Multipulse Initiation in Pulsed Laser and Quenched Instationary Polymerization: Determination of the Propagation and Termination Rate Coefficients for Dicyclohexyl Itaconate Polymerization

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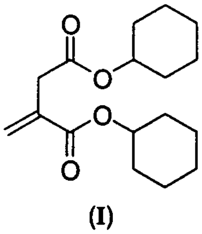
ABSTRACT: The commonly used pulsed laser polymerization technique and the recently introduced method of quenched instationary polymerization were successfully adapted for the measurement of kinetic coefficients in the bulk polymerization of the highly hindered monomer dicyclohexyl itaconate (DCHI) in the temperature range 20−50 °C. The need for very high free radical concentrations in the polymerization system was met via a multipulse laser initiation, in which a burst of laser pulses substitutes for the commonly used single laser pulse. Thus, two new methods are at hand for the investigation of the kinetic parameters. The chain length distributions that are obtained can be easily analyzed, and the data for the propagation rate coefficients, calculated via these two techniques, show excellent agreement. The activation parameters for k_p were calculated as $E_a = 22.0$ kJ mol^{-1} and $A = 1.74 \times 10^4$ L mol^{-1} s^{-1} for the first method and as $E_a = 22.8$ kJ mol^{-1} and $A = 2.49 \times 10^4$ L mol^{-1} s^{-1} for the second method. The activation energy is comparable with the methacrylate series of monomers. The frequency factor is relatively small and reflects the steric hindrance in the transition state caused by the bulky substitution in the monomer (and/or the radical). The quenched instationary polymerization method was utilized to determine the termination rate coefficient, yielding very low values (200−1000 L mol^{-1} s^{-1} in the temperature range 20−50 °C). The low k_t may well be related to the monomer viscosity. The temperature dependence of k_t shows the same extent as that of the viscosity, indicating the diffusion control of the termination reaction. Modeling of the chain length distributions obtained by the quenched instationary polymerization experiments indicates about 25% termination via combination.

Introduction

The determination of the rate coefficients that govern free radical polymerizations has been revolutionized by the invention of pulsed laser polymerization (PLP) which allows with subsequent analysis of the polymeric product via size exclusion chromatography (SEC) for the accurate evaluation of propagation rate coefficients, k_p. Since the invention of PLP−SEC[1] many different monomers have been studied with respect to their propagation rate coefficients, and benchmark values have been collated for styrene,[2] methyl methacrylate (MMA),[3] and alkyl methacrylates[4] by an IUPAC working party. The application of pulsed laser polymerization for the determination of the termination rate coefficients, k_t, and its chain length dependence was realized by the introduction of the single pulse PLP[5] and techniques dealing with the chain length distribution (CLD) formed by the pulsed laser polymerization process.[6] The situation is much less satisfactory in respect to the so-called “hindered” monomers, which have only been studied by electron spin resonance (ESR).[7−9] This is not too surprising as these monomers are generally characterized by low termination rate coefficients, allowing the generation of high radical concentrations, favoring the application of the ESR technique. However, our group recently published values for the propagation rate coefficients[10,11] and termination rate coefficients[12] of dimethyl itaconate evaluated via the PLP−SEC technique, showing in detail that this method is also capable of determining rate coefficients for hindered monomers with low termination rate coefficients. In particular, the low values of k_t for these types of monomers are of specific interest, because they provide deeper insights into the termination process, which is still far from being understood in depth. This current work was inspired by an idea to extend pulsed laser polymerization to the field of the highly hindered monomers with k_p values near unity and k_t values of about 1000 L mol^{-1} s^{-1} and lower. The monomer dicyclohexyl itaconate (DCHI) (**I**) with reported values of k_p and k_t in this range ($k_p = 2.3$ L mol^{-1} s^{-1} and $k_t = 1900$ L mol^{-1} s^{-1} at 60 °C in benzene)[13] was chosen as the subject of this kinetic analysis. Two new techniques which allow for the determination of propagation and termination rate coefficients are introduced and applied. The first one is an adaptation of the common PLP−SEC technique; the second one is a modification of the quenched instationary polymerization, recently introduced by Schnoell-Bitai.[14,15] Both are based on the concept of a multipulse initiation.



(I)

Multipulse Initiation in PLP. The laser-induced termination process in free radical polymerization is essential for the PLP−SEC technique, because it results in the formation of characteristic peaks which occur in the CLD. These characteristic peaks reflect an increased termination probability of the growing chains at the

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moment of a laser flash resulting from the formation of a large free radical population. The evaluation of these peaks is the basis for the calculation of the propagation rate coefficient k_p, according to the well-known eq 1[16]

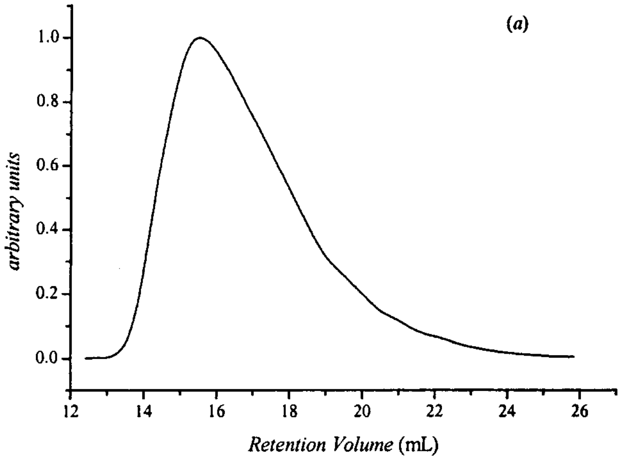
$$L_{0,i} = k_{p,i}[M]t_0 \tag{1}$$

where $L_{0,i}$ is the kinetically relevant chain length obtained from either the first ($i = 1$) or second ($i = 2$) inflection point preceding a maximum of the distribution, [M] is the monomer concentration, and t_0 is the laser repetition time. To get well-resolved additional peaks in the PLP–CLD, one has to carefully balance experimental input parameters. The theory of pseudo-stationary pulsed laser polymerization[17] shows that the shape of the distribution is only governed by the dimensionless product

$$C = \rho k_t t_0 \tag{2}$$

with ρ being the free radical concentration produced by each laser pulse. A typical value of C is 0.5–10, whereas higher values of C yield more pronounced first additional peaks (high termination limit). The shape of a PLP distribution can (in principle) be held constant by balancing the product of the laser period t_0 and the free radical concentration ρ to give constant values of C. Hence, if the termination rate coefficient k_t is low, e.g., with hindered monomers, the product of t_0 and ρ has to be high to get well-structured distributions. This can be achieved by decreasing the laser frequency or increasing the laser intensity and the initiator concentration, respectively. For experimental reasons, however, there are evident limits to this procedure: (i) The laser repetition time t_0 is responsible not only for the shape of the distribution but also for the absolute position of the additional peaks on the chain length axis according to eq 1. An experiment involving DCHI with k_p values of about 2 L mol^{-1} s^{-1} and k_t of about 200 L mol^{-1} s^{-1} (see below) at 20 °C and common values for ρ of approximately 2×10^{-6} mol L^{-1} must be performed with a dark time of 2500 s to obtain a structured CLD with a value of $C = 1$. The corresponding inflection point would occur at a molecular weight of $M = 5 \times 10^6$ g mol^{-1}, a region that is barely accessible via free radical polymerization as transfer to monomer reactions become significant, thereby limiting the maximum number-average degree of polymerization. (ii) The absorption of laser light by the initiator within the sample should be minimized to get a homogeneous initiation profile. The maximal initiator concentration should therefore not exceed a value which leads to an absorption of more than 10–20%, e.g., about 1×10^{-2} mol L^{-1} DMPA (ϵ(355 nm) $\cong$ 6000 cm^2 mol^{-1} [18] and a path length of 1 cm). In addition, it was reported recently that a large increase of the photoinitiator and laser intensity may disturb the kinetic measurements, as free radicals with different initiation reactivity are formed.[19,20] The increase of laser power may also lead to uncontrollable thermal effects and may cause degradation of the polymer and/or monomer.

One prospect is to increase the value of the product C to get well-structured CLDs, not by increasing the free radical concentration generated by each laser pulse, but instead to sum up the concentrations of several pulses, that are applied over a very short time interval. Because of the low values of k_p for the monomer DCHI, the uncertainty caused by the extension of the initiation period—10 ns in normal PLP and 1 s in this work—is nearly negligible. The burst of 20 laser pulses within 1 s leads to a primary free radical concentration that is nearly 20 times as high as in normal PLP, an amount not accessible by a single laser pulse. The laser bursts are separated by the repetition time t_0. Figure 1 shows impressively the improvement of the resulting CLD.



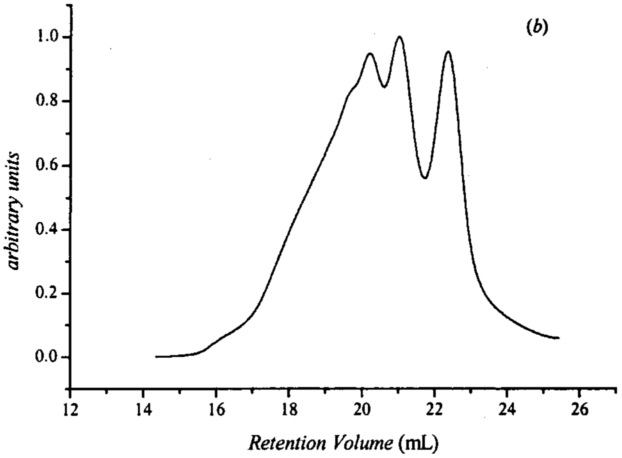


Figure 1. SEC traces of pulsed laser polymerization of dicyclohexyl itaconate in bulk at 25 °C, repetition time of $t_0 = 10$ s. (a) Initiated with a single laser pulse; (b) multipulse laser initiation (20 pulses in 1 s).

Both experiments were performed under the same experimental conditions, excepting a change from the normal laser single pulse initiation to a rapid burst of 20 laser pulses. Whereas the additional peaks in Figure 1a are not visible, the CLD in Figure 1b exhibits well-resolved PLP peaks. Olaj and Zifferer[21] have shown by simulations that arbitrary periodic initiation profiles, even such with discontinuities, lead to CLDs with additional peaks and to the correct values of k_p. In this present work, simulations carried out with the program package PREDICI[22] using specific experimental input parameters for the bulk polymerization of DCHI will be used to complement the experimental study. The type of initiation with laser bursts separated by a longer dark time is similar to the so-called "railroad" experiment, introduced and studied by Buback and co-workers.[23] However, the intention of their experiment was the determination of propagation and transfer rate coefficients simultaneously within one experiment.

Multipulse Initiation in Quenched Instationary Polymerization. Quenched instationary polymerization systems, introduced by Schnoell-Bitai,[14,15] are characterized by the complete deactivation of all radicals that are generated via a single initiation pulse by reaction with an inhibitor after a certain dark time. The method is based on the intentional limitation of the maximum active chain length L_q the radicals can achieve. Therefore, the kinetic scheme for the free radical polymerization is extended by the quench reaction with the rate constant k_q. The 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) free radical is known as an extremely fast and efficient scavenger ($k_q > 10^9$ L mol^{-1} s^{-1}).[24] This high rate coefficient ensures that the quench reaction is complete within a short time span. Hence, the radical population present in the moment of the quench reaction is immediately converted into inactive polymeric product. A similar approach has also been taken by Karatekin et al.[25] for the study of the living chain molecular weight distribution in free radical polymerization. The obtained CLD is the sum of the chains which are terminated via the normal termination process during the dark period and the CLD of the quenched radicals. These radicals have chain lengths defined by a Poisson distribution. Schnoell-Bitai's experimental setup was based on a flow system in which a photopolymerizable mixture passes through a capillary system where it is irradiated at a specific location and polymerizes in the capillary during a well-defined dark period until it drops into a quenching bath. We have changed the technique to a batch operation. Encouraged by the success of the multipulse initiation technique, we applied the same initiating laser burst as a substitute for the single pulse. This increases the concentration of initiated chains, thereby increasing the monomer to polymer conversion, which is normally very low in a single-pulse experiment. After a time t_q, the time between the beginning of the initiation period and the quenching process, a solution of TEMPO in THF is added to the reaction mixture. Measuring the CLD by size exclusion chromatography reveals a structured shape that allows to determine k_p using eq 3. This technique relates the active lifetime of a growing macroradical with its maximum active chain length, L_q.

$$L_q = k_{p,q}[\mathrm{M}]t_q \tag{3}$$

One difference to the PLP−SEC technique is that the peak maximum is the most accurate measure for L_q. Figure 2 shows the SEC distributions of the bulk polymerization of DCHI at 20 °C performed via the multipulse initiated quenched instationary polymerization for different quench times. The shift of the peak maxima to higher molecular weights with longer quench times can be seen clearly.

Keeping in mind that the obtained CLD is a sum of the dead polymer produced during the dark time and the dead polymer generated via the quenching, which is strictly speaking the "mirror" of the radical CLD, it is possible to separate these two distributions with respect to their peak areas. With accurate SEC measurements where the peak areas are calibrated, the absolute polymer concentration in the sample and the monomer to polymer conversion can be calculated.[26] Hence, the amount of polymer generated by the quenching, which is equal to the radical population present at the moment of quenching, is accessible. The molar free radical concentration can then be calculated with the average chain length of the radicals at the moment of the quenching by evaluation the peak maximum of the CLD. The loss of radical concentration [R] in a single pulse experiment simply follows a second-order rate law:

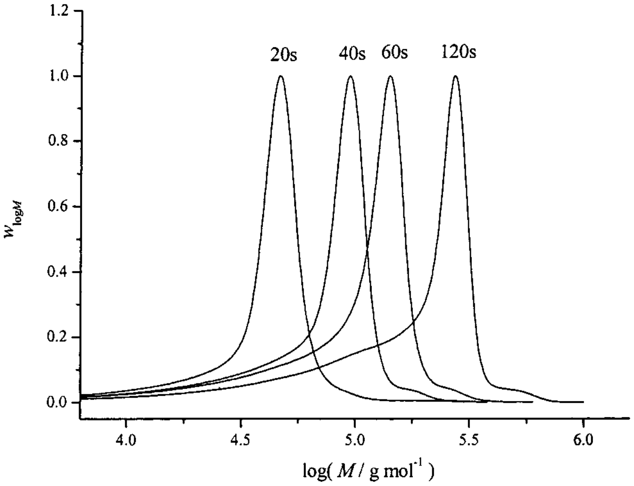


Figure 2. SEC distributions of quenched instationary polymerizations of dicyclohexyl itaconate in bulk at 20 °C; different quench times t_q are indicated.

$$-\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = k_t[\mathrm{R}]^2 \tag{4}$$

The integration of eq 4 over time from 0 to t_q yields

$$\frac{1}{[\mathrm{R}]} = \frac{1}{[\mathrm{R}]_0} + k_t t_q \tag{5}$$

According to eq 5, a linear plot of the inverse free radical concentration, $[\mathrm{R}]^{-1}$—obtained from experiments under exactly the same experimental conditions, except the quenching times t_q—vs the quench time t_q gives an average termination rate coefficient k_t as the slope and the inverse radical concentration directly after the initiating period, $[\mathrm{R}]_0{}^{-1}$, as the intercept. Simulations will again be used to complement the experimental approach.

Experimental Section

Materials. Dicyclohexyl itaconate was prepared by esterification of itaconic acid with a 4-fold excess of cyclohexanol with 0.5 wt % *p*-toluenesulfonic acid according to ref 27 and purified by distillation under reduced pressure ($\mathrm{bp}^{1\,\mathrm{mmHg}} \approx 140$ °C) to give a highly viscous colorless oil. The purity was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR (CDCl$_3$): δ 1.2−1.4 (m 12H), 1.63 (m 4H), 1.72 (m 4H), 3.22 (s 2H), 4.71 (m 2H), 5.56 (s 1H) 6.20 (s 1H). ^{13}C NMR (CDCl$_3$): δ 23.4, 24.0, 31.4, 35.5, 38.1, 70.2, 73.0, 127.4, 134.7, 165.5, 170.1. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Aldrich, 99%) and 2,2,6,6-tetramethylpiperidine-1-oxyl, free radical (TEMPO) (Aldrich, 98%), were used as received. Tetrahydrofuran (THF) for SEC measurements was refluxed over potassium, distilled, and stabilized with 2,6-di-*tert*-butyl-*p*-cresol.

Polymerization. All samples were comprised of monomer (0.5 mL) with a photoinitiator concentration of about 5×10^{-3} mol L^{-1}, thoroughly deoxygenated with a nitrogen stream. A Continuum Surelite I-20-Nd:YAG pulsed laser system was used to generate a wavelength of 355 nm with a single pulse energy of 20 mJ and a beam diameter of 6 mm. Care was taken to ensure a homogeneous intensity profile over the whole optical cross section. The applied laser pulse patterns were controlled with an external digital pulse generator (Quantum Composers). Isothermal reaction conditions were maintained using a recirculating bath including a feedback loop through a thermocouple attached to the side of the reaction cell. The

Table 1. Viscosity of Dicyclohexyl Itaconate at Different Temperatures

T (°C)	η (mPa s)	T (°C)	η (mPa s)
22.5	179	40	63.1
25.5	147	45	50.2
30.5	108	50	42.6
35	79.4		

experimental rig employed is very similar to the one described earlier.[28] The samples for the multipulse initiated PLP were irradiated with 5−8 repetitive bursts of 20 laser pulses (20 Hz), leading to an overall polymerization time of 1−10 min, depending on the repetition times t_0. The samples for the quenched instationary polymerizations were irradiated with a single burst of 20 laser pulses (20 Hz), and later 0.5 mL of a cold solution of 2.5×10^{-2} mol L^{-1} TEMPO in THF was added with a syringe after the quench time t_q. Care was taken to complete the mixing in the shortest possible time (<1 s), and the mixture was cooled immediately after the quenching procedure.

Molecular Weight Analysis. CLDs were measured by size exclusion chromatography (SEC) on a Shimadzu modular system, comprising of an autoinjector, a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm), followed by three linear PL columns (10^5, 10^4, and 10^3 Å), and a differential refractive index detector. The eluent was THF at 40 °C with a flow rate of 1 mL min^{-1}. Calibration curves were generated using both poly(methyl methacrylate) and polystyrene standards. The Mark−Houwink−Kuhn−Sakurada (MHKS) constants of polystyrene and poly(methyl methacrylate)[29,30] were then used to create a universal calibration curve which, in conjunction with the MHKS constants of polydicyclohexyl itaconate (THF, $K = 23.3 \times 10^{-3}$ mL g^{-1}, $a = 0.580$),[27] provided access to absolute molecular weight distributions. The propagation rate coefficients, $k_{p,i}$, were determined on one hand using the inflection point molecular weights of the first and second additional peaks of the molecular weight distribution obtained via the multipulse initiated PLP, utilizing eq 1. On the other hand, the propagation rate coefficients, $k_{p,q}$, were determined by evaluation of the maxima of the CLD obtained via the quenched instationary polymerizations, according to eq 3. Conversions of monomer to polymer—which were used to determine the concentration of free radicals in the system—were determined via the calibrated area under the differential refractometer signal.

Density and Viscosity. The density, d, necessary for the calculation of the monomer concentration was measured with a DMA 5000 density meter (Anton Paar) in the temperature range of $T = 20-70$ °C:

$$d = 1.0751 - T \times 8.774 \times 10^{-4} + T^2 \times 5.940 \times 10^{-7} \text{ g mL}^{-1} \quad (6)$$

The viscosity was measured with a rotational digital viscometer, Brookfield model LVTDV-II (see Table 1).

Simulations. All simulations of CLDs and monomer conversion as a function of time were carried out with the program package PREDICI, version 5.36.3, on a Pentium III, 733 MHz IBM-compatible computer.

Results and Discussion

Simulations of Multipulse Initiated PLP. The simulations were outlined according to a kinetic scheme including pulsed initiation, propagation, chain transfer to monomer, and termination.[12] The CLDs of the multipulse initiated PLP experiments were simulated, subjected to an algorithm which simulates the SEC broadening ($\sigma(\log M) = 0.05$) and subsequently analyzed to obtain a k_p value. The initiation profile was a 20 pulse burst with a frequency of 20 Hz. The input parameters were $k_p = 3$ L mol^{-1} s^{-1}, $k_{t,d} = 150$ L mol^{-1} s^{-1}, $k_{t,c} = 50$ L mol^{-1} s^{-1} (indices d and c correspond to disproportionation and combination), and a primary free radical concentration generated by each laser pulse of 5×10^{-6} mol L^{-1}. Chain transfer to monomer was neglected in the initial simulations. Table 2 gives the chain lengths according to the first and second point of inflection, $L_{0,1}$ and $L_{0,2}$, respectively, and the values of the propagation rate coefficient derived from the first and the second point of inflection, $k_{p,1}$ and $k_{p,2}$.

Table 2. Simulated Multipulse Initiated PLP Data for Different Repetition Times t_0: Simulation Input of $k_p = 3$ L mol^{-1} s^{-1}; All Other Parameters Are Given in the Text

t_0, s	$L_{0,1}$	$L_{0,2}$	$k_{p,1}$, L mol^{-1} s^{-1}	$k_{p,2}$, L mol^{-1} s^{-1}
10	107.0	209.0	2.991	2.921
20	208.0	405.0	2.907	2.830
40	408.0	810.0	2.851	2.830
60	608.0	1224.0	2.832	2.851
120	1235.0	2386.0	2.876	2.779

Table 3. Simulated Multipulse Initiated PLP Data for Different Chain Transfer to Monomer Rate Coefficients, k_{tr}: Simulation Input of $k_p = 3$ L mol^{-1} s^{-1}, $t_0 = 40$ s; All Other Parameters Are Given in the Text

k_{tr}, L mol^{-1} s^{-1}	$L_{0,1}$	$L_{0,2}$	$k_{p,1}$, L mol^{-1} s^{-1}	$k_{p,2}$, L mol^{-1} s^{-1}
10^{-4}	209.0	415.0	2.921	2.900
10^{-3}	207.0	410.0	2.893	2.865
10^{-2}	204.0	408.0	2.851	2.851
10^{-1}	26.0		0.363	
1	3.0		0.042	

The results clearly show that the inflection point of the additional peaks is still a good measure—within 5% error—for the true L_0. However, the calculated values for k_p are slightly smaller than the input parameter, decreasing with increasing chain length and repetition time. This can be easily explained by the fact that with higher t_0 values—and all other parameters kept constant—the product C increases, too. At higher C values, the PLP peaks shift to lower chain lengths, increasing the underestimation of the true L_0 value by the point of inflection.

The next step was to investigate possible influences of chain transfer to monomer. Table 3 gives the calculated data for different values of chain transfer to monomer rate coefficients.

The validity of the evaluated k_p values remains up to relatively high values of k_{tr}. At high transfer constants, $C_M > 10^{-2}$, the distribution loses its PLP structure, and the evaluated inflection points are no longer a valid measure for L_0. Simulations with different contributions of disproportion to the overall termination and different amounts of chain length dependence of k_t showed no significant effect on the calculated k_p values.

Experimental Results of Multipulse Initiated PLP. Table 4 shows the experimental results for the multipulse initiated PLP for dicyclohexyl itaconate in bulk in the temperature range between 20 and 50 °C.

The values of $k_{p,1}$ and $k_{p,2}$—derived from the first and second point of inflection, respectively—are in very good agreement for each single experiment. The values are slightly decreasing with increasing repetition time, showing the same relative extent of about 5% that was observed with the simulation data. However, this effect is much smaller than the chain length dependence of k_p in PLP experiments recently observed with monomers like styrene and methyl methacrylate, where a decrease of 25% of k_p and more in the chain length regime of up to 1000 was revealed.[31] The k_p data are

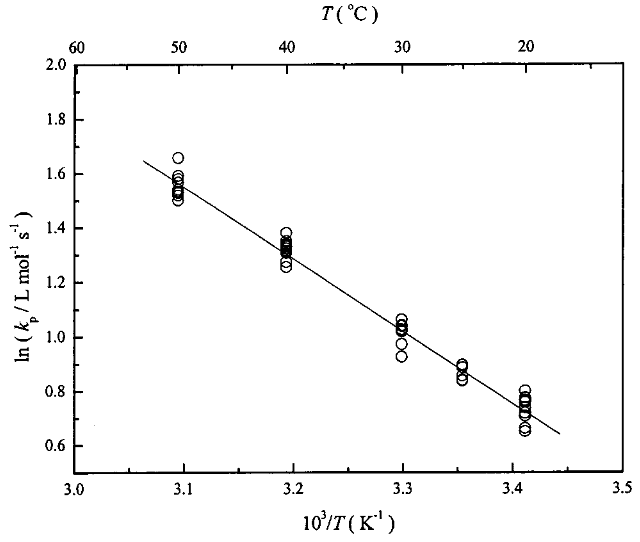


Figure 3. Arrhenius plot of the propagation rate coefficient, k_p, of the bulk polymerization of dicyclohexyl itaconate, determined via the multipulse initiated PLP.

Table 4. Experimental Multipulse Initiated PLP Data for the Bulk Polymerization of Dicyclohexyl Itaconate

T, °C	t_0, s	$L_{0,1}$	$L_{0,2}$	$k_{p,1}$, L mol^{-1} s^{-1}	$k_{p,2}$, L mol^{-1} s^{-1}
20	10	75.24	156.06	2.095	2.172
20	10	77.33	160.01	2.153	2.227
20	20	153.48	307.18	2.136	2.138
20	40	295.00	602.12	2.053	2.095
20	60	418.22	826.95	1.941	1.919
20	120	826.95	1751.85	1.919	2.032
25	10	87.73	165.40	2.452	2.311
25	60	526.70	1042.19	2.453	2.427
25	30	248.91	505.30	2.319	2.353
30	10	101.06	206.47	2.835	2.896
30	20	198.21	395.01	2.781	2.771
30	40	398.24	805.56	2.793	2.825
30	60	540.02	1080.73	2.525	2.527
30	120	1131.24	2476.69	2.645	2.895
40	10	136.49	269.89	3.860	3.816
40	20	261.30	526.70	3.695	3.724
40	30	398.24	805.56	3.754	3.797
40	60	758.05	1603.97	3.573	3.780
40	100	1240.73	2813.71	3.509	3.979
50	5	86.18	184.14	4.913	5.249
50	10	168.16	314.73	4.794	4.486
50	20	325.08	655.26	4.634	4.670
50	30	480.86	969.77	4.569	4.607
50	40	649.72	1362.75	4.630	4.856

presented as an Arrhenius plot in Figure 3, yielding an activation energy of $E_a = 22.04$ kJ mol^{-1} and a frequency factor of $A = 1.74 \times 10^4$ L mol^{-1} s^{-1}; the corresponding 95% joint confidence interval is given in Figure 4. Comparison with the simulated data may lead to the conclusion that the experimental results are slightly smaller than the true value of k_p; however, the activation energy will be unaffected by this error due to the averaging procedure in the calculation, but the frequency factor may be smaller than the real value.

Simulations of Multipulse Initiated Quenched Instationary Polymerization. The kinetic scheme of the polymerization was extended by the quench reaction, which describes the termination of living radicals with a quench molecule to give a polymeric product. The rate coefficient of the quench reaction, k_q, was chosen to be 10^9 L mol^{-1} s^{-1}. The other input values of the kinetic parameters were the same as in the simulations of the PLP distributions (described above), and the CLDs have again been subject to a subsequent SEC-broadening procedure. Table 5 gives the simulated chain length according to the maximum of the CLD, L_q, and the values of the propagation rate coefficient derived from that maximum, $k_{p,q}$.

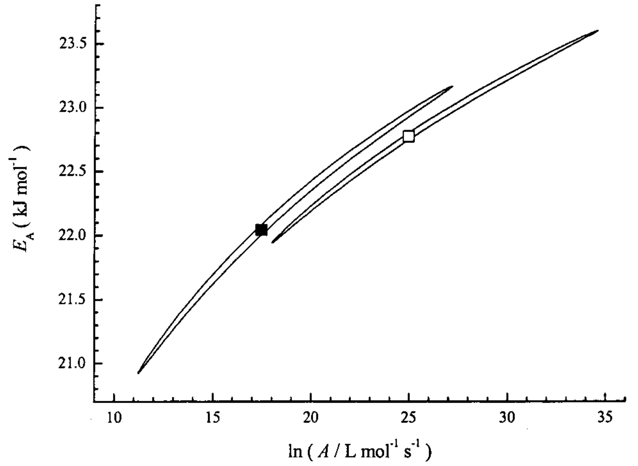


Figure 4. The 95% joint confidence intervals for the Arrhenius parameters of the propagation rate coefficients, k_p, of the bulk polymerization of dicyclohexyl itaconate; (■) PLP, (□) quenched instationary polymerization.

Table 5. Simulated Multipulse Initiated Quenched Instationary Polymerization Data for Different Quench Times t_q: Simulation Input of $k_p = 3$ L mol^{-1} s^{-1}; All Other Parameters Are Given in the Text

t_q, s	L_q	$k_{p,q}$, L mol^{-1} s^{-1}
10	104.0	2.907
20	211.0	2.949
40	420.0	2.935
60	639.0	2.976
120	1277.0	2.974

It is evident that the peak maximum is an excellent measure for the chain length of the radicals at the moment of their termination. In contrast to the simulated multipulse initiated PLP data (see above), the simulated k_p values of the multipulse initiated quenched instationary polymerization experiments are independent of the quench time and the chain length. The change of the initiation profile to a burst of pulses within 1 s does not significantly effect the measured values of k_p. The uncertainties caused by the Poissonian character of the radical distribution are only significant below a certain chain length of about 10, a chain length regime where the Poisson distribution is relatively broad (as extensively described in ref 32). However, this degree of polymerization is already present at the end of the initiation time. At the experimental conditions chosen the radical chains exhibit a minimum chain length of about 100 at the moment of quenching (see Table 5). The free radical distribution therefore exhibits a relative narrow dispersion at the moment of quenching, because of the decreasing relative dispersion of the free radical distribution, due to its Poissonian character. Although the free radical distribution is, strictly speaking, the sum of 20 Poisson distributions, each generated by one single laser pulse in the initiating burst, its shape and characteristics are very similar to a real Poisson distribution. The peak maximum is therefore a good measure of the mean average lifetime of the macroradicals, especially at long chain lengths. Table 6 gives simulated data for different chain transfer to monomer rate coefficients, k_{tr}.

Table 6. Simulated Multipulse Initiated Quenched Instationary Polymerization Data for Different Chain Transfer to Monomer Rate Coefficients, k_{tr}: Simulation Input of $k_p = 3$ L mol^{-1} s^{-1}; All Other Parameters Are Given in the Text

k_{tr}, L mol^{-1} s^{-1}	L_q	$k_{p,q}$, L mol^{-1} s^{-1}
10^{-4}	427.0	2.984
10^{-3}	422.0	2.949
10^{-2}	400.0	2.795
10^{-1}	52.0	0.363
1	7.0	0.049

Table 7. Experimental Multipulse Initiated Quenched Instationary Polymerization k_p Data for the Bulk Polymerization of Dicyclohexyl Itaconate

T, °C	t_q, s	L_q	$k_{p,q}$, L mol^{-1} s^{-1}
20	7	57.90	2.303
20	10	76.83	2.139
20	20	157.36	2.190
20	20	152.69	2.125
20	40	319.86	2.226
20	40	308.93	2.150
20	60	476.91	2.213
20	60	467.23	2.168
20	120	927.45	2.152
20	120	917.06	2.128
30	6.5	68.60	2.961
30	10	105.77	2.968
30	20	215.07	3.017
30	20	204.77	2.872
30	40	408.10	2.862
30	41	434.09	2.970
30	60	633.40	2.962
30	60	634.82	2.968
30	120	1264.08	2.955
30	120	1287.54	3.010
40	5.5	78.74	4.049
40	10	139.45	3.944
40	20	287.93	4.071
40	20	282.73	3.998
40	40	567.75	4.014
40	40	579.07	4.094
40	60	871.70	4.109
40	60	862.86	4.067
40	120	1786.85	4.211
40	180	2582.06	4.057
50	10	179.213	5.109
50	20	348.022	4.960
50	30	539.682	5.128
50	40	690.357	4.920
50	50	916.019	5.223

The influence of this side effect is again small up to relatively high values of k_{tr}, causing an error of about 7%, until the system becomes totally transfer controlled and loses its additional peak. Different contributions of disproportionation to the overall termination showed no significant effect on the calculated k_p values.

Experimental Results of Multipulse Initiated Quenched Instationary Polymerization. Table 7 summarizes the experimental results for different temperatures.

The k_p values exhibit an astonishingly small amount of scatter and show no change with chain length. With the results of the PLP data this confirms that there is no observable chain length dependence of k_p. The chain length dependence of k_p for common monomers like styrene and methyl methacrylate is believed to be caused by a progressive displacement of monomer from the proximity of the radical chain end by the rest of the chain, which builds up a statistical coil, thus decreasing the local monomer concentration which results in a formal decrease of k_p if the average monomer concentration is inserted into its calculation.[31] The sterically demanding cyclohexyl substituents in the DCHI molecule lead to extremely stiff polymer chains,[33] which are not easily able to form coils but rods instead. This loss of the coil characteristic may be responsible for the missing chain length dependence of k_p.

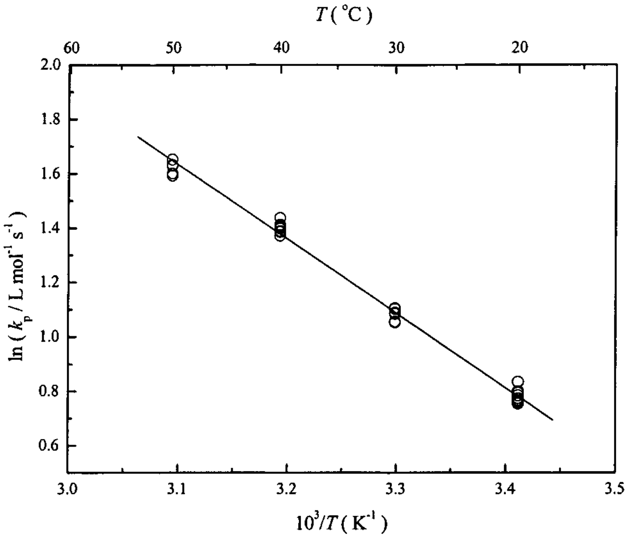


Figure 5. Arrhenius plot of the propagation rate coefficient, k_p, of the bulk polymerization of dicyclohexyl itaconate, determined via the multipulse initiated quenched instationary polymerization.

The corresponding Arrhenius plot (Figure 5) leads to an activation energy of $E_a = 22.77$ kJ mol^{-1} and a frequency factor of $A = 2.49 \times 10^4$ L mol^{-1} s^{-1}; the corresponding 95% joint confidence interval is given in Figure 4.

The activation energies obtained from the two different methods match within an error of only 3%. The frequency factor from the quenching experiments is higher than that from the PLP measurements, which was believed to be underestimated. The obtained value for E_a is very similar to that obtained for methyl methacrylate (22.36 kJ mol^{-1})[3] and other methacrylates.[34] Hence, the low values of the propagation rate coefficient can be attributed solely to steric hindrance for the radical addition reaction.

The experimental CLDs of the quenched instationary polymerizations (see Figure 2) clearly exhibit a small shoulder at the high molecular end of the distribution. Because this shoulder occurs exactly at double the peak molecular weight, it may be assigned to the product that terminated during the dark period via termination by combination. This observation confutes the common opinion that hindered monomers, especially itaconates,[35] terminate solely via disproportionation because of the bulky substituents in the neighborhood of the reactive center. Modeling of the experimental CLD (see below) indicates about 25% termination via combination, a value which is also known for methyl methacrylate. Hence, the congestion at the radical centers seems to have no influence on the termination mode.

The CLDs were subjected to a procedure that allows for the separation of the peak areas contributed by the polymer produced during the dark time and by the amount of polymer which was generated at the moment of quenching. The rising edge of the CLD at low molecular weights was fitted according to the theoretical equation[36] which describes the chain length distribution generated via a single pulse experiment. Integration of

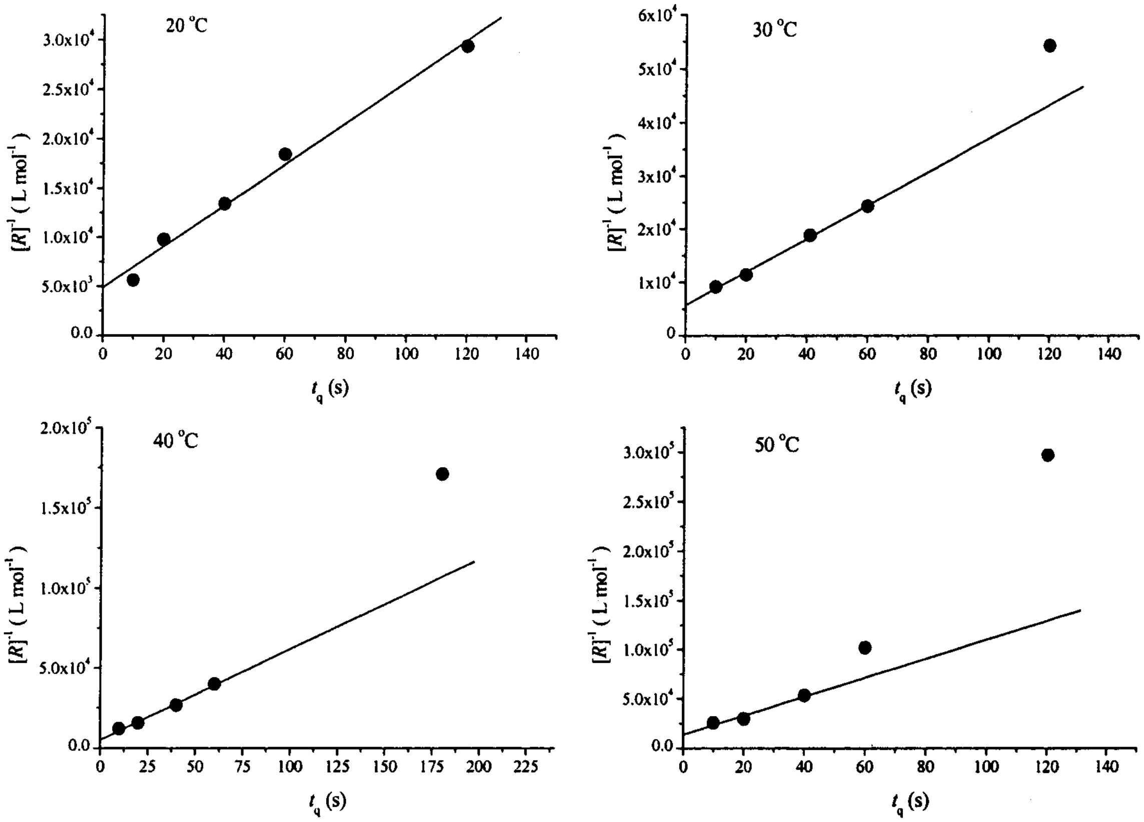


Figure 6. Inverse free radical concentration $[R]^{-1}$ vs quench time t_q for different temperatures, determined via the multipulse initiated quenched instationary polymerization. Tangential linear fits are described in the text.

Table 8. Experimental Multipulse Initiated Quenched Instationary Polymerization k_t Data and Initial Free Radical Concentration for the Bulk Polymerization of Dicyclohexyl Itaconate

T, °C	k_t, L mol^{-1} s^{-1}	$[R]_0$, 10^{-4} mol L^{-1}
20	208.4	2.05
30	311.8	1.76
40	563.8	1.91
50	960.2	1.07

this function from zero to the maximal chain length L_{max} yields the correct amount of dead polymer. The comparison with simulated distributions shows that the errors made with this procedure were below 3%. The peak areas obtained were used to calculate the free radical concentration at the moment of the quenching, which was plotted inversely vs t_q, to give values for an average k_t at different temperatures (see Figure 6 and resulting k_t values in Table 8).

At 20 °C, the linear fit worked reasonably well; however, at higher temperatures, the deviation from linearity increased, especially at longer quenching times. This can be explained by chain transfer to monomer, which on one hand increases at elevated temperatures. On the other hand, the chains become longer due to the increased k_p value. Hence, when the same quench time is applied, the probability of a transfer event is increased. Transfer to monomer produces short radicals in the dark period, which are transformed into dead polymer, too, but which cannot be separated from the rest of the dead polymer in the low molecular weight part of the CLD. Hence, the calculated free radical concentration is too low. To overcome this problem, the only points used in the calculation of k_t were those which withstood a statistically "runs test", that proves the significance of the linearity. The resulting lines therefore reflect the fit in the chain length regime where transfer to monomer seems to have no big influence. The resulting errors in the k_t values are rather low for low temperatures (approximately 20%) and reach a factor of 2 at 50 °C. Calculation of the Arrhenius parameters (see Figure 7) gives an activation energy of $E_a = 40.7$ kJ mol^{-1} and a frequency factor of $A = 3.4 \times 10^9$ L mol^{-1} s^{-1}.

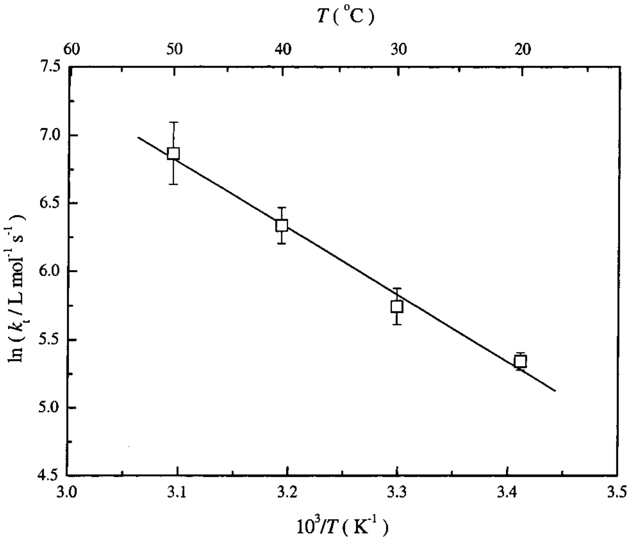


Figure 7. Arrhenius plot of the termination rate coefficient, k_t, of the bulk polymerization of dicyclohexyl itaconate, determined via the multipulse initiated quenched instationary polymerization.

This value for E_a seems very high; however, the activation energy of the flow, calculated by the viscosity data of Table 1, is $E_a(\eta) = 42.3$ kJ mol^{-1}. These values

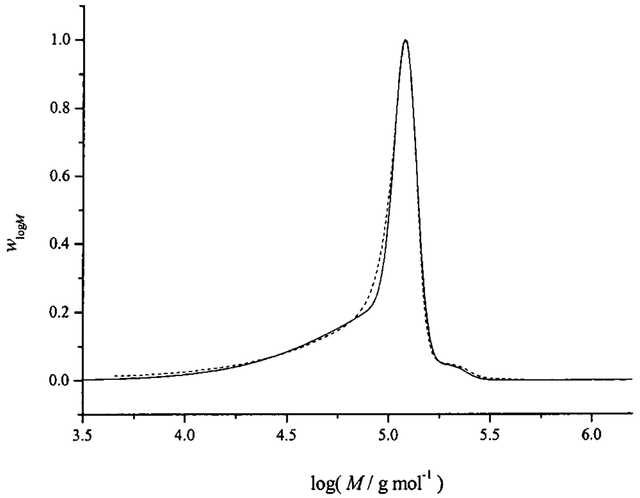


Figure 8. SEC distribution of a quenched instationary polymerization experiment of dicyclohexyl itaconate in bulk at 30 °C: (– – –) experimental, (—) simulated.

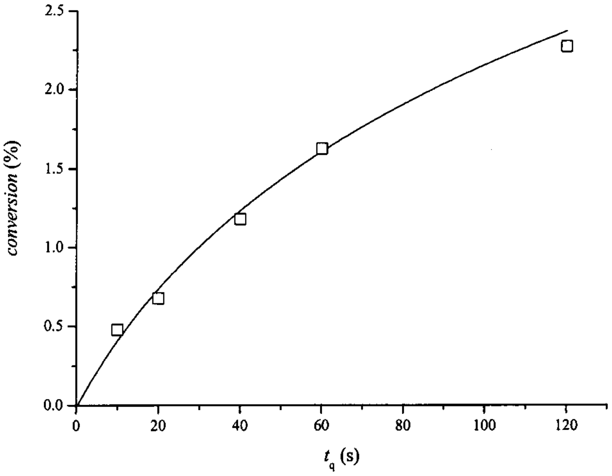


Figure 9. Monomer to polymer conversion vs quench time for a quenched instationary polymerization experiment of dicyclohexyl itaconate in bulk at 30 °C: (□) experimental, (—) simulated.

match well within the experimental errors and indicate the possibility of viscosity control of the termination rate coefficient. The low value of the termination rate coefficient of DCHI may therefore be interpreted by the very high viscosity of the monomer (see Table 1) and not by a chemically controlled termination reaction. However, we have not established a direct (causal) link between monomer viscosity and the k_t value, and further work is required before definite conclusions can be drawn. There is no obvious evidence for a chain length dependent termination rate coefficient, for the decrease of k_t with chain length—and time—should increase the concentration of free radicals, leading to a negative deviation of the plots $[R]^{-1}$ vs t. This possible lack of a chain length dependence—recently also observed with the sterically hindered dimethyl itaconate[12]—may be also explained by the chain stiffness. All theoretical investigations on the chain length dependence of a diffusion-controlled k_t normally deal with statistical Gaussian chains. The rigid shape of the chains formed by these hindered monomers may change their behavior and preclude a chain length dependence of k_t. This opens up a discussion over translational vs segmental diffusion control in these hindered monomers, which we will pursue in subsequent papers.

The evaluated values for $[R]_0$ range from 1×10^{-4} to 2×10^{-4} mol L^{-1} (see Table 8). This concentration is the summation of the radical concentration of 20 single laser pulses, minus the concentration of radicals terminated within the initiation period of 1 s. The termination during the first second can be neglected due to the small termination rate coefficient. Hence, the twentieth part of this radical concentration is a good measure for the primary radical concentration generated by one laser pulse, ρ, which therefore ranges from 5×10^{-6} to 1×10^{-5} mol L^{-1}. This order of magnitude concurs with previous published data,[12,37] although its exact value is of course dependent on the initiator concentration and the laser intensity.

To finally prove the relevance of the experimentally obtained kinetic data, an experiment was modeled, where the termination mode was the only unknown parameter. Figure 8 shows the simulated ($k_p = 2.9$ L mol^{-1} s^{-1}, $k_t = 311$ L mol^{-1} s^{-1}, $\rho = 1 \times 10^{-5}$ mol L^{-1}) and experimental CLDs, and Figure 9 gives the corresponding simulated monomer to polymer conversion vs time curve and the measured conversion values. These two figures impressively demonstrate the relevance of the kinetic parameters obtained in this study.

Conclusion

The commonly used pulsed laser polymerization technique and the recently introduced method of quenched instationary polymerization are successfully adapted for the measurement of kinetic coefficients of the highly hindered monomer dicyclohexyl itaconate. The need for very high free radical concentrations in the polymerizing system is achieved via a multipulse laser initiation, where a burst of laser pulses substitutes the commonly used single laser pulse. The obtained chain length distributions are readily analyzed with respect to their characteristic shapes. Data for the propagation rate coefficient, calculated via these two different techniques, show excellent agreement. The activation energy of the propagation reaction is very similar to the one obtained for other methacrylates, without substituents on the α-position; the low values of k_p can therefore be attributed to steric factors. There was no chain length dependence of k_p observed, which was assigned to the fact that the chains formed by this highly substituted monomer are very rigid. The instationary quenched polymerization method was also used to calculate the termination rate coefficients of this monomer system in the low conversion regime. The measured k_t values are very low, exhibiting a temperature dependence which is very close to the one for the monomer viscosity. This finding implies a diffusion control of the termination reaction. A therefore expected chain length dependence of k_t could not be observed. Modeling of the chain length distributions obtained by the quenched instationary polymerization experiments indicates about 25% termination via combination. The new techniques, which expand the commonly used pulsed laser experiments for the mechanistic investigations of free radical polymerization to the field of highly hindered monomers, will be used for further studies.

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