Termination Rate Coefficient of Dimethyl Itaconate: Comparison of Modeling and Experimental Results

Philipp Vana, Lachlan H. Yee, Christopher Barner-Kowollik, Johan P. A. Heuts, and Thomas P. Davis*

Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia

Received August 28, 2001; Revised Manuscript Received November 9, 2001

ABSTRACT: The termination kinetics of dimethyl itaconate (DMI) in bulk free radical polymerization at 40 °C have been studied by both experimental and theoretical approaches. The chain length distributions obtained from pulsed laser polymerization experiments have been analyzed in combination with rate measurements to extract chain length dependent termination rate coefficients. The full chain length distributions were modeled using a comprehensive kinetic scheme with both experimentally determined and adjustable kinetic parameters. The chain length average termination rate coefficient, k_t, was found to be close to 5.5×10^5 L mol^{-1} s^{-1}. Termination occurs almost exclusively via disproportionation. Such low k_t values are typical for sterically hindered monomers. The chain length dependence associated with the termination rate coefficient is almost negligible. The reasons for the very weak chain length dependence may be due to the solvent quality of the monomer toward its own polymer or due to the rigid structure of the formed polymer chains, therefore preventing the formation of a statistical coil.

Introduction

The determination of 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 situation is much less satisfactory with respect to the termination rate coefficients, k_t, for different monomer systems. Whereas several groups arrived in the past few years at accurate values for the termination rate coefficient and its chain length dependence of the "popular" monomers such as styrene and methyl methacrylate (using techniques that take advantage of the pulsed laser polymerization), few investigations have been done on other groups of monomer systems, in particular, the so-called "hindered" monomers, which have only been studied by electron spin resonance (ESR).[5,6] 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 of dimethyl itaconate[7,8] 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 monomer are of specific interest, because they provide deeper insights into the termination process, which is still far from being understood in depth.

To arrive at accurate values for the termination rate coefficient of DMI at 40 °C two different pathways were chosen, both relying on the careful determination of the chain length distribution of a polymer generated via a PLP experiment. In the first part of this work, we established a modeling method which allows for the evaluation of kinetic parameters by iterative optimization of a simulated model to the experimental chain length distribution. A comprehensive amount of mechanistic information can be gained about the overall system when a simulated model is applied. In particular, investigations can be conducted on how the kinetic coefficients might influence a specific system, and it is also possible to determine how sensitive these values are in describing the overall shape of the chain length distribution. The simulation program PREDICI[9] was used to perform model fitting to the PLP−SEC experimental data as well as to determine the average termination rate coefficient, k_t. The rate coefficient of the termination rate law of the form $-\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = k_t[\mathrm{R}^\bullet]^2$, where the factor of 2 is incorporated into the k_t value was used.

To verify the relevance of the kinetic data obtained by the described modeling procedure, experiments to determine the termination rate coefficient, k_t, were carried out. Two techniques, recently introduced by Olaj and co-workers,[10] were used to evaluate k_t via a careful analysis of the chain length distributions. These methods are capable of determining the rate coefficient of bimolecular termination, k_t, in free radical polymerizations and its chain length dependence. In both methods an average experimental $\overline{k_t}$ is defined and assigned to the mean chain length of the radical population that is characteristic of the experimental conditions chosen. In the first case the average $\overline{k_t^{\mathrm{m}}}$ is calculated from the equation relating the product of the weight average degree of polymerization $\bar{P}_w$ and the rate of polymerization R_p with kinetic coefficients[11]

$$\bar{P}_w R_p = \frac{k_p^{\,2}}{\overline{k_t^{\mathrm{m}}}}[\mathrm{M}]^2(3 - \delta) \qquad (1)$$

10.1021/ma011535v CCC: $22.00

with k_p being the rate coefficient of chain propagation and [M] being the monomer concentration. The quantity δ represents the contribution of disproportionation to overall termination.

In the second method to determine $\overline{k_t}$, another average termination rate coefficient, $\overline{k_t^*}$, is calculated via the rate expression derived for pulsed laser pseudo-stationary polymerization[12]

$$R_p = \frac{k_p[M]}{\overline{k_t^*}t_0}\ln\left\{1 + \frac{\rho\overline{k_t^*}t_0}{2}\left[1 + \left(1 + \frac{4}{\rho\overline{k_t^*}t_0}\right)^{0.5}\right]\right\} \quad (2)$$

with ρ being the concentration of free radicals produced in each pulse and t_0 the time elapsed between two successive laser pulses. The quantity ρ is determined as follows: In systems with negligible chain transfer the following relation holds true

$$\rho = 2R_p t_0/(\bar{P}_n(1 + \delta)) \quad (3)$$

with the number average degree of polymerization, $\bar{P}_n$, data being taken from the chain length distribution. Both methods are designed in such a way that they give an average k_t for each single experiment which is then attributed to the mean chain length of the terminating radicals ν', with $\nu' = \bar{P}_n((1 + \delta)/2)$. The results may be represented in the form of a power law

$$\overline{k_t} = A(\nu')^{-b} \quad (4)$$

where the exponent b is a measure for the chain length dependence of k_t. The prefactor A should not be confused with the termination rate coefficient for small radicals, because its value is obtained via an extrapolation of data that refers to macroradicals which show characteristics of a polymer chain. Hence, factor A refers to a termination rate coefficient of a polymer chain with unity chain length. Equations 1 and 2 were originally derived for chain length independent termination,[13,14] and they refer to systems with negligible chain transfer. Both methods rely on an accurate value of the propagation rate coefficient k_p, which can be easily determined via the PLP−SEC method.

Experimental Section

Materials. Dimethyl itaconate (Aldrich) was purified by distillation under reduced pressure ($bp^{5mmHg} \approx 80$ °C). The purity was confirmed by ^{1}H NMR spectroscopy. The photoinitiator 2,2′-azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. Tetrahydrofuran (THF) for GPC measurements was refluxed over potassium, distilled and stabilized with 2,6-di-*tert*-butyl-*p*-cresol.

Pulsed Laser Polymerizations. 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. Pulsing rates of 4−0.1 Hz were used. 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 experimental setup employed is very similar to the one described earlier.[15] Samples were deoxygenated by purging with nitrogen gas for a period of 10 min. The AIBN concentration was about 1×10^{-2} mol L^{-1}. Conversions of monomer to polymer were kept below 3%.

Molecular Weight Analysis. Chain length distributions were measured by size exclusion chromatography (SEC) on a Shimadzu modular system, comprising of an auto injector, 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 tetrahydrofuran (THF) at 40 °C with a flow rate of 1 mL min^{-1}. Calibration curves were generated using both polymethyl methacrylate and polystyrene standards. The Mark−Houwink−Kuhn−Sakurada (MHKS) constants of polystyrene and polymethyl methacrylate[16,17] were then used to create an universal calibration curve which, in conjunction with the MHKS constants of polydimethyl itaconate,[7] provided access to absolute molecular weight distributions. The propagation rate coefficients, k_p, were determined using the inflection point molecular weights of the primary peak of the molecular weight distribution, utilizing eq 5,[1]

$$L_0 = k_p[M]t_0 \quad (5)$$

where L_0 is the kinetically relevant chain length obtained from the inflection point preceding a maximum of the distribution, [M] is the monomer concentration, and t_0 is the time between consecutive laser pulses. Conversions of monomer to polymer—which were used to determine the rate of polymerization, R_p—were determined via the calibrated area under the differential refractometer signal. Number average degrees of polymerization, $\bar{P}_n$, and weight average degrees of polymerization, $\bar{P}_w$, were calculated from the molecular weight distributions.

Dilatometry. The density change of the polymerization system was followed in a volume calibrated dilatometer. The volume change was followed via the computer controlled observation of the meniscus of a solvent in a capillary on top of the reaction mixture. The conversion, $x(t)$, was calculated via eq 6,

$$x(t) = h(t)\frac{a}{m_0 f} \quad (6)$$

where $h(t)$ is the meniscus height, the cross sectional area of the capillary tube is a, the initial mass of monomer is m_0, and f is the contraction factor.

Simulations. All simulations of chain length distributions were carried out with the program package PREDICI, version 5.36.3, on a Pentium III, 733-MHz IBM-compatible computer. A total of 20 simulated laser pulses were used in the modeling procedure. The molecular weight distribution used in the modeling procedure was obtained via a PLP experiment with an initial initiator concentration of 3.46×10^{-3} mol L^{-1} and a dark time of 2.5 s at 40 °C.

Results and Discussion

PREDICI is a comprehensive simulation package for the treatment of kinetic equations in models of polyreactions, which allows the computation of chain length distributions of macromolecules generated via polymerization processes—combined with the simulation of additional reaction components and reactor variables. It is this treatment of simultaneous kinetic equations that allows detailed investigations of the mechanisms that occur during polymerization viz. initiation, propagation, chain transfer and termination. As well as this, values for the various rate coefficients that relate to these mechanisms can be optimized for. To simulate a chain length distribution for a typical PLP experiment a proper set of reactions has to be chosen, which contains the basic reaction types of free radical polymerization, (pulsed) initiation (A), propagation (B), transfer (C), and termination (D) (see Scheme 1).

To calculate the exact chain length distribution all rate coefficients and the initial concentration of the monomer and the initiating radicals have to be known. However, if the true chain length distribution is determined via SEC, the parameters—or combination of parameters—can be calculated via a modeling procedure. The simplest model for the pulsed laser polymer-

Scheme 1. Reaction Scheme of the Free Radical Polymerization Process Implemented into the PREDICI Simulation Program (for Details, See Text)

$$I^{\bullet} + DMI \xrightarrow{k_i} macrorad(1) \tag{A}$$

$$macrorad(i) + DMI \xrightarrow{k_p} macrorad(i+1) \tag{B}$$

$$macrorad(i) + DMI \xrightarrow{k_{tr}} PolyDMI(i) + macrorad(1) \tag{C}$$

$$macrorad(i) + macrorad(j) \xrightarrow{k_{td}} PolyDMI(i) + PolyDMI(j) \tag{D1}$$

$$macrorad(i) + macrorad(j) \xrightarrow{k_{tc}} PolyDMI(i+j) \tag{D2}$$

$$macrorad(i) + I^{\bullet} \xrightarrow{k_i} PolyDMI(i) \tag{D3}$$

ization already includes five variables, making it impossible to find a unique solution for the given chain length distribution if one tries to optimize simultaneously for all variables. Some of the parameters are well-known, especially the monomer concentration, [M] and the propagation rate coefficient, k_p, which can be easily determined via the PLP−SEC technique. For the other parameters reasonable initial values have to be assumed:

The rate coefficient of initiation, k_i, was assumed to be 10 times that of the rate coefficient of propagation, k_p. This is generally considered a sound assumption as it is well-known that short chain propagation occurs at a faster rate than long chain propagation.[18−20] It should also be noted that the size of k_i does not play a major role in forming the shape of the simulated PLP chromatograms.

Propagation rate coefficients k_p were taken from ref 7. Although it has recently been described that the propagation rate coefficient k_p is not chain length independent,[21] a constant value for all simulations was used. However, the effect of chain length dependence of k_p in the bulk polymerizations of DMI is rather small (the k_p value decreases about 10% in the chain length range of 0−500 and remains constant at higher chain lengths).[22] Neglecting this effect for the simulation procedure will cause little error.

The value used for the transfer to monomer rate coefficient, k_{tr}, is close to the numbers reported for methyl methacrylate (MMA).[23] The transfer reaction has been included in the model to give a more complete picture of the reacting system. We are aware of the fact that DMI may have a slightly different (higher) value for the transfer to monomer rate coefficient. However, we believe that the overall physical picture presented in this study is only marginally affected by the transfer to monomer rate coefficient, as its influence on the final molecular weight distribution is negligible as long as its value is relatively small.

The value for the concentration of free radicals formed at each laser pulse, ρ, was obtained by applying several formulas to arrive at a reasonable starting value.[24] This is important to minimize the computation time and to ensure that the optimized parameters are corresponding to the global minimum of the iteration. Equation 7 gives an expression for determining the initiator radical concentration[25]

$$\rho = 2\Phi \frac{n_{abs}}{V} \tag{7}$$

where Φ is the primary quantum yield, n_{abs} is the number of absorbed photons, and V is the irradiated volume. The primary quantum yield is calculated as the product of laser efficiency—assumed to be one in our simulations—and initiator efficiency f_i.[26] The number of absorbed photons is calculated via the Lambert−Beer law:[25]

Table 1. Physical Parameters and Procedure for the Calculation of Energy per Mole of Laser Photons

energy of generated photons	formula/ symbol	value
laser wavelength	λ	3.55×10^{-7} m
speed of light	c	3×10^{8} m s^{-1}
frequency of laser light	$\nu = c\lambda^{-1}$	8.45×10^{14} s^{-1}
Plank's constant	h	6.63×10^{-34} J s
single photon energy	$E_\lambda = h\nu$	5.60×10^{-19} J
photon energy/mol photons	$E_\lambda{}^{m} = E_\lambda N_A$	3.37×10^{5} J mol^{-1}

$$n_{abs} = \frac{E_p}{E_\lambda}(1 - 10^{-\epsilon[I]d}) \tag{8}$$

with E_p being the energy of one laser pulse and E_λ the energy of one mole of photons at the laser wavelength λ; ϵ is the molar absorption coefficient of the initiator molecule at the laser wavelength, [I] is the photoinitiator concentration, and d refers to the optical path length. Tables 1 and 2 give detailed information for the calculation procedure of E_λ, n_{abs} and the concentration of free radicals produced by one laser pulse, ρ.

Because the decrease of the laser light intensity within the sample due to absorption and the consumption of photoinitiator during the polymerization process was not taken into account, this value for ρ represents an upper limit. The estimated values of about 5×10^{-6} mol L^{-1}—depending on the photoinitiator concentration—are in very good agreement with those reported by the CSIRO group,[27] who measured the concentration of free radicals produced by one laser pulse, ρ, with AIBN as the photoinitiator via trapping experiments with nitroxides.

The initial value for the termination rate coefficient, k_t, was determined via steady-state experiments. Monomer conversions (up to a maximum of 10%) with respect to time were determined using dilatometry leading to an apparent rate coefficient, k_{obs}—according to eq 9—which gives a value for the average termination rate coefficient, k_t, of

$$\ln\frac{1}{1-x} = k_{obs}t \text{ with } k_{obs} = k_p\left(\frac{2f\,k_d[I]}{k_t}\right)^{0.5} \tag{9}$$

where x is the overall monomer conversion, f is the initiator efficiency, k_d is the rate of initiator decomposition,[26,28] k_p is the propagation rate coefficient obtained from PLP−SEC experiments, and k_{obs} is the observed rate coefficient of polymerization, which is equal to the slope from a plot of $\ln(1/(1-x))$ vs t. The experimental data are given in Table 3 leading to an value for k_t of about $(4.6 \pm 1.4) \times 10^{5}$ L mol^{-1} s^{-1}.

To keep the number of unknown parameters as small as possible, the chain length dependence of k_t was neglected. As will be shown later, this assumption is in excellent agreement with our experimental data which indicates that k_t is indeed chain length independent for chain length exceeding 80 units. However, it should not be ruled out a priori that termination is fast for small radicals. Thus, the simplest form of a chain length dependent termination rate coefficient was introduced

Table 2. Physical Parameters and Procedure for the Calculation of the Concentration of Free Radicals Produced by One Laser Pulse

primary radical concentration	formula/symbol	value
applied single pulse energy	E_p	0.02 J
AIBN extinction coefficient at λ^a	ϵ	12881.8 $cm^2\ mol^{-1}$
initial AIBN concentration	[I]	3.46×10^{-6} mol cm^{-3}
optical path length	d	1.3 cm
primary quantum yield	Φ	0.54
number of absorpt photons/laser pulse	$n_{abs} = E_p E_\lambda^{-1}(1-10^{-\epsilon \cdot [I] d})$	7.4×10^{-9}
irradiated volume	V	1.7×10^{-3} L
radical concentration/laser pulse	$\rho = 2\Phi n_{abs} V^{-1}$	$\approx 5 \times 10^{-6}$ mol L^{-1}

[a] The molar extinction coefficient ϵ was determined experimentally by measuring the absorbance of AIBN at 355 nm via Beer–Lambert's Law.

Table 3. Experimental Data of the Dilatometric Rate Measurements: [I], Initiator Concentration; k_{obs}, Observed Rate Coefficient; k_t, Average Termination Rate Coefficient

[I]/mol L^{-1}	$k_{obs}/10^{-5}\ s^{-1}$	$k_t/10^5$ L $mol^{-1}\ s^{-1}$
0.01	1.0	7.0
0.03	2.8	3.8
0.04	2.7	4.4
0.07	3.8	4.0
0.09	4.6	3.6

Table 4. Optimized Kinetic Parameters for the Bulk Polymerization of Dimethyl Itaconate at 40 °C, Evaluated via Modeling the Experimental Chain Length Distribution (for Details See Text)

parameter	value
k_i/L $mol^{-1}\ s^{-1}$	160
k_p/L $mol^{-1}\ s^{-1}$	16.0
k_{tc}/L $mol^{-1}\ s^{-1}$	3×10^4
k_{td}/L $mol^{-1}\ s^{-1}$	3×10^5
k_1/L $mol^{-1}\ s^{-1}$	1×10^8
k_{tr}/L $mol^{-1}\ s^{-1}$	5×10^{-3}
ρ/mol L^{-1}	2×10^{-6}

with the reaction (D3) in Scheme 1, the primary radical termination reaction, with the rate coefficient k_1, which is estimated to be in the order of 10^8 L $mol^{-1}\ s^{-1}$. If k_t is assumed to be chain length independent the overall shape of a PLP distribution is only governed by the product $k_t \rho t_0$.[1] Modeling for the individual parameters k_t and ρ would therefore not be possible. The introduction of the primary radical termination reaction, however, allows for the optimization of each of these variables. Inspection of Figure 1 clearly indicates that k_t and ρ can indeed be separated to some extent by the modeling procedure. The figure shows two molecular weight distributions where k_t is changed within 1 order of magnitude but the product of k_t and ρ is kept constant. The MWD given by the full line (corresponding to an overall k_t of 3.3×10^5 L $mol^{-1}\ s^{-1}$) clearly shows a distinct first peak, whereas the MWD represented by the dashed line (corresponding to an overall k_t of 3.3×10^6 L $mol^{-1}\ s^{-1}$) only has a shoulder at this position. An SEC broadening of $\sigma(\log M) = 0.05$ has been applied to the distributions.

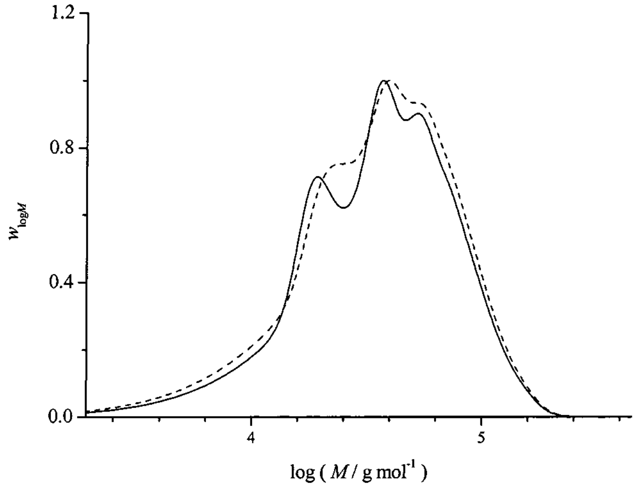

Figure 1. Simulated SEC trace for two free radical DMI bulk polymerizations with a pulse repetition rate of 1 Hz. An SEC broadening of $\sigma(\log M) = 0.05$ has been applied to the distributions. The MWD represented by the full line was obtained using the numbers given in Table 4; the dashed line corresponds to a MWD calculated with an increased (factor 10) overall k_t. The product of ρ and k_t was kept constant for both simulations.

The termination rate coefficient of very small radicals, k_1, is believed to be much higher than those of macroradicals. However, the difference between the termination rate coefficient for very small radicals and that for long macroradicals for so-called "high termination" monomers such as styrene or methyl methacrylate does not exceed 1 order of magnitude. Therefore, the kinetic schemes for such monomer systems do not often account for this type of reaction. Due to the very low termination rate coefficient of DMI the difference between these two termination rate coefficients may be much higher—3 orders of magnitude or more—if one assumes that the reactivity of the small radicals is not lowered in the DMI system. Keeping in mind that the termination process in the free radical polymerization of many conventional monomers in the low conversion regime is controlled by segmental diffusion,[29] this assumption seems reasonable.

Having obtained (through external methods) starting values for the rate coefficients and the primary free radical concentration, the remaining rate coefficient, k_t, was optimized for. The model then underwent iterative improvement/matching with experimental values until the optimal values for the various kinetic parameters were determined. A multidimensional grid for the parameters k_{tc}, k_{td}, k_1, and ρ was used for systematic variations of these different kinetic coefficients and the quality of the fit was determined via two main criteria: (i) the relative height of the first and second additional peak and the minima between them of the chain length distribution had to match and (ii) the low and high molecular area were subsequently fitted without changing the proportion of the additional peaks. The parameters k_i, k_p, and k_{tr} were held constant, assuming that they already represent reasonable values. Table 4 gives the results for this modeling procedure for the pulsed laser polymerization of DMI at 40 °C. It should be mentioned that the modeling procedure is subject to larger errors than the experimental procedure outlined

Table 5. Compilation of Experimental Data and Kinetic Quantities for the Pulsed Laser Polymerization of Dimethyl Itaconate at 40 °C, Calculated for $k_p = 16.0$ L mol^{-1} s^{-1} and $\delta = 0.9$

t_0/s	$R_p/10^{-4}$ mol L^{-1} s^{-1}	$\bar{P}_n$	$\bar{P}_w$	$\rho/10^{-6}$ mol L^{-1}	$\overline{k_t^m}/10^5$ L mol^{-1} s^{-1}	$\overline{k_t^*}/10^5$ L mol^{-1} s^{-1}
0.25	2.6790	80	173	0.8849	5.651	6.092
0.50	2.0964	108	235	1.0205	5.319	5.666
0.75	1.9485	113	253	1.3606	5.322	5.700
1.00	1.6539	126	273	1.3767	5.819	5.901
1.50	1.3924	154	329	1.4250	5.718	5.592
2.00	1.1344	176	410	1.3537	5.635	5.849
2.50	1.0352	177	460	1.5404	5.505	6.099
3.00	1.0602	168	483	1.9906	5.121	5.872
3.50	0.9882	168	484	2.1729	5.480	6.002
4.00	0.6552	300	778	0.9190	5.148	5.756
5.00	0.4881	392	948	0.6553	5.666	5.975
7.00	0.4507	412	1100	0.8060	5.290	5.723
8.50	0.3937	462	1227	0.7624	5.432	5.702
9.90	0.3999	428	1239	0.9738	5.293	5.594

below. The numbers given in Table 4 for k_t and ρ are associated with an error of at least ±50%.

It is noteworthy that the value obtained for ρ is acceptably close to the initial value calculated through the given formulas. This lends credit to the modeling procedure that was applied to deduce ρ, since the calculation procedure only involves known physical constants and should thus yield correct numbers. The only unknown quantity is Φ, the primary quantum yield. In addition, the experimentally obtained monomer conversion for the corresponding PLP–SEC experiment matched the calculated conversion (using the parameters given in Table 4 and experimental conditions described in the section Experimental/Simulations) which further underpins the validity of the obtained parameters.

The termination was originally thought to be solely by disproportionation, referring to the work of Popovic and co-workers[30] using thermogravimetric investigations. In addition, considering that this study involves the polymerization reactions of a "hindered" monomer species, one would expect to see very little termination by combination. However, it is very difficult to deduce the ratio of combination to disproportionation solely from the molecular weight distribution via a modeling approach. The sensitivity of the shape of the chain length distribution toward the mode of termination is not very high, but at least a small amount of termination by combination seems to occur. It is for this reason that we included 10% termination by combination into the model. Recent experiments, dealing with the termination mode of hindered monomers, underpinned the above assumption.[31]

The termination rate coefficient was subsequently determined via the techniques introduced by Olaj and co-workers.[10] Table 5 lists the data obtained for $\overline{k_t^m}$ and $\overline{k_t^*}$, respectively, evaluated for $\delta = 0.9$. The result of the linear fit to the data—shown in Figure 2—worked fairly well and leads to

$$\overline{k_t^m} = (6.03 \pm 1.2) \times 10^5 \bar{P}_n^{-(0.02\pm0.02)}$$

$$\overline{k_t^*} = (6.34 \pm 0.9) \times 10^5 \bar{P}_n^{-(0.02\pm0.01)}$$

where the 95% confidence intervals are given.

The observed absolute values lie within a range of 5.1×10^5 to 6.1×10^5 L mol^{-1} s^{-1} exhibiting an almost negligible chain length dependence described by exponents of about −0.02 in the corresponding power laws for the chain length regime of 80 to 500. Comparison of $\overline{k_t^m}$ and $\overline{k_t^*}$ shows that the former quantity is always smaller (by about 3–5% on average). This appears to be a genuine effect which was observed by simulation data[12] where this difference was monitored as a function of the extent of the chain length dependence of k_t. However, the differences are very small, reflecting the weak chain length dependence. There are two possible reasons for the negligible chain length dependence of k_t: (i) It is well-known that in systems where the surrounding media is a thermodynamically bad solvent the exponent b of the power law becomes very small, assuming that a shielding effect of the polymer chain is responsible for the chain length dependence of k_t. In theory this shielding effect should nearly vanish in a Θ system ($b \approx 0.05$).[32] Considering the errors of the exponents (i.e., ±0.02), the obtained values of b may well be ascribed to a reduced solvent quality of the monomer toward the polymer in the bulk polymerization of DMI at 40 °C. (ii) The negligible chain length dependence may be caused by the lack of the above-mentioned shielding effect. This may be explained by the hindered structure of the monomer that forms very stiff polymer chains.[33] All theoretical investigations dealing with the shielding effect of diffusion controlled termination reactions so far used the concept of statistical Gaussian coils. The rodlike structure of the polymer chains formed by a hindered monomer—therefore not fully capable of forming statistical coils—may be responsible for this different behavior and preclude a chain length dependence of k_t.

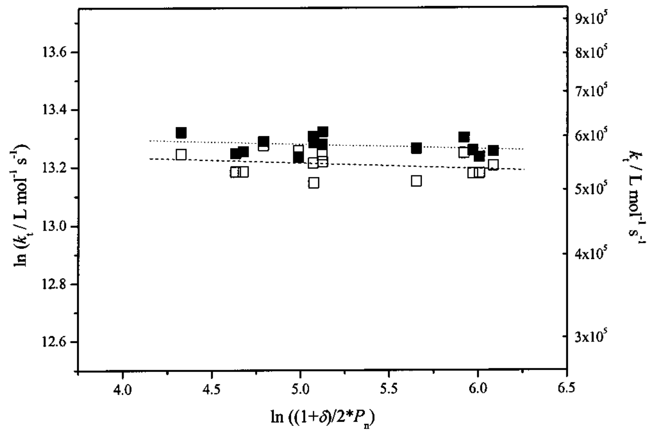

Figure 2. Double logarithmic plots of $\overline{k_t^m}$ (□) and $\overline{k_t^*}$ (■)—calculated from experimental data of dimethyl itaconate polymerization at 40 °C according to eq 1 and eq 2—vs the number average chain length of the radicals at the moment of their termination $\nu' = \bar{P}_n((1 + \delta)/2)$, for contribution of disproportionation to overall termination $\delta = 0.9$ and $k_p = 16$ L mol^{-1} s^{-1}. Best linear fits are indicated.

The comparison of the termination rate coefficients, k_t, of DMI at 40 °C obtained via modeling of the complete chain length distribution—i.e., $k_t = 3.3 \times 10^5$ L mol^{-1} s^{-1}, see Table 4—with those evaluated experimentally—i.e., $k_t = 5.5 \times 10^5$ L mol^{-1} s^{-1}, see Table 5 and $k_t = 4.6 \times 10^5$ L mol^{-1} s^{-1}, see Table 3—shows the good agreement of these two methods; despite the large numbers of parameters which were necessary to model the PLP distribution, the result is quite satisfactory. The difference of a factor of about 1.75 is comparatively small if one takes a look at the scatter

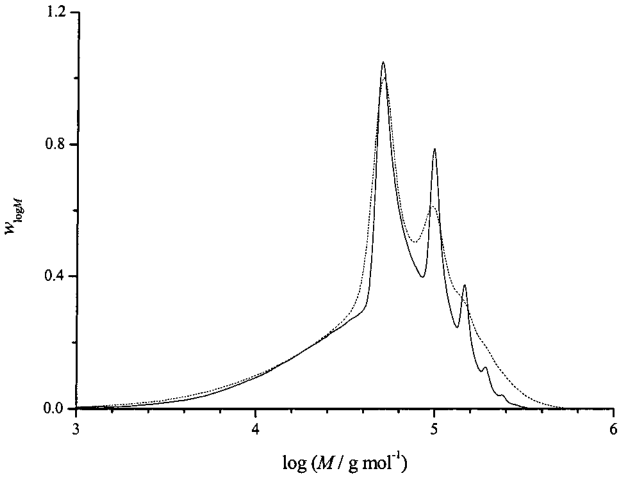

Figure 3. Experimental (- - -) and simulated (—) chain length distribution (SEC-trace) for a pulsed laser polymerization of dimethyl itaconate at 40 °C, $t_0 = 2.5$ s, and $\rho = 1.54 \times 10^{-6}$ mol L^{-1}, where k_{td} and k_{tc} are 5.4×10^5 and 0.6×10^5 L mol^{-1} s^{-1}, respectively. All other parameters are given in Table 4.

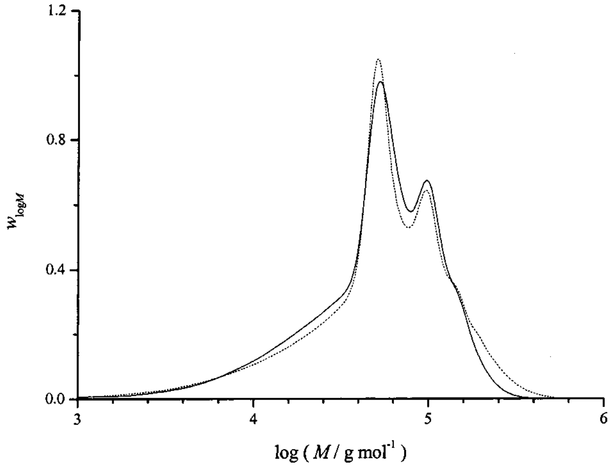

Figure 4. Experimental (- - -) and simulated (—) chain length distribution (SEC-trace) for a pulsed laser polymerization of dimethyl itaconate at 40 °C. The same parameters were used as in Figure 3; the simulated chain length distribution was subject to a Gaussian broadening with $\sigma_{\log M} = 0.05$.

which is normally associated with literature data of k_t.[23] Hence, the modeling procedure may constitute an appropriate tool for the determination of kinetic coefficients, especially the rate coefficient of termination. Due to the fact that the chain length distribution is modeled as a whole, errors occurring in the baseline of the size exclusion chromatography or low molecular weight material can easily be excluded by taking only the "important" regions—like the additional peaks and the adjacent rising edges—into account. The critical part of the modeling procedure is the estimation of the free radical concentration ρ, due to its coupled nature with k_t. However, the comparison of the experimentally obtained values with the estimated and afterward optimized values shows them to be in very good agreement. Our successful estimation of the concentration of the free radicals produced by each laser pulse, ρ, makes the modeling procedure capable of determining kinetic parameters of polymerization systems, where the primary radical termination reaction is not as pronounced as in this low termination system. The negligible chain length dependence of the system, which was determined experimentally, justifies the assumption of chain length independent k_t which was made in the simulation model. However, the concept of a chain length dependent termination reaction will be inserted into the model for future studies. Figure 3 shows an experimental chain length distribution of a pulsed laser polymerization of the DMI system at 40 °C together with a simulated one, using the experimental values of k_t and ρ. Figure 4 shows the same chain length distribution as Figure 3, but after a mathematical treatment[34] which simulates the SEC broadening ($\sigma(\log M) = 0.05$). The distributions nearly match exactly, indicating the quality of the model which was used for the simulations.

There are very few data in the literature our results can be compared with and the interpretation under the concept of chain length dependent k_t is missing in all cases. However, due to the very weak or nonexisting chain length dependence of k_t the good agreement with data obtained by methods which do not account for the chain length dependence is quite satisfactory. One example where a fairly reasonable comparison can be made is given by the work of Sato et al.[5] which contains data collected at 50 °C in benzene by means of electron spin resonance spectroscopy (ESR) combined with steady-state data. They arrived at a value of k_t of 5.9×10^5 L mol^{-1} s^{-1}, which is in excellent agreement with our data, although a direct comparison is not straightforward due to the different temperature, the used solvent and the fact that the chain length regime of their measurements is not specified. The same holds true for the work of Otsu et al.,[6] who determined k_t of DMI at 60 °C in benzene via ESR. They stated a slightly lower value of 3.6×10^5 L mol^{-1} s^{-1}, which is, however, still in good agreement with our data. Literature data[23] for k_t of monomers such as methyl methacrylate or styrene which exhibit a more or less pronounced chain length dependence are spread over 1.5 orders of magnitude. This enormous scatter occurs mostly because the chain length dependence of the termination rate coefficient was not accounted for. It is therefore no surprise that in a system with negligible chain length dependence of k_t like DMI the data obtained via different methods must match better.

Conclusion

The method of determining kinetic parameters, especially the rate coefficient of termination, k_t, via modeling the chain length distributions obtained by pulsed laser polymerization shows remarkably good agreement with experimentally evaluated data. The success of the modeling procedure relies on the careful estimation of the free radical concentration, which is produced by each laser pulse. The experimental verification of the modeling results lead to values of the termination rate coefficient which exhibit only a negligible chain length dependence. This effect may be assigned to a low solvent quality of dimethyl itaconate toward its polymer or to the formation of rodlike polymer chains that prevent the formation of statistical polymer coils. Future investigations will try to elucidate the termination reactions of dimethyl itaconate and other "hindered" monomer systems.

Acknowledgment. P.V. acknowledges the generous support by the Austrian Science Fund (Project No. J1965). Financial support by Uniqema (ICI) and the CRC for Polymers is gratefully acknowledged. The Australian Research Council is acknowledged for generous funding.

References and Notes

(1) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.
(2) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
(3) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; Van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545.
(4) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355.
(5) Sato, T.; Takahashi, Y.; Seno, M.; Nakamura, H.; Tanaka, H.; Ota, T. *Makromol. Chem.* **1991**, *192*, 2909.
(6) Otsu, T.; Yamagishi, K.; Matsumoto, A.; Yoshioka, M.; Watanabe, H. *Macromolecules* **1993**, *26*, 3026.
(7) Yee, L. H.; Coote, M. L.; Davis, T. P.; Chaplin, R. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2192.
(8) Yee, L. H.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 3581.
(9) Wulkow, M. *Macromol. Theory Simul.* **1996**, *5*, 393.
(10) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 433.
(11) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **1997**, *18*, 997.
(12) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **1998**, *19*, 89.
(13) Olaj, O. F.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2569.
(14) Olaj, O. F.; Zifferer, G. *Eur. Polym. J.* **1989**, *25*, 961.
(15) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.
(16) Rudin, A.; Hoegy, H. L. W. *J. Polym. Sci., Part A1* **1972**, *10*, 217.
(17) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D.; Zilliox, J. J. *Chim. Phys.* **1966**, *63*, 1507.
(18) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *Macromolecules* **1995**, *28* (26), 8771.
(19) Deady, M.; Mau, A. W. H.; Moad, G.; Spurling, T. H. *Makromol. Chem.* **1993**, *194* (6), 1691.
(20) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864.
(21) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913.
(22) Vana, P.; Davis, T. P. Manuscript in preparation.
(23) Brandrup, A.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; Wiley-Interscience: New York, 1999.
(24) Buback, M.; Huckestein, B.; Leinhos, U. *Makromol. Chem., Rapid. Commun.* **1987**, *8*, 473.
(25) Buback, M.; Busch, M.; Kowollik, C. *Macromol. Theory Simul.* **2000**, *9*, 442.
(26) Buback, M.; Huckestein, B.; Kuchta, F.-D.; Russel, G. T.; Schmid, E. *Macromol. Chem. Phys.* **1994**, *195*, 2117.
(27) Moad, G.; Shipp, D. A.; Smith, T. A.; Solomon, D. H. *J. Phys. Chem. A* **1999**, *103*, 6580.
(28) Moad, G.; Rizzardo, E.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 793.
(29) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859; Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
(30) Popovic, I. G.; Katsikas, L.; Weller, H.; Schroetter, S.; Velickovic, J. S. *J. Appl. Polym. Sci* **1993**, *50*, 1475.
(31) Vana, P.; Yee, L.; Davis, T. P. *Macromolecules* **2001**, submitted for publication.
(32) Khokhlov, A. R. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 633.
(33) Matsumoto, A. *Macromol. Symp.* **1995**, *98*, 139.
(34) Laemmel, R. A. Ph.D. Thesis, Goettingen, Germany, 1997.

MA011535V