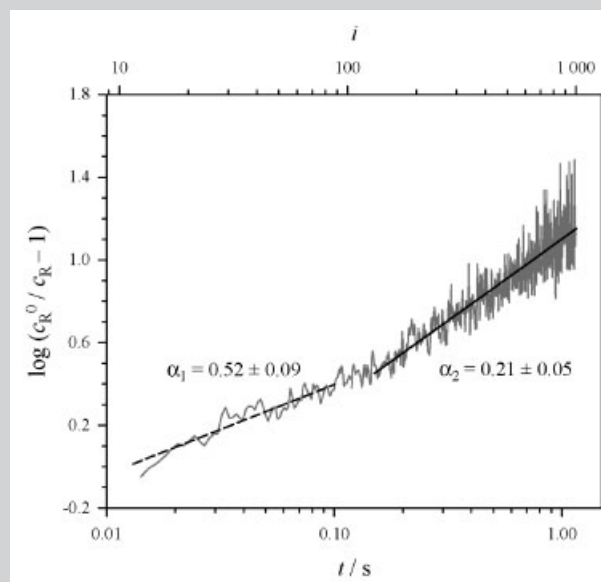


**Summary:** A novel method for measuring termination rate coefficients,  $k_t$ , in free-radical polymerization is presented. A single laser pulse is used to instantaneously produce photoinitiator-derived radicals. During subsequent polymerization, radical concentration is monitored by time-resolved electron spin resonance (ESR) spectroscopy. The size of the free radicals, which exhibits a narrow distribution increases linearly with time  $t$ , which allows the chain-length dependence of  $k_t$  to be deduced. The method will be illustrated using dodecyl methacrylate polymerization as an example.

Two straight lines provide a very satisfactory representation of the chain-length dependence of  $k_t$  over the entire chain-length region ( $c_R$  = radical concentration).



## Free-Radical Termination Kinetics Studied Using a Novel SP-PLP-ESR Technique

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### Introduction

The detailed understanding of diffusion-controlled termination processes in free-radical polymerization (FRP) is both scientifically attractive and technically relevant. Several laser-assisted techniques for measuring the termination rate coefficient,  $k_t$ , have been developed since the late 1980s.<sup>[1]</sup> The so-called SP-PLP (single-pulse pulsed-laser polymerization) method allows  $k_t$  to be measured as a function of both monomer conversion and free-radical chain length.<sup>[2]</sup> In SP-PLP, monomer conversion as a function of time  $t$  after applying a laser pulse (of about 20 ns width) at  $t = 0$ ,  $c_M(t)$ , is monitored by online near-infrared (NIR) spectroscopy with a time resolution of microseconds.<sup>[3]</sup> Under ideal polymerization conditions, that is, when a “perfect” photoinitiator (one which decomposes into two growing primary radical species) is used,<sup>[4]</sup> and as

long as chain transfer may be neglected, the SP-PLP experiment yields a close-to-monodisperse radical chain-length distribution (CLD) with the degree of polymerization,  $i$ , linearly increasing with time  $t$ . The expression for  $i$  reads:  $i = k_p c_M t$ , where  $k_p$  is the propagation rate coefficient. The SP-PLP technique allows the chain-length dependence of  $k_t$  to be analyzed within an extended region of monomer conversions.<sup>[2]</sup> The primary experimental quantity from SP-PLP is  $k_t/k_p$ .  $k_t$  is obtained by implementing  $k_p$  values from independent experiments by the IUPAC-recommended pulsed-laser polymerization size-exclusion chromatography (PLP-SEC) technique.<sup>[5,6]</sup> The measurement of  $k_t$  by SP-PLP is indirect in that the time-dependence of monomer concentration, rather than that of radical concentration, is measured. Time-resolved measurements of macroradical concentration,  $c_R$ , by electron spin resonance (ESR) spectroscopy were first carried out by Westmoreland

et al.<sup>[7]</sup> and by Zhu et al.<sup>[8]</sup> Westmoreland et al. measured  $c_R$  during high-conversion semi-continuous emulsion copolymerization processes. Nonstationary conditions were achieved by shutting down the flow of a redox initiator. Absolute radical concentration was determined from ESR peak heights. Zhu et al. carried out time-resolved ESR measurements on methyl methacrylate bulk polymerizations at 25 °C under “post-effect” conditions, which were created by switching off the UV lamp used for inducing 2,2'-azoisobutyronitrile (AIBN) decomposition. The decay in radical concentration was monitored by measuring the height of the central line of the ESR spectrum.

The ESR studies into  $k_t$  carried out in those works were limited in that: (i) initiation could not be instantaneously stopped; (ii) the CLD of radicals at  $t = 0$  (that is, at the moment when either photoinitiation or the addition of an initiator ceased) was broad. These limitations may be overcome by using time-resolved ESR spectroscopy in conjunction with initiation by a single laser pulse, in which case primary radicals are produced (almost) instantaneously. There is no initiation in the dark-time period as initiation starts sharply at  $t = 0$ . Moreover, the free-radical CLD is close to monodisperse (of Poisson-type) throughout the entire experiment unless chain-transfer processes come into play. Under ideal conditions, termination kinetics follows Equation (1):

$$-\frac{dc_R}{dt} = 2 \cdot k_t(i, i) \cdot c_R^2 \quad (1)$$

in which  $k_t(i, i)$  is the rate coefficient for termination of two radicals of identical size,  $i = k_p c_M t$ . As the dependence of  $k_p$  on chain length (CL) will be restricted to lower values up to  $i = 10$ , it seems justified to use constant  $k_p$  for modeling the extended CL region up to  $i = 1000$ . To distinguish the novel technique from the existing SP-PLP method, it will be referred to as SP-PLP-ESR, whereas the established method will be referred to as SP-PLP-NIR. An important advantage of SP-PLP-ESR over SP-PLP-NIR is that  $k_t(i, i)$  can be determined by a single differentiation of  $c_R$ , see Equation (1), whereas  $c_M(t)$  data from SP-PLP-NIR need to be differentiated twice to yield  $k_t(i, i)$ . Thus, even a model-free determination of  $k_t(i, i)$  may come into reach using SP-PLP-ESR.

The intention of the present paper is to demonstrate the potential of the new technique toward measuring the dependence of  $k_t$  on both chain length and monomer conversion. The experiments were carried out on dodecyl methacrylate (DMA) at ambient pressure, 0 °C, and monomer conversions up to 30%. The DMA conversion induced by a single laser pulse is typically around 0.05%.  $k_t$  of DMA has already been investigated using SP-PLP-NIR at 40 °C and 1000 bar.<sup>[9]</sup> Increasing temperature and pressure enhance the propagation rate and thus favorably affect the quality of the SP-PLP-NIR signal. No such enhancement is required for SP-PLP-ESR studies into  $k_t$ .

## Experimental Part

ESR spectra were recorded on a Bruker Eleksys® E 500 series CW-EPR spectrometer. The sample solution was contained in a quartz tube of 5 mm outer diameter and of 4 mm inner diameter. 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. The laser energy per pulse was around 50 mJ. The cylindrical axis of the sample tube was perpendicular to the direction of the laser beam. The ESR spectrometer and the excimer laser were triggered by a pulse generator (Scientific Instruments 9314). The decay in radical concentration after a single laser pulse was measured in a fixed magnetic field by the central line of the ESR spectrum (see Figure 1).<sup>[7,8]</sup> That the intensity at the peak maximum is proportional to the double integral of an ESR spectrum, which is an accurate measure of radical concentration, was carefully checked before each experiment. Absolute radical concentrations were calibrated using 2,2,6,6-tetramethylpiperidine-*N*-oxy (TEMPO, 99%, Aldrich Chemie) dissolved in DMA under conditions as close as possible to those of the actual SP-PLP-ESR experiment.

In order to improve the signal-to-noise ratio, up to 20 individual  $c_R(t)$  traces from independent SP-PLP-ESR experiments (carried out within a short time interval in which overall monomer conversion increases by one to two per cent) were co-added. In between applying such series of laser pulses, the ESR tube was inserted into the sample chamber of an IFS 88 FT-NIR spectrometer (Bruker) and the absolute (overall) monomer concentration was measured by the absorbance at around  $6160 \text{ cm}^{-1}$  of the first C–H stretching overtone (at the C=C double bond).<sup>[10]</sup> IR absorbance is reproducibly measured by passing an IR light beam of 1 mm diameter through the central part of the ESR tube at right angle to the cylindrical axis.

The photoinitiator  $\alpha$ -methyl-4(methylmercapto)- $\alpha$ -morpholinopropiophenone (MMMP, 98%, Aldrich Chemie) was used as received at initial concentrations of about  $3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ . In a glove box, under an argon atmosphere, MMMP was added to DMA and the solution was filled into

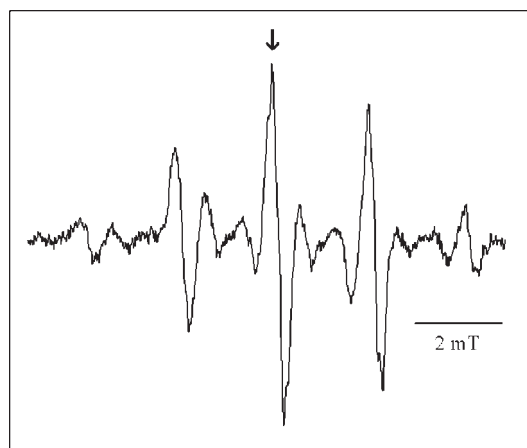


Figure 1. Spectrum of DMA macroradicals from quasistationary polymerization initiated by laser pulses applied at a repetition rate of 20 Hz and carried out at 0 °C. The arrow indicates the magnetic field at which the time-resolved experiments were carried out.

an ESR sample tube. Dodecyl methacrylate (DMA, >95%, stabilized with hydroquinone monomethyl ether, Fluka Chemie) was purified with an inhibitor remover (Aldrich Chemie) and then distilled under reduced pressure. The monomer was treated by several freeze–pump–thaw cycles to remove dissolved oxygen.

The software Xepr v1.0 (Bruker), which also controls the spectrometer settings, was used for primary data acquisition. The integration of the spectra and the calculation of absolute radical concentrations were carried out using Matlab.  $k_t$  values were deduced from  $c_R(t)$  data using the software packages Matlab and Origin.

## Results and Discussion

Figure 1 shows a typical 13-line ESR spectrum for low-conversion DMA polymerization. Nine-line spectra, as reported for methacrylates by other groups,<sup>[8]</sup> were observed for DMA at conversions above 30%, which is beyond the conversion range of the present study. The spectrum was recorded under quasistationary polymerization conditions with excimer laser initiation at a pulse repetition rate of 20 Hz. Kamachi and Kajiwara assigned the 13-line spectrum of methyl methacrylate to two conformations that can be converted into each other by rotation around the  $C_\alpha$ – $C_\beta$  bond at the free-radical chain end.<sup>[11,12]</sup> In SP-PLP-ESR experiments, the peak height of the line with maximum intensity (indicated by the arrow in Figure 1), which is a measure of radical concentration (see Experimental Part), was recorded at constant magnetic field.

Shown in Figure 2 is a  $c_R(t)/c_R^0$  trace, with  $c_R^0$  being the radical concentration at time  $t = 0$ , measured for a DMA polymerization at 0 °C. This trace refers to a polymer concentration of 14% (from preceding polymerization). The signal-to-noise quality that may be reached with the currently available experimental setup is not yet sufficient for obtaining high-quality first-derivative curves of  $c_R(t)$  data. So, the first-derivative strategy based on Equation (1) was not applied. Instead, integrated forms of Equation (1) were fitted to experimental data.

The integrated expression which can be derived from Equation (1) under the assumption that the kinetics is ideal ( $k_t = \text{constant}$ ) reads [Equation (2)]:

$$\frac{c_R(t)}{c_R^0} = (1 + 2 \cdot k_t c_R^0 t)^{-1} \quad (2)$$

According to Equation (2),  $c_R(t)$  data may be analyzed by plotting the reciprocal of radical concentration versus time. If  $k_t$  remains constant and thus independent of chain length, such a plot will yield a straight line which should intersect the ordinate at  $c_R(t)/c_R^0 = 1$ .  $k_t$  can be obtained from the slope of this straight line provided that  $c_R^0$  is known. The insert in Figure 2 shows such a  $c_R^0/c_R(t)$  versus  $t$  plot. No

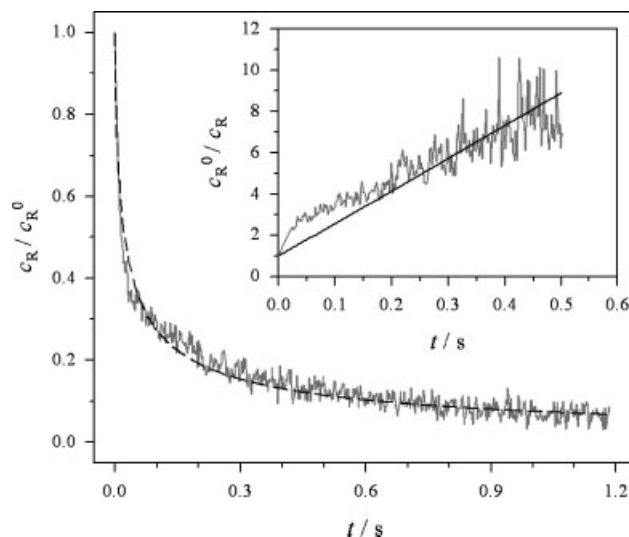


Figure 2. Decay in radical concentration after applying a laser pulse at  $t = 0$  as measured by ESR for a DMA bulk polymerization at 0 °C and 14% of polyDMA from preceding DMA photopolymerization. The associated DMA concentration is  $c_M = 2.9$  M. The  $k_p$  value from PLP-SEC for the above conditions is  $256 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ . The dashed line represents the best fit of Equation (3) to the  $c_R(t)/c_R^0$ . Plotted in the insert is the reciprocal of radical concentration versus time. The straight line is the best linear fit that intersects the ordinate at  $c_R(t)/c_R^0 = 1$ . Because of diminishing signal quality, the analysis presented in the insert was restricted to the time region  $t \leq 0.5$  s.

satisfactory linear fit can be obtained, which suggests that  $k_t$  is chain-length dependent. This observation is in full agreement with the now generally accepted picture.<sup>[1]</sup>

A simple and frequently used way of taking the chain-length dependence of  $k_t$  into account is by employing the power-law model:  $k_t(i, i) = k_t^0 \cdot i^{-\alpha}$  for termination of two macroradicals of identical chain length  $i$ . Substitution of this power-law expression into Equation (1) and subsequent integration yields [Equation (3)]:

$$\frac{c_R(t)}{c_R^0} = \left( \frac{2 \cdot k_t^0 \cdot c_R^0 \cdot t_p^\alpha}{1 - \alpha} \cdot t^{(1-\alpha)} + 1 \right)^{-1}, \quad (3)$$

where  $t_p = (k_p \cdot c_M)^{-1}$  is the so-called propagation time, that is, the time interval between two successive propagation steps. The dashed line in Figure 2 represents the fit of Equation (3) to the  $c_R(t)/c_R^0$  data. The fit is rather satisfactory with the exception of the early time region,  $0 < t < 0.3$  s. The parameters deduced from fitting Equation (3) to the data within the chain-length interval  $1 < i < 1000$  are:  $\alpha = 0.34 \pm 0.05$ . With pulse-induced initial radical concentrations,  $c_R^0$ , of about  $5.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  being obtained by ESR calibration, according to the procedure described above, and with the  $k_p$  and  $c_M$  values given in the legend to Figure 2,  $k_t^0$  is found to be  $(3.8 \pm 0.7) \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

From the SP-PLP-ESR signals measured at other conversions,  $\alpha$  and  $k_t^0$  values have been found that agree with the values given above within the limits of experimental accuracy. The literature value for  $k_t^0$  from SP-PLP-NIR experiments for DMA carried out at 40 °C and 1 000 bar is:  $k_t^0 = (4.0 \pm 0.6) \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  which, after extrapolation to 0 °C and to ambient pressure using the measured activation volume (for  $k_t$ ) of  $10.8 \text{ cm}^3 \cdot \text{mol}^{-1}$  and the estimated activation energy of  $E_A(k_t) = 5 \text{ kJ} \cdot \text{mol}^{-1}$ , yields  $k_t^0 = (4.6 \pm 0.8) \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ . The agreement between the  $k_t^0$  values from the two independent SP-PLP techniques is remarkable and very satisfactory but should not be overestimated until further tests for other polymerization conditions and monomers have been carried out. Moreover, it needs to be noted that the  $\alpha$  value from SP-PLP-ESR is higher than the SP-PLP-NIR value of  $\alpha = 0.15 \pm 0.04$ .<sup>[13]</sup> This is probably due to the fact that the NIR technique, which is applied at higher temperatures, primarily catches the chain-length dependence of  $k_t$  for larger radicals, which is weaker than the one for small radicals (see below).

As has been mentioned above, the quality of fits of Equation (3) to  $c_R(t)/c_R^0$  data is reduced at low  $t$  (at  $t < 0.3 \text{ s}$ ), which suggests that a more refined model for the chain-length dependence of  $k_t$  should be used.  $k_t^0$  in Equation (3) refers to the termination of radicals with chain length unity. On the other hand, the power-law dependence was derived for large coiled radicals.<sup>[14]</sup> Thus,  $k_t^0$  characterizes the termination behavior of a fictitious species which is large and coiled but of chain length  $i = 1$ . It comes as no surprise that  $k_t^0$ , which is extrapolated from the data obtained for macroradicals, does not coincide with the experimentally determined radical–radical combination rate coefficients for small radicals. This problem has recently been addressed by Smith et al.<sup>[15]</sup> who proposed to use a “composite model” with the theory-based value of  $\alpha = 0.16$  for long-chain radicals<sup>[14]</sup> and with  $\alpha$  being larger, for example, around  $\alpha = 0.5$ , for small-chain radicals. The larger  $\alpha$  value represents the appreciable initial lowering of  $k_t$  from experimental radical–radical combination rate coefficients of two small radicals up to the onset of the weaker chain-length dependence that is expected for larger coiled radicals. The authors assumed that the transition between the regions of smaller and larger  $\alpha$  occurs at around  $i = 100$ . Indications for composite-type  $k_t$  models have already been seen in the experimental studies by de Kock et al.<sup>[16]</sup> and by Vana et al.<sup>[17]</sup>

In order to test whether the kinetic data from SP-PLP-ESR are consistent with such a composite model, the following rearranged form of Equation (3) may be used [Equation (3a)]:

$$\frac{c_R^0}{c_R(t)} - 1 = C \cdot t^{(1-\alpha)}, \quad (3a)$$

where  $C = (2 \cdot k_t^0 \cdot c_R^0 \cdot t_p^\alpha) / (1 - \alpha)$  if the termination kinetics follows the power law with a single exponent  $\alpha$  from the very beginning, that is, from  $t = 0$  on. Plotting  $\log(c_R^0/c_R(t) - 1)$  versus  $\log(t)$  in this case should yield a straight line with the slope  $1 - \alpha$ . For the two-exponent composite model proposed in reference<sup>[15]</sup>, there should be two linear regions with slopes  $1 - \alpha_1$  (for  $t < t_c$ , where  $t_c$  refers to the cross-over chain length from  $\alpha_1$  to  $\alpha_2$  behavior) and  $1 - \alpha_2$  (for  $t \gg t_c$ , where simulation indicates that an almost accurate  $\alpha_2$  value is obtained by fitting Equation (3a) to the data within the entire range of  $t > t_c$ ). Figure 3 shows such a double logarithmic plot for the DMA data shown in Figure 2. On the abscissa,  $\log i$  is plotted as well as  $\log t$ . The two variables are proportional to each other:  $i = k_p c_M t$ .

The data plotted in Figure 3 clearly show that a single straight line can not be adequately fitted to the data within the entire chain-length region, whereas two straight lines provide a very satisfactory representation. The line fitted to the data at low  $i$  has a weaker slope, which is associated with a larger value of  $\alpha$ . The opposite is true for the data at higher  $i$ . The precise location of the crossover point between the regions of high and low  $\alpha$  is difficult to identify. This is most likely because of the fact that the transition is not at all sharp. As Figure 3 suggests, the assumption that such a transition occurs at  $i = 100$ , as proposed by Smith et al.,<sup>[15]</sup> is a very reasonable one. The chain-length interval  $0 < i < 1000$  was subdivided into two chain-length intervals, below and above  $i = 100$ . The best linear fits to the data within each of these two chain-length intervals are shown in Figure 3. The exponents  $\alpha_1$  and  $\alpha_2$ , calculated from the slopes of the lines, are  $0.52 \pm 0.09$  and  $0.21 \pm 0.05$  for the

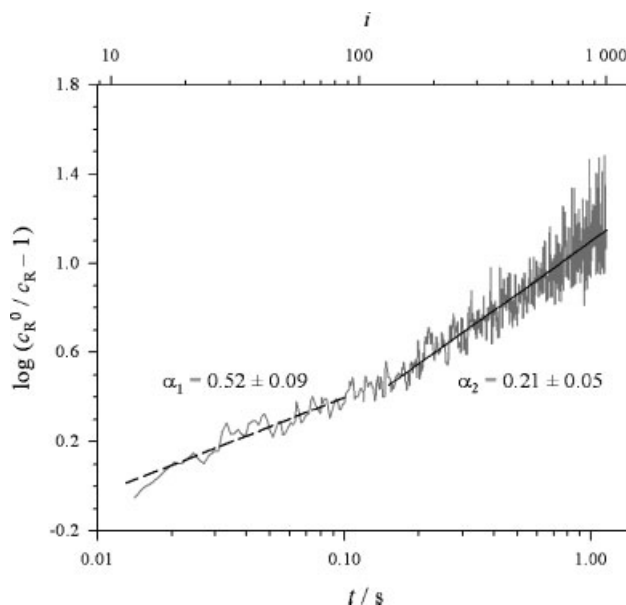


Figure 3. Double-log plot, according to Equation (3a), of the DMA trace from Figure 2. The straight lines are best linear fits within the chain-length intervals  $8 < i < 100$  (---) and  $100 < i < 1000$  (—), respectively.



low  $i$  and high  $i$  regions, respectively. The same procedure was applied for fitting the entire set of experimental SP-PLP-ESR traces obtained for DMA bulk polymerizations at 0 °C, ambient pressure, and with monomer conversions up to 30%, and for two MMMP photoinitiator concentrations, 0.0063 and 0.0255 M. The resulting  $\alpha_1$  and  $\alpha_2$  values are plotted against monomer conversion,  $X$ , in Figure 4. The absolute experimental error in monomer conversion is estimated to be below 3%. Although there may be a weak dependence on conversion, arithmetic mean values for the conversion range under investigation were calculated:  $\alpha_1 = 0.48 \pm 0.09$  and  $\alpha_2 = 0.18 \pm 0.04$ . These results are in remarkably good agreement with the composite model of Smith et al.,<sup>[15]</sup> in that bi-exponential behavior, above and below  $i = 100$ , is seen with  $\alpha_2 = 0.16$  and with  $\alpha_1$  being significantly larger, around 0.5. Figure 4 illustrates that the novel SP-PLP-ESR method allows  $k_t(i, i)$  to be investigated over a wide chain-length region, covering the ranges of high and low  $\alpha$ . The new SP-PLP-ESR technique, therefore, provides access to detailed analysis of  $k_t$  as a function of chain length and degree of monomer conversion. Correlation between the  $k_t$  data for macroradicals and the radical-radical reaction rate coefficients for small radicals, according to the lines of arguments of reference [15], appears to be particularly attractive. Within subsequent SP-PLP-ESR studies, the applicability of this novel method to several other free-radical polymerization systems will be tested.

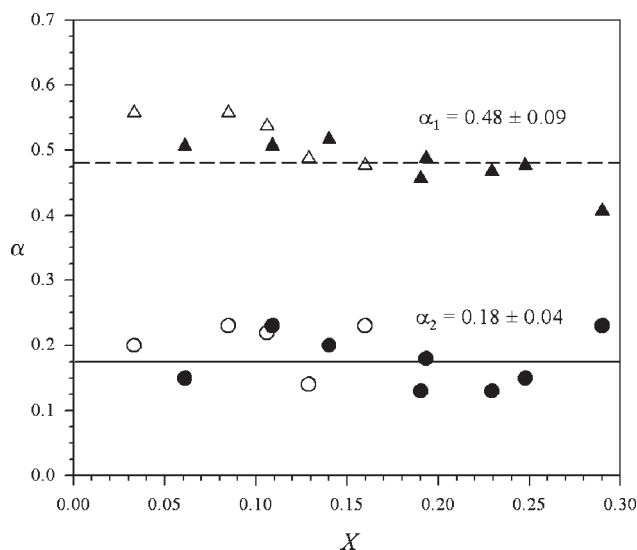


Figure 4. Conversion ( $X$ ) dependence of the power-law exponent  $\alpha$  for DMA bulk homo-polymerization at 0 °C measured by SP-PLP-ESR with MMMP used as the photoinitiator. The experiments were carried out at two initial MMMP concentrations: 0.0063 M (open symbols) and 0.0255 M (full symbols). The straight lines represent the arithmetic mean values of the low  $i$  and high  $i$  exponents, respectively, for the monomer conversion range under investigation.

## Conclusion

SP-PLP-ESR is a novel pulsed-laser polymerization method for detailed measurements into termination rate coefficients,  $k_t$ . Single-pulse initiation is combined with time-resolved ESR detection of the decay in pulse-laser-induced radical concentration. The first results for DMA bulk polymerization show close agreement with the literature  $k_t$  data obtained using the established SP-PLP-NIR technique. With the radical concentration being directly monitored, SP-PLP-ESR should allow for more detailed studies into  $k_t$ . The results obtained so far provide strong support for the recently proposed composite model, in which termination rate coefficients, starting from small radicals, first considerably decrease, for example, with a power-law exponent of  $\alpha_1 = 0.5$ , and subsequently, for example, at chain lengths above  $i = 100$ , decrease to a weaker extent, for example, with the theoretically predicted power-law exponent  $\alpha_2 = 0.16$ . Further studies will be carried out to identify whether this type of behavior also occurs with other monomers, including styrene, and within wider ranges of monomer conversion. SP-PLP-ESR is particularly well suited for studies into the termination kinetics of low  $k_p$  and low  $k_t$  monomers, such as DMA or itaconates. Within subsequent experiments, different types of sample cells and irradiation geometries will be tested. With ESR spectrometers of enhanced time resolution being available, SP-PLP-ESR should become widely applicable toward the detailed analysis of free-radical termination kinetics.

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