A Novel Method for the Measurement of Chain Transfer to Monomer Constants in Styrene Homopolymerizations: The Pulsed Laser Rotating Reactor Assembly

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Received October 31, 2000

ABSTRACT: The chain transfer to monomer constants (C_m) in styrene bulk polymerizations have been determined in the temperature range between 25 and 90 °C using both thermal polymerization and the novel pulsed laser polymerization (PLP) with extended dark times. This novel technique determines transfer to monomer rate coefficients by combining a pulsed laser setup with a rotating reactor/cuvette assembly. The resulting transfer controlled molecular weight distributions (MWD) were analyzed by the well-known Mayo and chain length distribution (CLD) methods. The results of both experimental methods agree well, which indicates that PLP with extended dark times is a reliable technique to determine transfer to monomer constants. For this reason, we report average values for the activation parameters determined from both thermal and extended dark times PLP experiments: $E_a = 21.6$ kJ mol^{-1} and $A = 0.22$ L mol^{-1} s^{-1}. These numbers are in excellent agreement with those reported in the literature.

Introduction

The evaluation procedures and theoretical basis for the determination of transfer to monomer constants, C_m, have been extended and perfected over the past decade, and a great number of transfer constants have been determined by various research groups (see for example refs 1 and 2 or the multiple entries in the *Polymer Handbook*[3]). The transfer (to monomer) constant is defined by eq 1 as the ratio of the transfer rate coefficient, k_{tr}, to the propagation rate coefficient, k_p.

$$C_m = k_{tr}/k_p \tag{1}$$

The classical procedure for transfer constant measurement (to the monomer itself, any other added substance or deliberately added transfer agent, such as a thiol or a catalytic chain transfer agent) has always been the Mayo method.[4] However, Gilbert recently introduced the chain length distribution (CLD) method[5] as an alternative way to determine transfer constants. The Mayo and CLD methods in themselves also provide different choices of data analysis, and these differences will be addressed later in this paper. Both methods have been carefully compared and thoroughly discussed with the conclusion that both are theoretically equivalent.[6]

In terms of applied experimental procedures, there are only two conceptually different methods available. The first one is the conventional or classical polymerization via thermal polymerization experiments with specific amounts of thermally decaying initiator present in the reaction mixture. Various groups have used this technique to determine transfer constants as the impressive collection of data in ref 3 indicates. Kukulj et al.,[7] for example, investigated the transfer to monomer constant of methyl methacrylate (MMA), styrene, and α-methylstyrene (AMS) at 50 °C using thermal polymerization. To generate a sufficiently low radical flux to achieve transfer dominated reaction conditions, the stock solution of the initiator in monomer was successively diluted. This gave a series of solutions with decreasing initiator concentrations yielding increasing molecular weights upon polymerization. In many cases and when the initiator concentrations are chosen correctly, a limiting molecular weight is reached which may then be used to determine the transfer to monomer constant via either the Mayo or the CLD method.

A second and more recent experimental technique became possible with the advent of pulsed laser systems: pulsed laser polymerization (PLP) in combination with subsequent size exclusion chromatography (SEC) of the resulting polymer is the standard and IUPAC recommended technique for the determination of propagation rate coefficients, k_p.[8] However, several research groups have used PLP to determine transfer rate constants to a range of chain-transfer agents. For example, Hutchinson and co-workers[9] determined the transfer coefficients for transfer to *n*-dodecyl mercaptan in methyl methacrylate (MMA), styrene, ethyl methacrylate (EMA), and butyl methacrylate (BMA) homopolymerizations in the temperature range between 20 and 80 °C. By adding sufficient transfer agent, these authors were able to generate transfer dominated conditions, as seen by the loss of the PLP characteristics in the molecular weight distributions (MWD) obtained by SEC analysis of the polymers. In addition, Buback and co-workers[10] designed a method to determine the value of the propagation rate coefficient, k_p, and the transfer to monomer rate coefficient ($k_{tr,\ mon}$) from a single PLP experiment. Packages of high-frequency pulses separated with long dark time intervals gave rise to two polymer distributions. The polymer produced during the high-frequency pulse packages could be used

10.1021/ma001871w CCC: $20.00

to determine k_p, while the polymer produced in the longer dark time could be used to determine C_m. The validity of the method was demonstrated using the PREDICI simulation program.[10,11]

Pulsed laser polymerization, however, is normally not the method of choice for measuring transfer to monomer rate coefficients via the CLD method, because the CLD method requires termination to be an unimportant or even absent route of radical chain stoppage as compared to transfer to monomer. In addition, the radical flux must be low enough so that transfer, rather than termination, is the main chain-stopping event, so that the polymerization is truly transfer dominated. Up to now PLP has essentially been used as a flickering termination rate technique, i.e., as a technique that makes essential use of effective termination. PLP can, however, be made applicable for studying even transfer to monomer, if combined with a rotating reactor/cuvette assembly as will be presented in the present communication. This assembly permits time efficient experiments with very long pulse periods and thus enables high molecular weight material to be produced at very low radical concentrations or termination rates, respectively. The main problem that is associated with extended dark times is the slow rate of polymerization. The rotating reactor/cuvette (which will be described in detail in the Experimental Section of this paper) allows for acceptable polymerization rates even for slowly propagating monomers such as styrene.

The present paper reports the use of this novel PLP experiment with extended dark times to determine the transfer to monomer constant, C_m, in styrene bulk homopolymerizations. As the frequency of the pulsed laser decreases and the dark time increases, the concentration of radicals in the system during polymerization decreases. At sufficiently long dark times, the radical flux should be so low that the main chain-stopping event is transfer to monomer rather than termination. This decrease in radical flux should be reflected in the shape of the SEC chromatogram as a loss of the characteristic PLP structure, which may be observed under non-transfer-controlled conditions. Such samples should therefore give accurate values of the chain transfer constants when the CLD method (or Mayo method) is used to analyze the data.

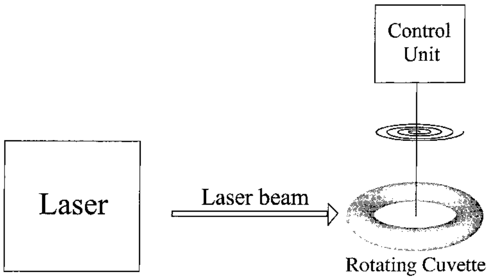
The validity of the method is tested by comparing the results to transfer to monomer rate coefficients obtained by the conventional thermal polymerization method. Transfer-dominated molecular weight distributions from thermal polymerizations can be analyzed via either the CLD or Mayo methods. The C_m values given in this paper will therefore be based on those two methods. The evaluation procedure will be discussed in detail later.

Experimental Section

Materials. Styrene (Aldrich, 99%) used for the PLP experiments was purified by washing the monomer with NaOH solution to destabilize the inhibitor. The aqueous phase was discarded, and the monomer was then passed through a short column of Baylith TE 144 (Bayer) and alumina (aluminum oxide 90, Merck). The photoinitiator for the extended dark time pulsed laser experiments was 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Aldrich, 99%). Methanol used to precipitate polystyrene from the samples was of chromatographic grade from Merck. Polymer samples were dissolved in dichloromethane (chromatographic grade, Merck) for GPC analysis.

The thermal experiments were carried out using 2,2-azobis(isobutyronitrile) (AIBN, Aldrich) as a thermally decaying initiator. AIBN has been recrystallized twice from methanol prior to use. Styrene (Aldrich, 99%) used for these experiments was dried over calcium hydride (Aldrich) before being distilled under reduced pressure. The distilled styrene was then passed through a column of basic alumina (Aldrich). Polymer samples were dissolved in THF (Aldrich, 99.9%) for GPC analysis.

Scheme 1. Schematic Drawing of the Experimental Apparatus Used at Bayer AG, Leverkusen, for the Pulsed Laser Rotating Reactor Experiments[a]



[a] The setup is comprised of the laser, the rotating cuvette (which is embedded in a thermostated water bath), and the control unit for the motor rotating the cuvette.

The Pulsed Laser Rotating Reactor Assembly. The pulsed laser rotating reactor assembly was developed and constructed at Bayer AG, Leverkusen. All polymerizations (except those at 10 Hz, which were performed in a stationary vial) were carried out in the specially designed cuvette/reactor to allow for acceptable effective polymerization rates, i.e., acceptable rates of production of polymer, even at pulse periods of 100 s. The reactor essentially consisted of a hollow quartz tube (see Scheme 1) in the form of a ring, which was slowly and quasi-continuously rotated around a vertical axis through the center of symmetry of the ring by an electronically controlled step motor. The laser light was directed onto the quartz ring in a horizontal plane perpendicular to the axis of its rotation. The inner diameter of the reaction tube was 8 mm, and the outer diameter of the ring was about 80 mm. This allowed the initiation of polymerization in up to around 20 well-separated sectors of the tube, which allowed about a 20-fold increase in polymer generation, provided that the diameter of the laser beam was limited to below 10 mm by an aperture mounted in front of a quartz tube. The laser pulse period and the period of revolution of the spinning cuvette were electronically synchronized to ensure that individual initiation volumes were always exactly hit again by subsequent laser pulses once they had been selected by suitable combinations of periods of laser pulses and cuvette revolutions.

The number of positions (sectors) at which the pulse from the laser struck the cuvette, the cuvette rotation time, and the total number of cuvette rotations during which the laser pulsed were entered into the control unit of the motor. It was also possible to adjust the frequency of the pulse in each sector by adding cuvette rotations when the laser did not fire, between each rotation during which the laser was firing. Scheme 1 shows a schematic picture of the experimental setup.

The kinetically relevant pulsed laser frequency was identical within each sector and calculated according to eq 2,

$$f_s = \frac{1}{t_c(1 + n_p)} \tag{2}$$

where f_s is the frequency of the laser in each sector, t_c the period of revolution of cell, and n_p the number of nonlaser pulsing rotations between each firing rotation.

The laser used in these experiments was a pulsed excimer laser (RD-EXC-150, Radiant dyes) operated at 308 nm (XeCl) and used in conjunction with a dye laser (Radiant dyes) to produce pulses at 355 nm of approximately 20 ns duration. The laser pulse frequency was controlled automatically once the number of sectors and cuvette rotation time had been set.

The outer surface of the tube on the inner side of the ring was blackened so as to absorb transmitted residual energy and

Table 1. Experimental Parameters Used To Control the Pulsed Laser Frequency by Which the Individual Sample Sectors Are Irradiated[a]

frequency of laser pulse in each sector, f_s (Hz)	**10**	**1**	**0.1**	**0.01**
frequency of laser pulse (Hz)	10	10	1	1
sectors	0	10	10	10
period of cell revolution, t_c (s)	0.1	1	10	10
nonpulsed revolutions between each pulsed revolution, n_p	0	0	0	9

[a] The actual (i.e., effective pulse frequency, f_s) is given in bold in the first row of the table.

Table 2. Individual Laser Pulsing Times for Different Effective Laser Frequencies, f_s, at Three Different Temperatures[a]

T (°C)	f_s (Hz)	*t* (min)
25	10	15
	1	120
	0.1	240
	0.01	420
60	10	15
	1	30
	0.1	150
	0.01	210
90	10	5
	1	15
	0.1	15
	0.01	15

[a] The pulsing times were selected such that the overall monomer conversion was well below 5% in each case.

prevent it from reaching the opposite sector of the tube after the laser pulse had passed the quartz tube once. The cuvette was thermostated at the desired temperatures to within ±0.2 °C by a water bath.

Polymerizations. a. Pulsed Laser Polymerization Using the Rotating Reactor Assembly. The monomer and initiator were mixed, and the mixture was subsequently degassed with helium for 5 min before being poured into the cuvette. The concentration of initiator (DMPA) was close to 1.0×10^{-3} mol L^{-1}. Table 1 gives the experimental parameters that have to be selected to achieve a specific frequency, i.e., the frequency that the sample actually sees. This specific frequency, f_s, is given in the top of the table in bold. In all samples except those at 10 Hz, the sample was subjected to 2−3 min of 10 Hz laser pulsing to remove any impurities left in the sample. The individual polymerization times for the selected temperatures (i.e., 25, 60, and 90 °C) are given in Table 2. The indicated times ensured that the final monomer conversion, under the given experimental conditions, stayed below 5%.

Immediately after the laser pulsing was stopped, the polymer was precipitated in methanol. The mixture was shaken to form large particles. The precipitate was allowed to settle, and the supernatant was decanted off. The polymer was again washed with methanol to remove any residual monomer. The supernatant was again decanted. The solid was then dried under an air stream before being subjected to molecular weight analysis.

b. Thermal Polymerizations. Thermal polymerizations using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator were performed in bulk at 40, 60, and 90 °C. The method described by Kukulj et al.[7] was used to obtain a series of solutions with different initiator concentrations. A stock solution of AIBN (1.0×10^{-2} mol L^{-1}) in styrene was prepared. Successive 1 in 10 dilutions of this stock solution were then carried out. The reaction mixtures were purged with high-purity nitrogen gas for 10 min prior to polymerization to ensure that no oxygen was present in the polymerizing system. All polymerizations were performed in sealed glass bottles in a thermostated water bath.

After the preset reaction time, the mixtures were poured into aluminum pans containing a small amount of the inhibitor hydroquinone (99%, Aldrich). The unreacted monomer was at first allowed to evaporate in a fume cupboard and subsequently dried under reduced pressure until constant weights were obtained. Monomer conversions were measured gravimetrically and were in all cases well below 5%.

It should be noted that the experiments using the pulsed laser rotating reactor assembly were carried out at Bayer AG, Leverkusen, whereas the thermal polymerizations described earlier were performed at the Centre for Advanced Macromolecular Design at the University of New South Wales in Sydney.

SEC Analysis. The SEC system used at Bayer AG for the analysis of polymers obtained via the extended dark time technique consisted of an autosampler and controller (Shimadzu), pump (Knauer), refractive index detector (Merck), UV detector (Waters), one Waters column HMW6E (mixed bed), and two Waters columns HMW7 (107 Å). The eluent was dichloromethane at room temperature (20 °C), at a flow rate of 0.6 mL min^{-1}. Calibrations were performed with narrow polydispersity polystyrene standards. The data were collected and the calibrations performed using PSS WinGPC Scientific software.

SEC analysis of polymers generated in the thermal polymerizations was carried out at the Centre for Advanced Macromolecular Design on a Shimadzu modular system, comprising an autoinjector, two Polymer Laboratories PLgel 10μ mixed-B columns, and a differential refractive index detector. The SEC columns were thermostated at 30 °C. The eluent was tetrahydrofuran (THF) at 1 mL min^{-1}, and the system was calibrated with polystyrene standards ranging in molecular weight from 200 to 10^7 g mol^{-1}.

Results and Discussion

Temperature Dependence of C_m(Styrene) from Thermally Initiated Polymerizations. Figure 1 shows a series of molecular weight distributions obtained in thermal bulk polymerizations of styrene at 90 °C and different initiator concentrations. (The AIBN concentration was varied from 6.4×10^{-3} to 0 mol L^{-1} (see the legend to Figure 1 for individual values).) Final monomer conversions were well below 5% for all samples. Inspection of Figure 1 shows an increase of molecular weight with decreasing initiator concentration. This behavior can be observed at each individual temperature (i.e., 40, 60, and 90 °C). Figure 1 also indicates that a limiting molecular weight is reached; i.e., the molecular weight distribution does not shift further to higher molecular weights, within the experimental error, when the initiator concentration is further decreased. This behavior can be seen at each temperature for the samples with the lowest concentration of initiator and the sample with no added initiator.

C_m was determined at each temperature using two methods. Initially the molecular weight distributions have been analyzed using the Mayo method. This method requires knowledge of either the weight or number molecular weight average of the corresponding distribution, M_w or M_n. Using M_w is considered more reliable than using M_n. Experimental and theoretical evidence for this conclusion is given in refs 12 and 13. The reason for this is that M_w is less sensitive to baseline selection errors in the SEC analysis procedure. When a limiting molecular weight is reached in such an initiator concentration series, the Mayo equation gives the value of C_m as the inverse of the average (number) degree of polymerization, 1/DP$_n$. Within the present work DP$_n$ (and subsequently C_m) was calculated via eq 3,

$$\mathrm{DP_n} = \frac{M_w}{2M_0} \Rightarrow C_m = \frac{1}{\mathrm{DP_n}} = \frac{2M_0}{M_w} \qquad (3)$$

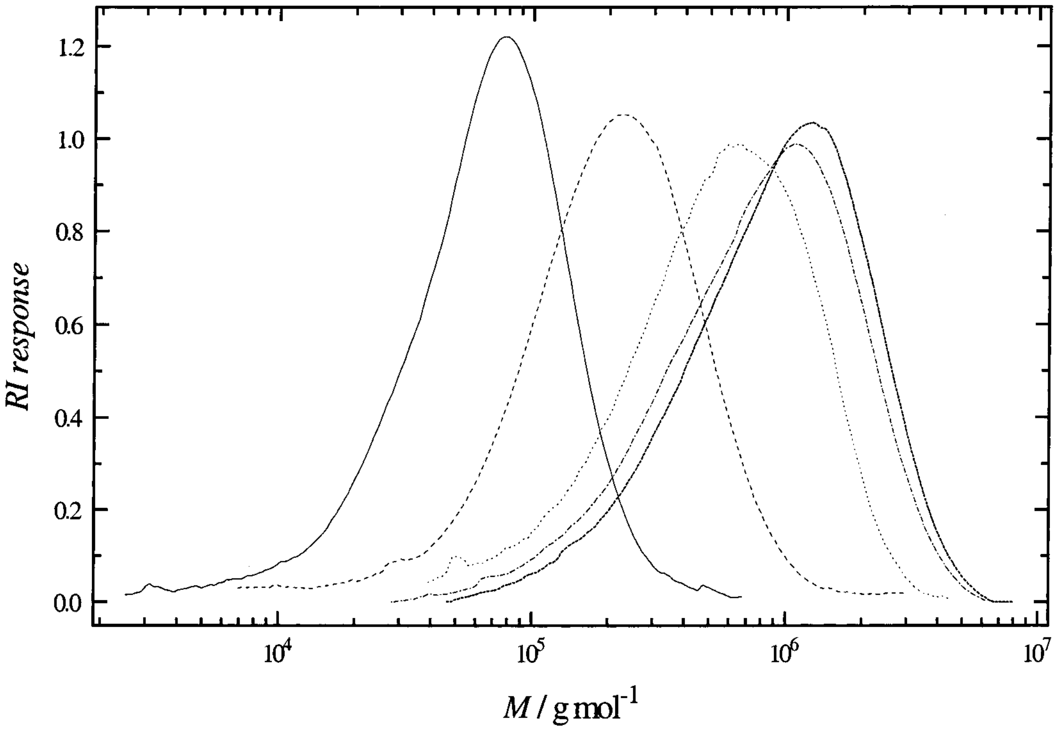


Figure 1. Molecular weight distributions obtained from thermal polymerization experiments of bulk styrene at 90 °C and varying initiator concentrations. The individual initiator concentrations were close to 6.4×10^{-3}, 9.0×10^{-4}, 1.0×10^{-4}, 1.0×10^{-5}, and 0 mol L^{-1}, respectively (from left to right). Monomer conversions were well below 5% in all cases.

where M_0 is the molecular weight of one styrene repeat unit. Equation 3 may be used in all cases when the molecular weight distribution is truly transfer controlled, and a Schulz–Flory distribution is generated. This is the case for all transfer controlled styrene homopolymerizations, regardless of whether the initiation occurs photochemically or thermally.

The second method used for molecular weight data analysis has become known as the chain length distribution (CLD) method, which was introduced by Gilbert and co-workers.[5] Although there is no theoretical a priori justification of the CLD method over the Mayo method,[6] it has some practical advantages which should improve the accuracy of the obtained C_m values. It is for this reason that the CLD method has also been employed to deduce C_m values. Nevertheless, we rate both methods as equal and will not put more emphasis on one or the other. The CLD method[5,6] has been extensively described in the past, and thus details on its theory and application will no be reiterated in this paper.

The usage of the CLD method requires plots of the natural logarithm of the number distribution, ln $P(M)$, vs the molecular weight, M. It has become standard practice to take the slope from the peak molecular weight region, Λ_{peak}, as well as from the high molecular weight region, Λ_{high}.[12–14] Again, there is no theoretical justification of the usage of one over the other, and in principle, they should both yield comparable results. In the present paper, both slopes were taken with similar results. We therefore restrict ourselves to report only numbers derived from the slope of the peak molecular weight region. A typical sample plot of ln $P(M)$ vs M is shown in Figure 2. The original molecular weight distributions were obtained from styrene bulk polymerizations at 90 °C and varying initiator concentrations (see Figure 2).

The region of the plot from which Λ_{peak} was taken is shown in bold. As the initiator concentration decreased, a limiting slope was reached for the last two molecular weight distributions corresponding to 1.0×10^{-5} and 0 mol L^{-1} AIBN. Inspection of Figure 2 clearly shows that the slopes of the last two samples are almost identical. The C_m value for each series was determined as the average of the last two samples, which contained 1.0×10^{-5} and 0 mol L^{-1} AIBN, and each polymerization series with varying initiator concentration was performed twice. Table 3 summarizes the results for C_m at different temperatures using the Mayo method (using M_w) and the CLD method (using Λ_{peak}).

The data given in Table 3 can be interpreted via an Arrhenius plot for the determination of the activation parameters. Figure 3 shows the temperature dependence of ln C_m obtained by the Mayo (M_w) and CLD (Λ_{peak}) method. Both dependencies were linearly fitted, and the activation energy, determined from the slope of the individual graphs, is close to 22.1 kJ mol^{-1} (full line and squares) based on the Mayo method and 24.3 kJ mol^{-1} for the analysis via the CLD method (dashed line and circles). Those two numbers are in excellent agreement within experimental error. It should be noted that an evaluation of the molecular weight data using the slope of the high molecular weight part of the distribution (i.e., Λ_{high}) yields, within experimental error, the same results for the transfer to monomer constants at the individual temperatures.

With a reference data set for the temperature dependence of the transfer to monomer constant being established from conventional thermal experiments, the rest of the paper will deal with a thorough discussion of the results obtained by the novel pulsed laser rotating reactor assembly.

Temperature Dependence of C_m(Styrene) from Experiments Using the Pulsed Laser Rotating

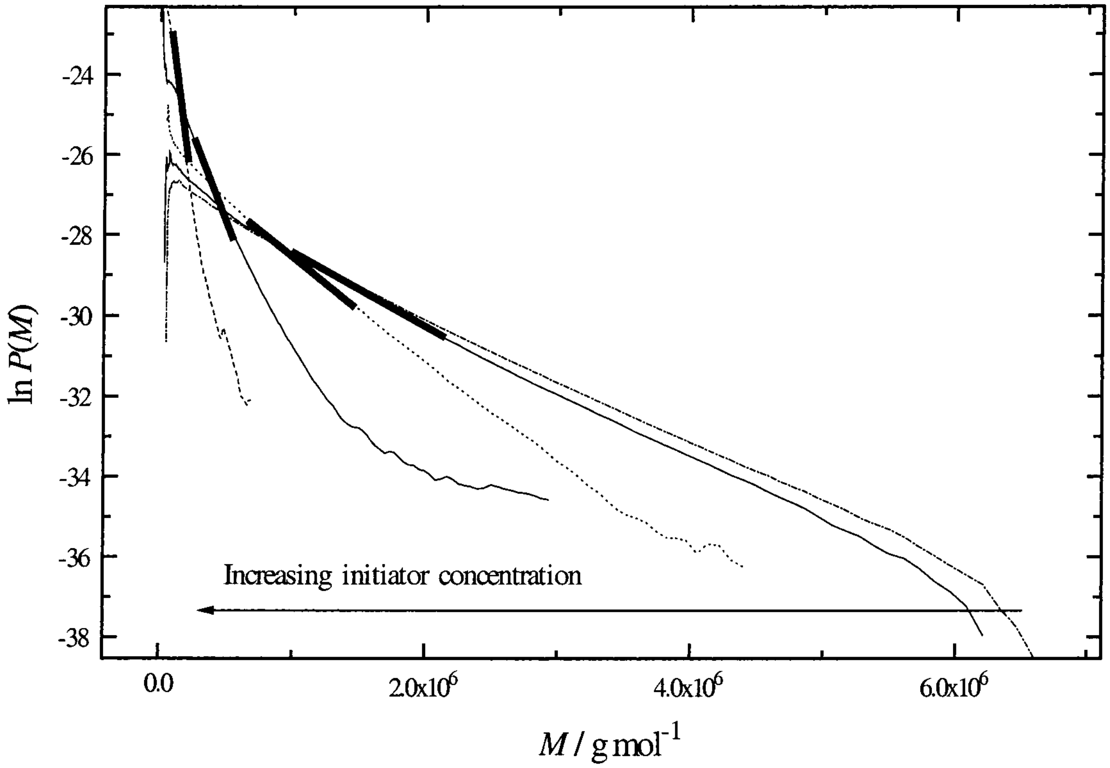


Figure 2. Example plot for the evaluation of the thermal bulk polymerizations of styrene at 90 °C using the well-known CLD method. Initiator (AIBN) concentrations were close to 4.0×10^{-3}, 9.0×10^{-4}, 1.0×10^{-4}, 1.0×10^{-5}, and 0 mol L^{-1}, respectively. The figure shows plots of ln $P(M)$ vs M for each individually obtained molecular weight distribution. The region of the plot where Λ_{peak} was taken from is given in bold. The results for the application of the CLD procedure toward the thermal experiments are given in Table 3.

Table 3. Experimental Transfer to Monomer Constants, C_m, Obtained from Thermal Styrene Bulk Polymerization Experiments[a]

T (°C)	$C_m \times 10^5$ from M_w	$C_m \times 10^5$ from Λ_{peak}
40	5.4	4.7
	5.8	5.1
average	5.6	4.9
60	10.1	10.1
	12.7	13.2
average	11.4	11.7
90	18.4	18.0
	18.0	18.2
average	18.2	18.1

[a] The second column gives transfer constants obtained using the Mayo method on the basis of M_w, whereas the third column gives values obtained by application of the CLD method based on Λ_{peak}. Each experiment has been performed twice, and an average value of the two individual runs is also given.

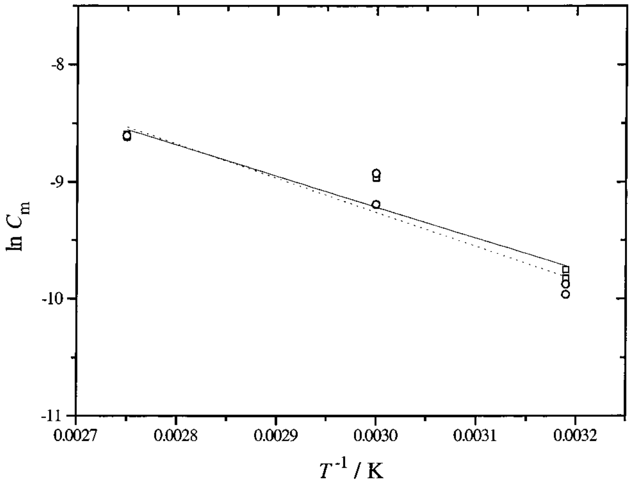


Figure 3. Individual Arrhenius plots for transfer to monomer constants obtained from thermal styrene bulk polymerizations. The graph shows results obtained from the Mayo method based on M_w (full line and squares) and the respective results obtained from the molecular weight distributions using the CLD method based on Λ_{peak} data (dotted fit and circles).

Reactor Assembly. The principal analysis of the molecular weight distributions obtained via the pulsed laser rotating reactor assembly was similar to the analysis carried out in the case of the conventional thermal polymerizations: first, a data analysis via the Mayo procedure and a subsequent evaluation of the molecular weight distributions via the CLD method.

Figure 4 gives a series of molecular weight distributions obtained at different frequencies using the pulsed laser rotating reactor assembly. The reaction temperature was 25 °C, and the initiator (DMPA) concentration was close to 1×10^{-3} mol L^{-1}. It should be noted that the pulsed laser experiments require a different initiator than the thermal experiments, i.e., DMPA instead of AIBN. The reactions have been carried out according to the frequency requirements given in Table 1. The individual reaction times for the corresponding frequencies range from 15 min for an actual frequency, f_s, of 10 Hz to 420 min for $f_s = 0.01$ Hz as detailed in Table 2.

Figure 4 reveals that the molecular weight distribution shifts to higher molecular weights with decreasing frequency, and the distributions lose their characteristic pulsed laser structure. Similar plots obtained at other temperatures (i.e., 60 and 90 °C) also clearly show that the molecular weights of the polymers increase as the actual frequencies decrease. Loss of the pulsed laser structure is presumably due to transfer rather than termination becoming the dominant chain-stopping

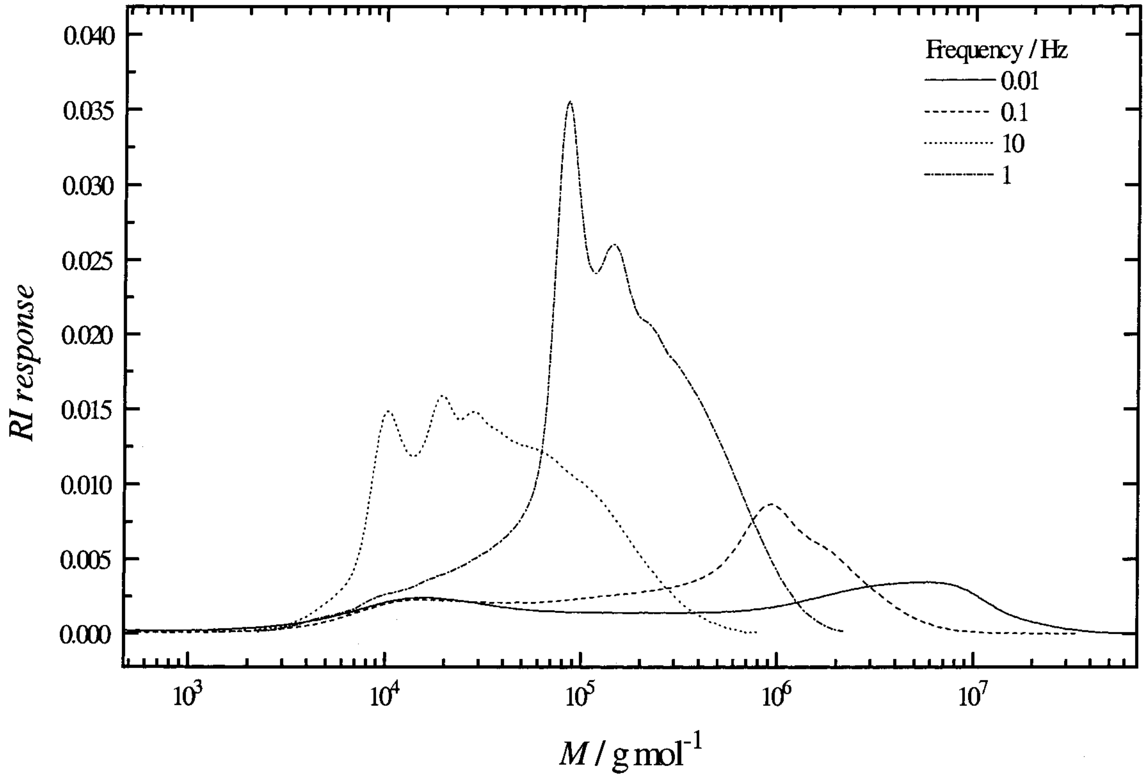


Figure 4. Molecular weight distributions obtained from rotating reactor PLP experiments at 25 °C showing the loss of PLP characteristics as the effective laser pulse frequency decreases. The photoinitiator was 2,2-dimethoxy-2-phenylacetophenone (DMPA), and its concentration was close to 1.0×10^{-3} mol L^{-1}. For details see text.

event. Although this paper is not centered on deriving k_p data from pulsed laser experiments, the propagation rate coefficients for styrene bulk polymerizations derived from the experimental distributions that show PLP characteristics agree well with data previously reported by an IUPAC working party.[15]

As the temperature is increased, the PLP structures become more and more indistinct at shorter dark times, as transfer becomes the dominant chain-stopping event. This is due to the higher activation energy of transfer relative to propagation (see below). At very long dark times (0.1, 0.01 Hz) a limiting molecular weight was reached for the samples polymerized at 60 and 90 °C, confirming that the polymerization was transfer dominated. It is thus feasible to use the polymerizations at 60 and 90 to determine the transfer to monomer constant by calculating the average number degree of polymerization via eq 3 and subsequent inversion of this value as has been detailed earlier.

The molecular weight distributions were also analyzed via the CLD method using Λ_{peak}. The results obtained are given in Table 4. Note that Table 4 does not include entries for 25 °C from the Mayo method, since no limiting molecular weight was reached. As in the case of the evaluation procedure for the thermal experiments, the Mayo procedure was carried out using M_w data.

The entries in Table 4 were individually potted as ln C_m vs $1/T$ to determine activation parameters. Figure 5 shows the Arrhenius plots using the CLD data (based on Λ_{peak}, dashed line and circles) and the Mayo method (based on M_w, full line and squares), yielding E_A as 21.2 and 18.7 kJ mol^{-1}, respectively. Both values show excellent agreement within experimental error.

The data for the activation parameters obtained by both methods (thermal polymerization and extended dark time PLP) and analysis procedures (Mayo method based on M_w and CLD method based an Λ_{peak}) are summarized in Table 5. All activation energies are close to each other within approximately 5.5 kJ mol^{-1}.

However, the preexponential factors obtained from the thermally initiated experiments are higher than those determined by the extended dark time pulsed laser polymerization technique. This may be because fewer sources of initiation were present in the PLP experiments, possibly due the cleaning procedure used in the pulsed laser experiments. By pulsing at 10 Hz for 1 min before beginning the long dark time polymerization, most of the impurities will be removed from the polymerization solution.[16] This certainly constitutes a more reliable way to remove impurities than drying, distillation, and filtration through basic alumina. Alternatively, shorter reaction times in the PLP experiments will result in smaller amounts of dimeric species being formed. Since most of the transfer in thermal

Table 4. Experimental Transfer to Monomer Constants, C_m, Obtained from Rotating Reactor PLP Experiments[a]

T (°C)	$C_m \times 10^5$ from M_w	$C_m \times 10^5$ from Λ_{peak}
25		4.59
		2.47
average		3.53
60	10.1	8.68
	7.25	6.83
average	8.68	7.76
90	15.3	17.1
	14.6	15.8
average	15.0	16.5

[a] The second column gives transfer constants obtained by using the Mayo method on the basis of M_w, whereas the third column gives values obtained by the application of the CLD method based on Λ_{peak}. Each experiment has been performed twice; thus, an average value of the two individual runs is also given.

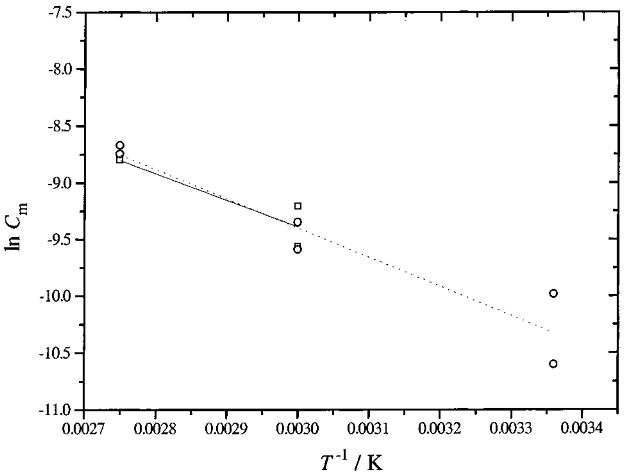


Figure 5. Individual Arrhenius plots for transfer to monomer constants obtained from rotating reactor PLP polymerizations. The graph shows results obtained from employing the Mayo method based on M_w (full line and squares) and the respective results obtained from evaluating the molecular weight distributions using the CLD method based on Λ_{peak} data (dotted fit and circles).

Table 5. Activation Energy, E_a, and Preexponential Factor, A, Obtained by Different Experimental Methods and Different Evaluation Procedures

	E_a (kJ mol^{-1})	A (L mol^{-1} s^{-1})
thermal polymerization		
Mayo method (M_w)	22.1	0.29
CLD method (Λ_{peak})	24.3	0.61
rotating reactor PLP		
Mayo method (M_w)	18.7	0.07
CLD method (Λ_{peak})	21.2	0.18

styrene polymerization is thought to be to styrene dimeric units rather than to the monomer itself, a reduction in dimer will lower the observed chain transfer to monomer constant.[17-20]

If we assume that the experimental methods are equivalent, it seems justified to average the activation parameters. Averaging yields the final values of $E_a = 21.6$ kJ mol^{-1} and $A = 0.22$ L mol^{-1} s^{-1}. These numbers agree well with those obtained by Tobolsky and coworkers with $E_a = 23.4$ kJ mol^{-1} and $A = 0.22$ L mol^{-1} s^{-1}.[21] Since the value of the activation energy for the transfer to monomer constant is positive, it can be immediately inferred by inspection of eq 1 that the activation energy for the transfer process is higher than for the propagation step. The activation energy for the transfer process is thus close to 54.1 kJ mol^{-1}, if the IUPAC accepted value for the activation energy for the propagation step of 32.51 kJ mol^{-1} is used.[15] This result is also confirmed by comparing the molecular weight distribution obtained at different temperatures, but at the same actual frequency, f_s: the higher the temperature, the less pronounced is the pulsed laser structure, indicating that transfer events become more pronounced. The derived average values for E_a and A may be used to calculate individual transfer rate coefficients (by use of eq 1) at any temperature allowing comparison to other values reported in the literature. Kukulj et al. report a k_{tr} value of 5.27×10^{-5} L mol^{-1} s^{-1} at 50 °C.[7] The value calculated from the present average values is close to 7.1×10^{-5} L mol^{-1} s^{-1}. Our value is also in good agreement with numbers reported by other authors, which range from to 6.0×10^{-5} to 7.8×10^{-5} L mol^{-1} s^{-1}.[22-24] The agreement at temperatures other than 50 °C is equally good.

Dropping the assumption of experimental equivalence, and thus averaging the numbers obtained from the extended dark time PLP experiments and the thermal polymerizations independently, yields $E_a = 20.0$ kJ mol^{-1}, $A = 0.11$ L mol^{-1} s^{-1} and $E_a = 23.2$ kJ mol^{-1} and $A = 0.42$ L mol^{-1} s^{-1}, respectively. The k_{tr} value (at 50 °C) calculated from the averaged Mayo and CLD method values associated with the PLP experiments is 6.7×10^{-5} L mol^{-1} s^{-1}, whereas the corresponding number from the thermal polymerizations is slightly higher with 7.5×10^{-5} L mol^{-1} s^{-1}.

It is difficult to conclude which method yields the correct values of the preexponential factor. However, the opportunity to clean samples in the laser and the shorter reaction times of the extended dark time PLP method are advantages over the thermal initiation technique. However, the equation used to derive C_m (eq 3) is strictly speaking only valid assuming steady-state initiation processes. Nevertheless, the flickering PLP technique, although providing changing radical profiles, comes close to this requirement.

Conclusions

In the present paper we have demonstrated that transfer to monomer rate coefficients can be determined for a slowly propagating monomer (i.e., styrene) with reasonable reaction times by using a novel rotating reactor pulsed laser polymerization procedure. The results thus obtained are in excellent agreement with numbers from conventional thermal polymerizations experiments in terms of the activation energy. There are discrepancies in the preexponential factor, resulting in lower transfer to monomer constants. However, we believe that the preexponential factors obtained by the novel method are more reliable, due to a more thorough in-situ cleaning procedure.

Acknowledgment. Financial support from the Australian Research Council is gratefully acknowledged. H.K.-D. acknowledges financial support by receiving an Australian Post graduate Award and by Bayer AG, Leverkusen, Germany.

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MA001871W