steel sample holder that was brought to temperature by a thermostat (VWR 1196D). Temperature was measured directly at the sample. The samples were allowed to equilibrate in temperature for about 5 min and were subsequently initiated by laser pulsing at constant repetition rates of up to 500 Hz. Laser initiation was achieved by a Xantos XS-500 (which is a compact version of the ExciStar EXS-500) operated at the XeF line of 351 nm. The laser beam, which was adjusted to an energy of close to 2.5 mJ/pulse hitting the sample, was redirected to illuminate the vial from the bottom. The laser pulsing causes an increase in temperature, which however was found to not exceed 1 °C with the number of pulses applied in the present work. After polymerization, hydroquinone/methanol solution was added to the samples, which were subsequently placed in a vacuum oven for the evaporation of the solvent and monomer. Monomer conversion was determined gravimetrically. Information on the materials and on SEC analysis can be found in the Supporting Information.

Results and Discussion. The choice of the pulsed laser light source for experimental PLP setups largely depends on three factors. One is of course the wavelength of the emitted light, one the energy level of each laser pulse, and the other the maximum pulse frequency. Criteria such as pulse width and energy stability, in other application areas such as lithography and pulsed laser deposition of paramount importance, need less consideration when performing pulsed laser polymerizations. Variations in laser energy (which for most laser systems are minimized to few percent) are averaged over the course of an experiment, and pulse widths (typically around ∼20 ns) are generally negligible on the time scale of polymerizations. The choice of wavelength depends on the employed photoinitiator, and usually lasers emitting light close to 350 nm are used, as this wavelength allows for the decomposition of most common initiators while the monomers themselves are not excited. High laser energies provide high initiating radical concentrations which are favorable for PLP experiments, although a fast decay of the initiator causes significant changes in radical concentrations over the course of a typical experiment and thus aids in

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* Corresponding authors: Tel +49 721 608-5641; Fax +49 721 608-5740; e-mail christopher.barner-kowollik@polymer.uni-karlsruhe.de, thomas.junkers@polymer.uni-karlsruhe.de.

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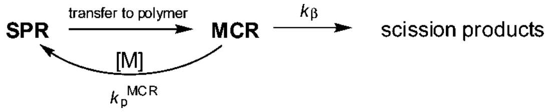
Scheme 1. Simplified Reaction Scheme for the Interconversion of Secondary Propagating Radicals (SPRs) and Midchain Radical (MCR) Species



obtaining well-structured molecular weight distributions.[15] However, by employing comparatively high initiator concentrations or by applying a larger number of laser pulses, also lower laser energies might be employed. In the case of BA k_p determination, pulse energies ranging from 2 to 60 mJ/pulse were employed in previous studies.[9]

The pulse frequency ν is somewhat related to the question of pulse energy. Generally, an increase in pulse frequency is bought in by a reduction of the individual pulse energy. Until recently, the technical limit for laser systems that allowed for reasonable pulse energies was around 100 Hz. For many monomers, frequencies below 100 Hz are used as the repetition rate must be chosen such as to allow for sufficient chain growth between two pulses in order to allow for good distinction between the overtones. The newest generation of excimer lasers that are commercially available are able to provide pulse frequencies of up to 500 Hz at the XeF line of 351 nm while yet providing pulse energies of several mJ/pulse. This technological advancement has immediate benefits: (i) k_p determination of ultrafast monomers becomes easier as the molecular weight range can be brought down to a more desirable range while concomitantly (ii) allowing for more degrees of freedom when the laser is used only to obtain polymer with limited molecular weight without the use of transfer agents.[20,21] (iii) More importantly, high-frequency pulsing allows for the determination of acrylate k_p in a wider temperature range. When lasers of up to 100 Hz are used, no k_p can be obtained from PLP−SEC on e.g. BA above ambient temperature, which is a consequence of the occurrence of transfer-to-polymer reactions in which the SPR is converted into an MCR. Different transfer mechanisms are in place, and a complex set of reactions results from the occurrence of MCRs. A thorough discussion of these reactions[11] is beyond the scope of this Communication.

Scheme 1 summarizes the effect that transfer to polymer reactions have. The SPRs are converted into MCRs. Those species can subsequently undergo termination reactions, monomer addition, or release a shortened radical via β-scission. Both monomer addition and β-scission convert an MCR back into a more reactive SPR; however, in both cases the time−chain length correlation that is strictly required for successful PLP−SEC is lost. This loss is due to the effective retardation in overall propagation caused by the much higher stability of an MCR and due to the chain breakage event of the scission reaction.

Thus, as the time−chain length correlation becomes increasingly distorted with time, faster pulsing should improve the situation as the terminating action of the next laser pulse can take place before too many MCRs are formed. Diminishing the effects from MCRs is hence a prerequisite for a successful PLP−SEC experiment, and in consequence, the k_p of the SPRs is determined rather than the actual effective propagation rate that would be found under stationary reaction conditions. Figure 1 depicts the difference in the experimentally observed PLP structures when the laser repetition rate is increased from 100 to 500 Hz. On the right-hand side, the poly(butyl acrylate) molecular weight distribution obtained from PLP at 100 Hz and 33 °C is shown (dotted line) in conjunction with the first derivative of the distribution. As can be seen, the molecular weight distribution shows some structuring as a result of the laser pulsing, and a shoulder on the high molecular weight side of the distribution is clearly visible. This shoulder translates into an inflection point that however converges into a saddle point due to broadening of the distribution. While the first point of inflection L_1 could in principle be used to determine k_p, the consistency criterion for reliable PLP experiments[5] is not fulfilled as exact positioning of L_2 is not possible. This observation is in good agreement with a large number of studies on the propagation rate of BA. Indeed, for the IUPAC paper on BA only data up to 20 °C were taken into consideration for deriving benchmark Arrhenius values.

A very different situation is at hand when the laser frequency is raised to 500 Hz. Not only is a shoulder for the higher molecular weight fractions observable, but even a multimodal distribution is obtained. When the first derivative is examined, three (if not four) points of inflection are observed with ease. The spacing between L_1 and L_2 adds up to 0.295 logarithmic units (factor 1.97), which translates to a match of almost 99% between k_p calculated from each individual point. The spacing between L_1 and L_3 (0.503 log-units, corresponding to a factor of 3.18) leaves a only slightly higher error. It should be noted that by IUPAC recommendation a variation of pulse frequency should be carried out to test for independence of k_p of the dark time between two pulses. Such additional check was not carried out for the present study as a change in the PLP distributions is indeed expected by the transfer reactions taking place as was

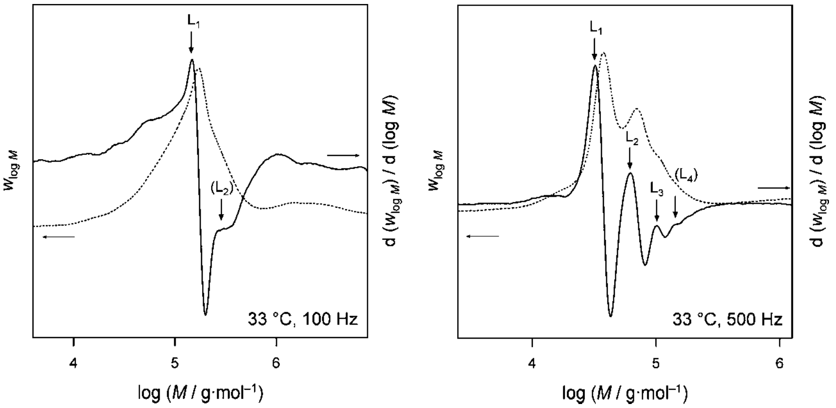


Figure 1. Molecular weight distributions and their derivatives from polymer generated by PLP of *n*-butyl acrylate at 33 °C. The left panel depicts a sample from laser pulsing at 100 Hz and the right panel from pulsing with 500 Hz and otherwise identical conditions.

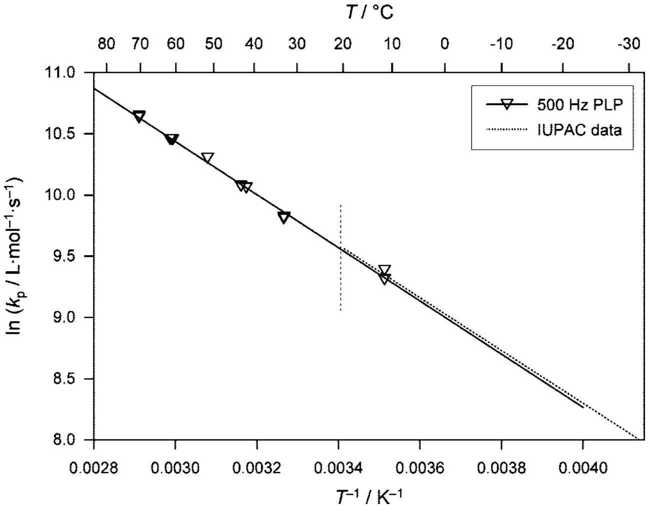


Figure 2. Arrhenius plot for the *n*-butyl acrylate k_p data obtained at 500 Hz. The dotted line represents the best fit of the IUPAC benchmark data. The vertical dashed line marks the temperature limit up to which k_p could be obtained with 100 Hz lasers.

shown by Nikitin et al.[17,19] Thus, all experiments were carried out at the maximum repetition rate of 500 Hz.

With increasing temperature, the PLP-derived molecular weight distributions slowly start to lose their characteristics. Such a behavior is expected, as backbiting and MCR follow-up reactions become more and more dominant, as even pulsing at 500 Hz is not fast enough to counteract the disturbing influences of MCR formation from a certain point on. (All molecular weight distributions and their derivatives used for k_p determination in the framework of the present study are shown in the Supporting Information alongside a table with all experimental data.) It is, however, not until 80 °C that no second point of inflection can be observed. However, already at 70 °C, another effect is observable in that a shoulder on the low-molecular-weight side of the distribution becomes visible. This shoulder, likely caused by the increasing importance of β-scission and/or the termination of radicals that have undergone an intramolecular transfer reaction, prevents an exact determination of the first inflection point already at 75 °C as the characteristic inflection point is absorbed by the rising shoulder. In principle, the second point of inflection could also be used to calculate k_p. However, an increasing discrepancy between $k_{p,1}$ and $k_{p,2}$ (that is, k_p obtained from L_1 and L_2, respectively) is observable with increasing temperature. Such difference is easily explainable by the retarding effect the MCRs have. As the chains at L_2 grew twice as long as the ones at L_1, they underwent more transformations into MCRs and back, thus resulting in shorter chains than anticipated. Thus, L_2 is no good measure for k_p at elevated temperatures (the difference between $k_{p,1}$ and $k_{p,2}$ at 70 °C is already 15%, which may be regarded to be the largest tolerable difference for a successful PLP−SEC experiment).

Figure 2 depicts the Arrhenius plot for k_p in the temperature range from 10 to 70 °C. Also shown are the IUPAC benchmark k_p data (dotted line).[9] It is immediately evident that the 500 Hz data are in excellent agreement with the benchmark data collated from data between −65 and 20 °C. The new data yield an activation energy of $E_A = 18.1$ kJ mol^{-1} and a frequency factor of $A = 2.31 \times 10^7$ L mol^{-1} s^{-1} whereas the IUPAC working group reported 17.9 kJ mol^{-1} and 2.21×10^7 L mol^{-1} s^{-1}.[9] It is hence not surprising to find that a joint fit of the 10−70 °C data with the data collected in the IUPAC benchmark publication yields very similar values of $E_A = 17.8$ kJ mol^{-1} and $A = 2.13 \times 10^7$ L mol^{-1} s^{-1} (see Figure S1 in the Supporting Information), hence giving validation to the extrapolated k_p data that are in use so far. Given the success of our high-frequency pulsing approach, it now seems to be a matter of priority to investigate a wide range of different acrylates with the new laser system at such frequencies and to provide reliable high temperature kinetic data for those other monomers, too.

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Supporting Information Available: Tabulated experimental data, molecular weight distributions, and their derivatives for all samples, a joint linear regression plot, and experimental details on SEC. This material is available free of charge via the Internet at http://pubs.acs.org.

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