Pulsed-Laser Polymerization Measurements of the Propagation Rate Coefficient for Butyl Acrylate

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ABSTRACT: The results are reported for a series of measurements of the propagation rate coefficient (k_p) of butyl acrylate obtained from pulsed-laser polymerization (PLP). Previous attempts reported in the literature to use PLP for this monomer have failed because the data did not satisfy the internal consistency tests afforded by PLP. The problem was obviated by carrying out measurements at very low temperatures and with very short times between laser pulses. Data for k_p were obtained over the range −65 to −7 °C which satisfy PLP consistency tests (invariance of the apparent k_p value to laser pulse frequency, etc.). The results fit k_p (dm^3 mol^{-1} s^{-1}) = $10^{7.2}$ exp(−17.3 kJ mol^{-1})/RT); the confidence ellipse for these parameters is provided. These data extrapolate to a value of $k_p = 2.7 \times 10^4$ dm^3 mol^{-1} s^{-1} at 50 °C. The higher value of the frequency factor of butyl acrylate compared to that of butyl methacrylate can be rationalized in terms of hindered rotations in the transition states.

1. Introduction

Reliable Arrhenius parameters of propagation rate coefficients for free-radical polymerizations are required for simulation and mechanistic understanding,[1] and with a view to developing theoretical models of the radical/molecule transition states for this process. Traditional means of obtaining the propagation rate coefficient (k_p), such as the rotating sector method, make subtle model-based assumptions (particularly about the nature of the termination process) which has as a result that tabulations of k_p data obtained under ostensibly the same conditions (e.g., ref 2) show wide variation. The relatively new technique of pulsed-laser polymerization (PLP)[3−6] is relatively free of such assumptions, and the technique also provides a set of internal consistency checks. It has therefore become the "method of choice" for measuring k_p and has been so recommended by the IUPAC Working Party on "Modeling of kinetics and processes of polymerization".[7−10]

PLP finds a value of k_p through initiation of polymerization from a photo-initiator illuminated by a pulsed laser. Some (but by no means all) chains initiated by any given laser pulse are terminated "instantly" by short radicals formed from the subsequent pulse. The degree of polymerization (ν_p) of those chains so terminated, the monomer concentration ([M]), the time between pulses (t_f), and the value of k_p are related by:

$$\nu_p = k_p[\mathrm{M}]t_f \qquad (1)$$

Simulations assuming that the only processes involved are initiation, propagation, termination (by combination and/or disproportionation), and transfer of a single species (including allowance for the chain-length dependence of some or all of these processes, in the absence of branching and cross-linking reactions) show that, over an extensive range of conditions, ν_p corresponds very closely (but not exactly) to the point of inflection on the molecular weight distribution of the polymer formed in the process.[3,4,11−13] A set of data obeying these assumptions to an acceptable accuracy is said to obey the "PLP precepts".

The PLP method provides a number of consistency checks for the value of k_p obtained (summarized in ref 7). These include the following: (a) that this point of inflection is slightly below the low-molecular-weight maximum in the GPC trace; (b) that at least one secondary peak (or shoulder) is observed above this maximum, the first of the secondary peaks having about twice the molecular weight of the point of inflection (due to termination by radicals generated two pulses after the initiating pulse; any other secondary peaks are associated with terminations of polymer chains after two pulses); and (c) the invariance of the apparent k_p value to initiator concentration, initiator type, laser power, laser wavelength, monomer concentration (provided no solvent effects are present), and pulse frequency.

The PLP method has been applied successfully to a number of monomers,[3,5,14−27] largely styrene and methacrylates. However, previous attempts to measure k_p for *acrylates* under a wide range of conditions failed to find a GPC trace with a clear point of inflection,[28] let alone one which satisfied the consistency criteria (although a PLP-derived value of k_p for butyl acrylate has been reported,[29] no GPC trace was published). The lack of reliable k_p values for butyl acrylate poses difficulties for modeling systems containing this common monomer. Moreover, it would be most useful to have Arrhenius parameters for this acrylate system so as to better understand the nature of the transition state for propagation,[30] by comparison with the Arrhenius parameters for methacrylates which are now available.[15,17,21]

Although a GPC trace will always show a low-molecular-weight point of inflection, seeing such a point of inflection in a sample prepared by PLP by no means implies that the corresponding degree of polymerization obeys eq 1: the point of inflection only obeys this equation if one or more of the various consistency criteria are satisfied. Carrying out such tests in turn requires being able to observe a point of inflection (and secondary point of inflection if possible) *with acceptable precision* over a range of, for example, laser pulse

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frequencies and initiator concentrations. One can identify the point of inflection from the maximum in the differential of the molecular weight distribution; however, under many conditions, this maximum is so broad that the uncertainty in the apparent ν_p is too big to carry out the consistency tests. It may be difficult to find conditions in a PLP experiment so that the independence of k_p to pulse frequency, etc., can be properly checked, since consistency may only occur over a comparatively small range of experimental parameters. The experimental parameters which can be independently controlled are monomer concentration, concentration of photo-initiator (or equivalently, the laser power), laser pulse frequency, total illumination time, and temperature (for which one needs a sufficient range to be able to obtain reliable Arrhenius parameters). Choice of these conditions is constrained by having to ensure that laser illumination of the sample is essentially uniform (including negligible attenuation of the laser beam over the length of the sample cell) and that [M] changes negligibly over the course of the experiment.[5,31] Both requirements restrict the total amount of polymer that can be formed, which can lead to problems in GPC analysis. As stated, no range of conditions where consistent PLP data for butyl acrylate are obtained have been reported in the literature.

The present paper aims to remedy this deficiency by using a number of variants on conventional PLP measurements. (1) The major variant originated when we postulated that whatever process might be causing the lack of a consistent point of inflection could be obviated by going to sufficiently low temperatures. One rationalization for this postulate was that the potential presence of low molecular weight species, e.g., from a transfer process, or the occurrence of a significant exotherm during laser illumination, would be diminished at low temperatures. (2) The second variant is to use very short times between laser pulses; the rationalization here was that the shorter the time between pulses, the less time there is for interference by whatever process causes the loss of a consistent point of inflection under conventional conditions (suggestions in this direction have been made by Hutchinson *et al.*[14]). For some of the present data, these very rapid pulses were achieved using illumination by two synchronized lasers.

Another reason for choosing low temperatures and short t_f comes from examining the relation between the point of inflection and the degree of polymerization ν_p given by eq 1, as follows. If termination is extremely fast, then ν_p would be at the *maximum* in the number molecular weight distribution (*not* the point of inflection of the corresponding GPC distribution).[23] However, because termination is never instantaneous, ν_p moves to lower molecular weights because the shorter terminating chain grows to finite length before it terminates. Indeed, simulations show[3,11,12] that, under "ordinary" PLP conditions, this effect, combined with Poisson broadening of the propagating radicals (both of the radical formed in the original pulse and the shorter one formed in the subsequent pulse), shifts the value of ν_p to molecular weights below the peak, as a result of which ν_p corresponds closely, *but not exactly*, to the point of inflection under "ordinary" conditions. Consistent with this, it has been shown[23] that the maximum is a better measure of ν_p than is the point of inflection, if termination is sufficiently rapid. Now consider a system with a very high k_p, such as butyl acrylate: here the relative rate of termination, compared to that of propagation, is less than that in an otherwise equivalent system with an "ordinary" value of k_p. It is now well established that the termination rate coefficient in general depends on the degrees of polymerization of each of the terminating radicals.[32] Suppose that propagation is so fast that chains grow very rapidly to a high degree of polymerization, so high that termination between pulses is very slow. The next pulse results in very short chains, some of which terminate "instantly", while those which do not so terminate grow rapidly to a much higher degree of polymerization with a low termination rate coefficient; by the time termination occurs, those chains that escaped instantaneous termination are part of a broad background. The chains formed by instantaneous termination on top of a broad background of chains formed by inter-pulse termination would move the value of ν_p from the point of inflection toward the *maximum* in the molecular weight distribution. That is, both very rapid termination and very rapid propagation (with chain length-dependent termination) can move ν_p from the point of inflection to higher molecular weights. Measuring k_p from the point of inflection in both cases will therefore result in an underestimate of its true value: the PLP precepts will not be obeyed. To regain the PLP precepts, conditions must return to more "ordinary" rates of termination and propagation. The rate of termination will be increased relative to that of propagation if (a) the temperature is lower (since termination, being diffusion-controlled, varies little with temperature, while k_p is relatively strongly temperature-dependent), and/or (b) the laser is rapidly pulsed. It is possible that recalcitrant systems (those with a high k_p, where the point of inflection may not correspond closely to ν_p) can move closer toward conditions where simulations indicate that ν_p corresponds to the point of inflection by reducing k_p (i.e., reducing the temperature) and/or increasing the pulse frequency.

2. Experimental Design

Materials. Butyl acrylate (Aldrich) was purified by repeatedly washing the monomer with 5% (w/v) NaOH until the aqueous layer showed no coloration. After drying the organic phase over anhydrous $CaCl_2$, the monomer was further purified by fractional distillation at reduced pressures. The purified butyl acrylate was stored below 5 °C until required; the absence of polymer was confirmed prior to use by adding a small sample of the monomer to methanol. Two photoinitiators were used over the course of the work: benzoin (Aldrich) was recrystallized from methanol, while Irgacure-651 (dimethoxyphenylacetophenone, Ciba-Geigy) was used as received. Two solvents were used: tetrahydrofuran (R.P. Normapur; AR grade) and toluene (R.P. Normapur; AR grade); both were fractionally distilled prior to use. Inhibitor for ensuring no polymerization after laser irradiation, 2,6-di-*tert*-butylphenol (Fluka; technical grade), was used as received.

Hardware. Photodecomposition of the initiator was induced by either one or two lasers, depending on the required repetition rate. Polymerization was carried out in cylindrical quartz cells of 1 cm external diameter; these cells were illuminated from below by the laser beam following the design of Davis *et al.*[5]

For frequencies of 30 Hz or less, a single excimer laser (Lambda Physik, Lextra-200 using XeCl) at 308 nm was employed for most runs. Some PLP experiments on undiluted samples were performed with a Lambda Physik LPX110iMC pulsed excimer laser at 351 nm, capable of frequencies of up to 100 Hz. The rectangular laser beam with dimensions of approximately 7 × 18 mm directly irradiated the sample in a jacketed quartz glass cell with the same dimensions as the laser beam. The optical path length was 5 mm. The temperature was kept constant to within 1 °C, as measured directly in the sample cell with a Pt-100 resistance element (Netsushin MG-1505).

Frequencies above 30 Hz were also obtained by utilizing an additional laser (Continuum Surelight I-20 Nd:YAG) at 355 nm. Both lasers were triggered at the same repetition rate, in this case 20 Hz, but out of phase. This allowed the production of any repetition rate greater than the native 20 Hz trigger frequency; a second frequency component f_2 will always be present in these experiments given by the equation $f^{-1} = f_1^{-1} + f_2^{-1}$, where f is the "native" laser frequency (20 Hz in the present case), and f_1 and f_2 are the two frequency components induced by the out-of-phase lasers. Unless the energies of the two lasers are set so that the same yield of radicals is generated at each pulse, it is not possible to remove the native 20 Hz frequency; contributions to the molecular weight distribution corresponding to this background frequency will always be observed. Now, while any combination of pulse frequencies can be so generated, the PLP precepts were deduced by modeling with a single uniform pulse sequence, and so strictly one can only use the two-laser sequence when the lasers are exactly out of phase and have the same intensity. While it may be possible that the PLP precepts are also obeyed with other pulse sequences (which can result in an arbitrarily short pulse imposed on a slower one), this cannot be verified until proper simulations have been performed. Hence data obtained with the two-laser method cannot be used in the fitting (at least until proper simulations have been performed); however, these two-laser data will be seen to be supportive of results obtained in other consistency checks.

The two lasers were overlapped spatially with a 308 nm dichroic reflector which reflects 100% of the 308 nm beam and transmits most of the 355 nm beam. Timing of the individual lasers was controlled by a digital delay generator (Stanford DG-135) which provided accurate delays with <1 ps jitter. The delay between the laser trigger and arrival of the pulse, however, is different for each laser. The accurate arrival of each laser pulse at the sample was calibrated by overlapping the laser pulses temporally and detecting them with a fast power meter. The trigger of one laser was adjusted until both lasers overlapped within their natural pulse duration (i.e., within ~5 ns). The delays were then varied using the delay generator and the total number of pulses per experiment timed with a stopwatch. The two lasers had quite different beam profiles; that of the excimer beam was rectangular (about 10 × 25 mm) while the Nd:YAG laser had a Gaussian profile (about 10 mm diameter). Both lasers were attenuated in size to the internal diameter of the cuvette (~6 mm), and the laser powers from each beam incident on the cell were adjusted to correct for the different absorption cross section of the initiator at 308 and 355 nm; this meant that the YAG laser (355 nm) operated at a laser power 2.5 times that of the excimer (308 nm).

For temperatures above −10 °C, ethylene glycol from an isothermal bath was circulated through a brass block (external diameter ~1.5 cm) which was in contact with the cell. For runs below −10 °C, various slush mixtures were used to maintain isothermal conditions in the cell: carbon tetrachloride/dry ice for −20 °C, acetone/dry ice for −30 °C, acetonitrile/dry ice for −48 °C, xylene/dry ice for −54 °C, and chloroform/dry ice for −63 °C. The sample cell was placed in the slush bath for about 4 min, after which the temperature had equilibrated, as measured with a thermocouple.

One possible origin of the difficulty reported in the literature in finding a consistent k_p for butyl acrylate might be the occurrence of a significant exotherm. To obtain an estimate of this, the temperature rise was measured for three replicate runs at −14 °C, for which the concentration of monomer was 2.4 mol dm^{-3} in THF, and 300 pulses were used. The exotherm was measured by inserting the thermocouple through the septa of degassed cuvettes and monitoring the temperature on pulsing with the laser; the exotherm so observed was less than 3 °C in each case; the exotherm measured for the same conditions in the absence of monomer was 1.7 °C.

Polymerization and Analysis. A typical sample consisted of a solution of butyl acrylate (2.4 mol dm^{-3}) and benzoin (2.4 × 10^{-4} mol dm^{-3}) in tetrahydrofuran. Concentrations were calculated with correction for temperature variation of the densities of both monomer and solvent using literature data, and with extrapolation by a second order polynomial fit; the data obtained from the online Beilstein data base were fitted as:

$$\text{density of butyl acrylate} = 0.045798 + \frac{417.06}{T} - \frac{48466}{T^2}$$

$$\text{density of THF} = 0.021436 + \frac{415.12}{T} - \frac{47121}{T^2}$$

where the density is in g cm^{-3} and T is in K. The effect of exotherms was not incorporated. The concentrations of components were such that only 10% of the power of the excimer laser incident on the sample was absorbed (due to the lens/directional system operating, only 15% of the total power of the laser was incident on the sample). For each experiment, equal amounts of this solution were placed into each of two sample cells, to a total depth of ~10 mm. Each of these solutions was then bubbled for 2 min with ultra-high-purity nitrogen, and a rubber septum was used to seal the system. The reaction mixture was brought to the desired temperature, and then irradiated with either one or two lasers. The total number of pulses was varied, but did not exceed 800; GPC data were only analyzed for experiments in which the limit of conversion did not exceed 5% of added monomer (as measured gravimetrically). Once irradiation was completed, 2,6-di-*tert*-butylphenol was added by syringe to ensure that polymerization was terminated.

GPC was carried out using tetrahydrofuran as the mobile phase (0.6 mL min^{-1}); 100 μL aliquots of each polymerized reaction mixture were injected (undiluted) onto a series of three (10^5, 10^4, and 10^3 Å) Waters Ultrastyragel GPC columns. The relative concentration of polymer at each elution volume was monitored using a Waters 401 differential refractometer. The standard GPC trace (which is effectively the weight distribution as a function of log(molecular weight), often denoted $W(\log M)$[33]) was obtained by using universal calibration[34] based on 12 polystyrene standards of peak molecular weights ranging from 2.35 × 10^3 to 1.46 × 10^6. GPC was performed directly on undiluted samples from the PLP experiments; this was found to be necessary to give sufficient signal to noise ratios, consistent with low conversions. If the concentration of polymer is such that separation of the polymer is not complete, the result will be a distortion of the molecular weight distribution and hence of the point of inflection. Conversions, and hence polymer concentration in the samples, were varied by altering either the energy of the laser or the total pulse times; no systematic correlation was found between the polymer concentration and the point of inflection in the samples reported in Table 1.

The Mark−Houwink parameters used in this analysis were taken from the literature:[35] $K = 7.4 \times 10^{-3}$ cm^3 g^{-1}, $a = 0.75$. These are close to new values ($K = 11.0 \times 10^{-3}$ cm^3 g^{-1}, $a = 0.708$) reported using triple-detection SEC.[36]

The point of inflection for the application of eq 1 is usually obtained from the GPC MWD. Alternatively, ν_p can be estimated from the number MWD, $P(M)$.[21] The relation between the two distributions is (for a linear GPC calibration curve):

$$P(M) = \frac{\text{GPC distribution}}{M^2} \equiv \frac{W(\log M)}{M^2} \qquad (2)$$

(the proof of eq 2, and extensions to nonlinear calibration curves, can be found in refs 33 and 37). However, for the low molecular weights typical of the point of inflection in PLP, the greater noise in the derivative of $P(M)$ compared to that in the GPC distribution means that it is hard to evaluate k_p from $P(M)$ data. Indeed, there is no optimum form of the MWD to evaluate k_p: as discussed above, simulations for "ordinary"

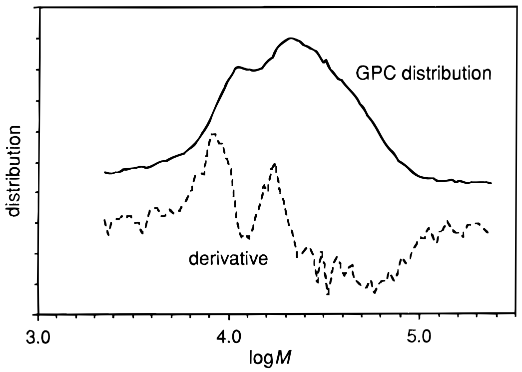

Figure 1. GPC trace and derivative (both in arbitrary units) from PLP on butyl acrylate at −47 °C; this is experiment 19 in Table 1. Conditions: initiation by a xenon chloride excimer laser operating at 40 mJ/pulse (at the sample), pulsed at 30 Hz, 500 pulses, initiator = 2.4×10^{-4} mol dm^{-3} benzoin, [M] = 2.4 mol dm^{-3} in tetrahydrofuran.

systems show that the ν_p of eq 1 corresponds closely but never exactly to the point of inflection on either form of the molecular weight distribution. In the present work, ν_p is obtained from the *W*(log *M*) ("GPC") distribution.

The GPC trace from a run which shows "desirable characteristics" for a PLP experiment is shown in Figure 1. This shows a clear point of inflection (as indicated by the low-*M* maximum in the derivative of the GPC trace), situated at a molecular weight slightly less than the low-*M* maximum in the GPC trace and whose molecular weight is about a factor of 2 less than that of the overtone (which corresponds approximately to the molecular weight of chains terminated by a radical arising from the second pulse after that which initiated the chain).

The range of variations in experimental conditions in the present studies are summarized in Table 1, together with the values for k_p calculated on the assumption that eq 1 holds for the degree of polymerization calculated from the point of inflection found for the low molecular weight side of the *W*(log *M*) form of the molecular weight distribution. The pulse energies refer to the energy of the beam incident to the sample and allow for the loss of signal prior to reaching the sample. The results are grouped according to similarity in reaction temperature (to facilitate comparison), and the discussion of the consistency checks that follows will focus on these temperature groupings.

Some two-laser data are included, but without simulation results there is no guarantee that such data should obey the PLP precepts, and hence these data were not used in the fitting. However, it is noted that these data in fact appear to obey the PLP consistency tests for sufficiently high frequencies.

3. Results

It is emphasized that the display of "desirable characteristics" in PLP-MWD data such as shown in Figure 1 is not sufficient to ensure consistency. As well as seeing a point of inflection, maximum and (preferably) overtone, it is essential that the value of k_p inferred from such data be shown to be invariant to experimental parameters such as pulse frequency, initiator concentration, etc.[7] As will become evident, the assumption of the applicability of eq 1 made in evaluating k_p from the point of inflection will be seen to be either incorrect or potentially inaccurate for some of the data in Table 1. As such, not all of these data were used in evaluating the Arrhenius parameters; data omitted from this evaluation are presented in italics.

Data are also given in Table 1 for experiments in which no photo-initiator was added and which do not conform to the precepts of eq 1; the relevance of these experiments will be discussed in a later section.

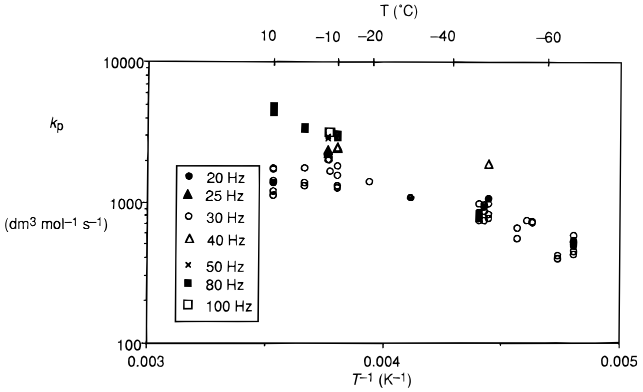

Figure 2. All apparent k_p values in Table 1 as an Arrhenius plot (the data cover the temperature range −67 to +10 °C).

Consistency Tests: Identifying Data Conforming to PLP Precepts. Applications of the consistency tests show that, for some of the data in Table 1, the point of inflection as a means of evaluating k_p is either incorrect or inaccurate.

Figure 2 shows the values for the propagation rate coefficient using all the data given in Table 1. It is immediately apparent that the apparent value of k_p sometimes depends on pulse frequency, etc., showing some data are inadmissible. For convenience of discussion, the data are broken into two general sets of experiments: those performed at temperatures below which the PLP precepts always seem to be obeyed (usually temperatures of −45 °C and below), and those performed above this temperature.

(a) Below −45 °C. The most complete assessment of data reliability was carried out at *ca.* −47 °C. By comparing the results of experiments carried out in both THF (runs 16−19) and toluene (runs 25 and 26), the propagation rate coefficient was found to be independent of solvent. All of the data at this low temperature show second overtones whose point of inflection are close to $2\nu_p$; however, the uncertainty in this second inflection point makes it difficult to use for consistency tests when considered in isolation. Runs 16−19, 21, 22, 27, and 28 show that the apparent value of k_p is also independent of laser power, laser frequency, initiator type, and wavelength. However, the difference in the apparent value of k_p measured at a monomer concentration of 2.4 mol dm^{-3} with the corresponding values found at 4.9 mol dm^{-3} (runs 29−34) indicates that data consistency must be tested. Since the apparent k_p value for 1.3 mol dm^{-3} monomer (run 20) is in agreement with those measured at 2.5 mol dm^{-3}, the data for the lower monomer concentrations are considered to be more reliable. This is consistent with the postulate that lowering the rate of propagation relative to that of termination (either by lowering the temperature, or by lowering the monomer concentration, or by increasing the pulse frequency) is one way to improve the validity of the PLP precepts.

At higher concentrations of monomer, reaction exotherms and the propagation rate are both higher, both of which may weaken the validity of the PLP precepts. The effect of the exotherm would be an apparently higher value for the propagation rate coefficient; the effect of a higher rate of propagation relative to termination may lead to an apparent value which is lower than the true value (because the value of ν_p may move from the point of inflection toward the peak maximum). There is also the possibility that side reactions involving the monomer can invalidate the PLP precepts. The

Table 1. Details of All PLP Runs[a]

run no.	T (°C)	laser frequency ($=t_f^{-1}$) (Hz)	[M] (mol dm^{-3})	[benzoin] (mol dm^{-3})	diluent	energy (mJ/pulse)	wavelength (nm)	overtone intensity ratio	k_p (dm^3 mol^{-1} s^{-1})
1	−62	30	2.6	2.4×10^{-4}	THF	40	308	0.43	719
2	−62	30	2.6	2.4×10^{-4}	THF	40	308	0.41	685
3	−65	30	2.6	2.4×10^{-4}	THF	25	308	0.50	1023
4	−65	30	2.6	2.4×10^{-4}	THF	25	308	0.48	930
5	−65	30	1.3	2.4×10^{-4}	THF	25	308	0.46	704
6	−65	30	1.3	2.4×10^{-4}	THF	25	308	0.43	737
7	−65	20	2.6	2.4×10^{-4}	THF	25	308	0.46	755
8	−65	20	2.6	2.4×10^{-4}	THF	25	308	0.50	947
9	−65	20	2.6	2.4×10^{-4}	THF	25	308	0.50	918
10	−54	30	2.6	2.4×10^{-4}	THF	40	308	0.50	1175
11	−54	30	2.6	2.4×10^{-4}	THF	40	308	0.44	965
12	−57	30	1.3	2.4×10^{-4}	THF	25	308	0.43	1255
13	−57	30	1.3	2.4×10^{-4}	THF	25	308	0.53	1113
14	−56	20	1.3	2.4×10^{-4}	THF	25	308	0.48	1350
15	−54	20	2.6	0	THF	40	308	too noisy	*1557*
16	−46	30	2.5	2.4×10^{-4}	THF	30	308	0.55	1763
17	−46	30	2.5	2.4×10^{-4}	THF	30	308	0.60	1826
18	−47	30	2.5	2.4×10^{-4}	THF	40	308	0.50	1640
19	−47	30	2.5	2.4×10^{-4}	THF	40	308	0.46	1562
20	−48	20	1.3	2.4×10^{-4}	THF	25	308	0.48	1518
21	−46	20	2.5	*1.9×10^{-4}	THF	40	355	0.50	1585
22	−46	20	2.5	*1.9×10^{-4}	THF	40	355	0.48	1525
23	−48	30	2.5	0	THF	40	308	too noisy	*3211*
24	−48	30	2.5	0	THF	40	308	too noisy	*3283*
25	−46	30	2.5	2.4×10^{-4}	toluene	50	308	0.58	1852
26	−46	30	2.5	2.4×10^{-4}	toluene	50	308	0.61	1884
27	−48	20	2.5	2.4×10^{-4}	toluene	50	308	0.71	1595
28	−48	20	2.5	2.4×10^{-4}	toluene	50	308	0.71	1802
29	−48	30	4.9	2.4×10^{-4}	toluene	50	308	0.46	*1476*
30	−47	30	4.9	2.4×10^{-4}	toluene	50	308	0.48	*1526*
31	−47	30	4.9	1.2×10^{-4}	toluene	50	308	0.46	*1526*
32	−47	30	4.9	1.2×10^{-4}	toluene	50	308	0.56	*1590*
33	−47	30	4.9	4.8×10^{-4}	toluene	50	308	0.48	*1578*
34	−47	30	4.9	4.8×10^{-4}	toluene	50	308	0.43	*1398*
35	−30	40	2.5	2.4×10^{-4}	THF	10.0, 10.0	308, 355	0.61	*3724*
36	−21	20	2.5	2.4×10^{-4}	toluene	50	308	–	*2096*
37	−20	20	2.5	2.4×10^{-4}	toluene	50	308	–	*2457*
38	−20	30	2.5	2.4×10^{-4}	toluene	50	308	0.48	*2769*
39	−19	30	2.5	2.4×10^{-4}	THF	40	308	0.46	*3597*
40	−19	30	2.5	2.4×10^{-4}	THF	40	308	0.43	*3778*
41	−19	30	2.5	2.4×10^{-4}	THF	40	308	0.45	*4032*
42	−19	40	2.5	2.4×10^{-4}	THF	10.0, 10.0	308, 355	0.61	*4698*
43	−7	30	2.5	2.4×10^{-4}	toluene	50	308	–	*4037*
44	−7	30	2.5	2.4×10^{-4}	toluene	50	308	–	*3279*
45	−10	30	2.5	2.4×10^{-4}	THF	30	308	–	*2535*
46	−10	30	2.5	2.4×10^{-4}	THF	30	308	–	*2137*
47	−10	30	2.5	0	THF	30	308	–	*3095*
48	−10	40	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.55	*4874*
49	−10	40	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.58	*4993*
50	−10	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.52	*5660*
51	−10	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.53	*5974*
52	0	30	2.5	2.4×10^{-4}	THF	30	308	–	*2675*
53	0	30	2.5	2.4×10^{-4}	THF	30	308	–	*2572*
54	0	30	2.5	0	THF	30	308	–	*3482*
55	0	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.61	*6510*
56	0	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	0.64	*6756*
57	10	20	2.5	2.4×10^{-4}	toluene	50	308	–	*3056*
58	10	30	2.5	2.4×10^{-4}	toluene	50	308	–	*3454*
59	10	30	2.5	2.4×10^{-4}	toluene	50	308	–	*3484*
60	10	30	2.5	2.4×10^{-4}	THF	30	308	–	*2149*
61	10	30	2.5	2.4×10^{-4}	THF	30	308	–	*2346*
62	10	30	2.5	0	THF	30	308	–	*2817*
63	10	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	–	*9747*
64	10	80	2.5	2.4×10^{-4}	THF	10.8, 26.8	308, 355	–	*8691*
65	−7.2	25	7.4	*5.0×10^{-3}	nil	5	351	–	*5131*
66	−7.2	50	7.4	*5.0×10^{-3}	nil	5	351	–	6617
67	−7.4	50	7.4	*5.0×10^{-3}	nil	5	351	–	6422
68	−7.5	100	7.4	*5.0×10^{-3}	nil	5	351	–	6838
69	−7.9	100	7.4	*5.0×10^{-3}	nil	5	351	–	6747

[a] Those with two energies per pulse are where two synchronized lasers were employed. Values of k_p which do not obey the PLP consistency criteria are italicized. The overtone intensity ratio should be close to 0.5 for the PLP precepts to be obeyed; the dash in this column indicates that no second overtone was observed (for two-laser data, it has yet to be proven that the PLP precepts could hold, and so these data are not considered in evaluation of k_p). (*) The initiator in these cases were Irgacure-651.

origin of the lower apparent value for k_p found with runs 29−34 might therefore relate to the influence of the increased monomer concentration. At higher pulse frequencies, the apparent values of k_p are higher and are independent of pulse frequency, suggesting that the increased termination rate arising from higher pulse frequency improves the validity of the PLP precepts.

Based on this analysis, the data obtained in runs 29−34 were deemed to be unreliable and were not used in evaluating the Arrhenius parameters for the propagation reaction. Even among those data deemed to satisfy the PLP precepts, there is a large scatter in values of k_p.

For polymerizations carried out at *ca.* −64 °C, the data (for runs 1−9) do not show any significant dependence on laser power, monomer concentration, or pulse frequency. At this lower temperature, the rate of propagation relative to termination is decreased, suggesting that these conditions are now in the "ordinary" regime where the PLP precepts are valid. Experiments involving the systematic variation of initiator concentration, initiator type, solvent type, and wavelength were not performed on the basis of the findings at *ca.* −47 °C. These results were all taken to be reliable and are used in evaluating Arrhenius parameters. At *ca.* −54 °C, the results of varying the monomer concentration confirm the reliability of the data for runs 10−14.

(b) Above −45 °C. At temperatures of 0 °C and above (runs 52−64), it was not possible (with the available equipment) to ascertain the reliability of the data. Hence these data were not used to calculate the Arrhenius parameters. At −7 °C the apparent values of k_p obtained at pulse frequencies of 25 and 30 Hz (runs 43, 44, and 65) are significantly lower than those obtained at 50 and 100 Hz (runs 66−69). Since the latter are in good agreement, they were taken as reliable and used in the evaluation of the Arrhenius parameters; this selection is again consistent with the hypothesis that increased rate of propagation relative to termination can invalidate the PLP precepts. However, none of these data exhibited overtone behavior.

In going from −46 to −7 °C, the pulse frequency had to be increased from 20 to 50 Hz in order to obtain reliable data; as the temperature of the experiment is increased, the lowest frequency at which frequency-independent data are obtained clearly increases. At −10 °C and above, there is a clear dependence of the measured value for k_p on the pulse frequency, with the value for the apparent rate coefficient increasing with frequency, for frequencies less than 50 Hz, and hence such data do not obey the PLP consistency tests.

At *ca.* −19 °C, runs 36−38 also show a relationship between the apparent value of k_p and the pulse frequency (this being seen also in run 42). While there was no evidence for solvent effects at temperatures below −45 °C, this need not be the case at all temperatures, as evident from the comparison of run 38 with runs 39−41; the latter cannot be attributed to differences in laser power because the higher power (which could result in a higher exotherm but also a higher termination rate) is not associated with the higher value for k_p.

All in all, it appears that the data obtained at frequencies less than 50 Hz are unreliable above −45 °C. The PLP precepts are most likely to be obeyed at high laser frequencies (provided that the degree of polymerization is not so small as to admit the possibility of the influence of chain length-dependent k_p, an effect which can be safely excluded from all of the present data). The apparent k_p values at the higher temperatures in Table 1 denoted as obeying the PLP criteria were all obtained at higher frequencies and show a temperature dependence consistent with that extrapolated from reliable data at lower temperatures. Note in this context that the apparent k_p obtained using the inflection point from two synchronized lasers, although not used in the fitting for reasons discussed above, also shows behavior consistent with these postulates.

Identifying the Origin of Inconsistent Data. It is evident that inconsistency in the applicability of eq 1 to the point of inflection can be identified by varying t_f, the frequency having to be greater to obtain reliable data at higher temperatures. As such, some light on the underlying cause for failure of experiments at low frequencies can be found by examining the effect of temperature on the apparent value for k_p with the frequency maintained at a constant value. Inspection of Figure 2 for experiments performed at a laser pulse frequency of 30 Hz shows that while the apparent k_p values at this fixed frequency show a linear Arrhenius behavior at lower temperatures, there is a significant nonlinearity at higher temperatures. Possible explanations for this observation at higher temperatures are the following:

(a) the value of k_p is somehow lowered due to changes within the system such as gross changes in solvent structure with temperature; and/or

(b) reaction(s) take place in this system *in addition* to those assumed in modeling studies which indicate that the ν_p in eq 1 can be associated with the point of inflection: initiation, propagation, termination (by combination and/or disproportionation), and transfer of a single species, in the absence of branching and cross-linking reactions. The unexpected occurrence of any additional process would invalidate the PLP assumptions: for example, (1) side reactions involving a second photo-initiated species could form low molecular weight species which could swamp the PLP point of inflection and/or (2) chain transfer to polymer (it is known[38,39] that butyl acrylate undergoes extensive chain transfer to polymer, and branched chains so formed would be seen in the GPC at elution volumes corresponding to unbranched chains of much lower molecular weight); and/or

(c) there is sufficient exotherm to broaden the molecular weight distribution so much that the proper point of inflection cannot be identified; and/or

(d) the ratio of termination and propagation rates is such that the data lie outside the range of "ordinary" conditions where modeling indicates that the point of inflection lies close to ν_p, independent of termination mechanism, etc.; and/or

(e) there is an abnormally large amount of transfer occurring at higher temperatures. Each of these possibilities is now considered.

The origin of the problem is unlikely to be chain transfer to another polymer chain, the latter being in low concentrations throughout. However, transfer to the same chain (back-biting) cannot be ruled out at this stage.

The second possibility was examined by reanalyzing the GPC data after transforming to the number molecular weight distribution, through eq 2. The number MWD should be sensitive to the presence of unsuspected reactions, branching, etc., since the rate equations expressing such events are in terms of the absolute

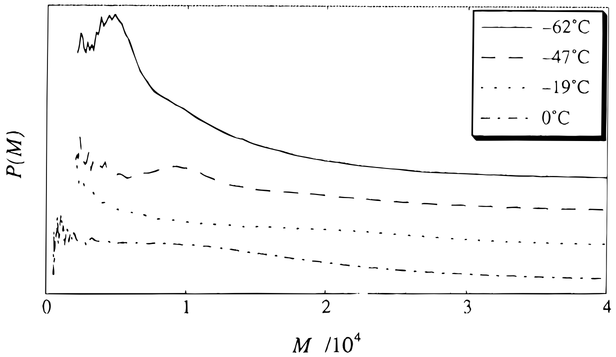

Figure 3. Number molecular weight distributions, *P(M)*, as obtained at different temperatures. These are the data corresponding to experiments 1, 18, 40, and 52 in Table 1 for which $\lambda = 308$ nm, pulse frequency = 30 Hz, [monomer] = 2.4 mol dm^{-3} (in tetrahydrofuran), and [benzoin] = 2.4×10^{-4} mol dm^{-3}.

number of chains. Figure 3 shows *P*(*M*) data for a range of temperatures from polymerizations performed at 30 Hz. For polymerizations carried out at −62 and −47 °C, the *P*(*M*) data show the expected form, *viz*., an early minimum, a steep rise to a maximum, and then a continuing decrease as molecular weight increases.[21] The overtone cannot be clearly distinguished in this *P*(*M*) plot, although it is apparent in the GPC distribution. However, for reactions performed under similar conditions at −19 °C and above, the *P*(*M*) data do not show the expected behavior. By comparing the systematic change in the shapes in these four traces, it seems that as the temperature of reaction increases, the number of chains of lower (apparent) molecular weights has increased to such an extent that it obscures the peak due to chains that grow for the period between consecutive pulses. This is particularly evident at 0 °C. This is consistent with, but does not prove, the presence of some unsuspected reaction process which might mask the low-*M* point of inflection arising from pure PLP considerations. Since the effect of solvent on the apparent values for k_p was not systematic at these higher temperatures, the possibility that it is transfer to solvent is minimal; however, the scatter in these data does not preclude the possibility that minor impurities within the solvents are involved to some extent.

The possibility that a low termination:propagation rate ratio was a possible origin of the invalidity of the PLP criterion has been discussed above, wherein it was shown that this is an admissible cause of the problem.

The occurrence of an abnormally high rate of transfer can also cause the observed effects;[14] if this were the case, then (because transfer has a higher activation energy than propagation) reducing the temperature would help restore the validity of the PLP precepts, as would increasing pulse frequency. However, modeling[14] shows that the transfer constant must take extremely large values for this to cause the observed effects. Whether this is indeed the case in the present system must await accurate measurements of this quantity, new techniques for which are now available.[37,40,41]

Data with No Added Photo-Initiator. To further investigate the potential importance of unsuspected radical formation process, a number of polymerizations were performed in the absence of added photo-initiator. Such radicals could be associated with photo-excitation of monomer and/or polymer and/or (trace) impurities and/or solvent. Figure 4 shows that polymer is formed on exposure to pulsed-laser irradiation of wavelength 308 nm in the absence of added photo-initiator, as previously reported in the literature.[42] This problem might better be avoided by working at 355 nm. However, for all experiments performed in the absence of added initiator, the irradiation period had to be much longer (typically by a factor of 10) to obtain sufficient polymer for GPC analysis. This indicates that the rate of polymer formation in the absence of added photoinitiator is small compared to that associated with added photo-initiator so that the effect of this is of little concern at all temperatures. Moreover, this generation of radicals occurs at the same time as generation of initiator-derived radicals, and therefore it would only be a problem if any non-initiator-derived radical were generated with a certain time delay.

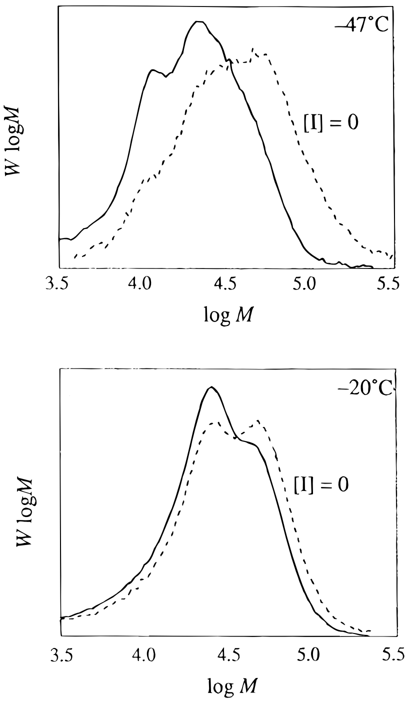

Figure 4. GPC molecular weight distribution for pulsed-laser polymerizations (data of Table 1) performed with (full line) and without (broken line) added photoinitiator at temperatures of −47 and −20 °C.

All in all, it does not seem possible to assign a single cause to the range of conditions where the PLP precepts are invalid. It is not unlikely that there is more than one such cause. However, the data suggest that, whatever the origin(s), the problem can be obviated by operating at sufficiently low temperatures and/or high pulse frequencies.

4. Final Rate Parameters and Error Analysis

For meaningful comparison with propagation rate coefficients for other monomers, for comparison with theory, and for extrapolation of the present low-temperature data to ordinary polymerization temperatures, it is essential to carry out a rigorous error analysis of the data deemed to obey the PLP precepts. This is especially important because the extrapolation to ordinary temperatures is a large one. Quantification of the uncertainty of the Arrhenius parameters and of extrapolated k_p values requires some estimate of the uncertainty in the values of both k_p and the temperature, as well as the variation of these uncertainties with temperature.

Internal consistency checks were used to identify those data, denoted as consistent in Table 1, which

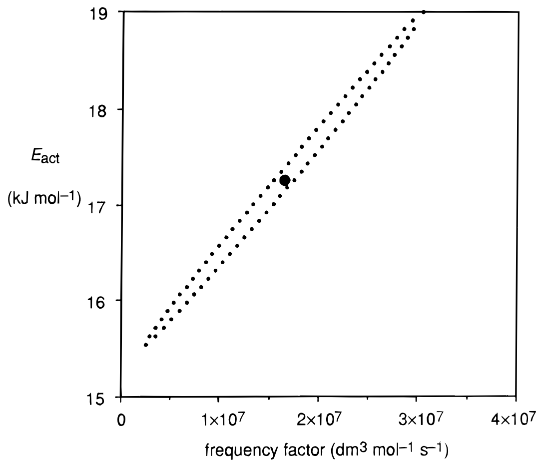

Figure 5. Confidence ellipsoid for Arrhenius activation energy (E_{act}) and frequency factor (A) fitting the data of Table 1 deemed to obey the PLP precepts, obtained using the error-in-variable method.[26]

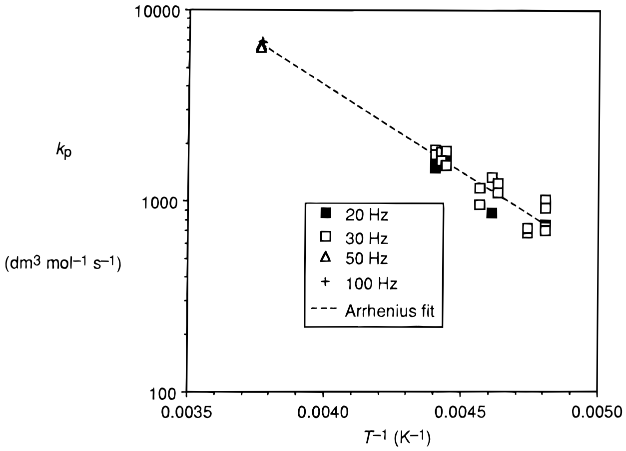

Figure 6. Arrhenius fit (using the frequency factor and activation energy from the center of the confidence ellipse in Figure 5) to the data of Table 1 deemed to obey the PLP precepts.

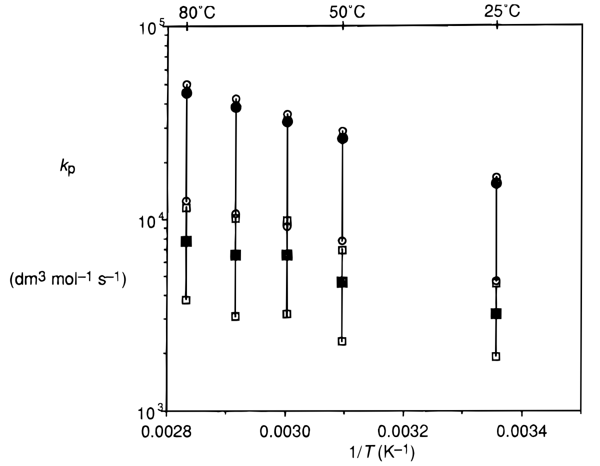

Figure 7. Comparison of the k_p data reported by Buback and Degener[29] (■) over the range 25−80 °C with those obtained by extrapolating the present results (●), obtained at much lower temperatures. The extrapolation and uncertainties of the present data were performed by using the extremes of the confidence ellipsoid of Figure 5. Uncertainties in the data of Buback and Degener were taken as those reported by those authors.

showed no dependences of k_p on frequency, initiator type and concentration, solvent type, and/or monomer concentration.

In order to fit the k_p data with the Arrhenius equation, we have used the error-in-variables method.[26] This takes into account the uncertainty in the temperature as well as the uncertainty in k_p. Given a set of consistent data, the uncertainties in both k_p and temperature must be identified. At the lowest temperatures of approximately −65 °C, the relative uncertainty in k_p is somewhat larger than that at higher temperatures. Closer inspection reveals that although there is no dependence of k_p on laser frequency, there is some dependence of the uncertainty in k_p on this frequency. At −65 °C the distribution in k_p values is larger for the 30 Hz data than for the 20 Hz data points. This is also the case at −47 °C, although the relative uncertainties are smaller. This can be explained by the fact that at lower temperatures (with a lower k_p value) and higher frequencies the polymer chains become smaller. In this particular case, the lowest molecular weights of polymer at the point of inflection were 2200. In this molecular weight region, the linearity of the Mark−Houwink equation becomes questionable, as a tends toward 0.5. As we depend on the Mark−Houwink relation to transform our GPC chromatograms into MWDs, in the lower molecular weight region the uncertainty in k_p becomes somewhat larger. For the lowest temperatures and higher frequency runs (runs 1−6), the uncertainty in k_p was set to 15%; the overall relative uncertainty for the k_p values of the other runs was set to 10%. For the solution experiments, the uncertainty in the temperature was set to 2 °C; the bulk (undiluted) experiments were done in a way that allowed control of the temperature to within ±1 °C. The fitting procedure resulted in:

$$k_p\,(\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 10^{7.22}\exp((-17.27\ \mathrm{kJ\,mol^{-1}})/RT) \qquad (3)$$

The 95% confidence ellipsoid for eq 3 is presented in Figure 5, and an Arrhenius fit of the consistent data of Table 1 shown in Figure 6.

An important use of k_p values is in modeling polymerization reactions. For reasons that have been discussed above, the present data could be obtained only at temperatures very much below those at which butyl acrylate is polymerized commercially. However, the general insensitivity of k_p to solvent effects[5,16,20,43−46] suggests that any temperature-induced changes in solvent structure and/or dynamics should have only a minor effect on propagation, i.e., that the Arrhenius parameters obtained over the range −65 to −7 °C can be employed to predict k_p at ambient temperatures. This gives a value of $k_p = 2.7 \times 10^4$ dm^3 mol^{-1} s^{-1} at 50 °C, with confidence limits, obtained from the extremities of the 95% confidence ellipse for the Arrhenius parameter, of (0.8−2.9) × 10^4 dm^3 mol^{-1} s^{-1}.

This 50 °C value of k_p is much higher than corresponding k_p values for the methacrylates, an inference which has some important ramifications in commercial polymerization processes involving butyl acrylate; the physical reasons for this high value are discussed in the next section.

Figure 7 compares the k_p values reported by Buback and Degener[29] over the range 25−80 °C with those from the present study, extrapolated to that temperature range and with the uncertainties as dictated by the confidence ellipse of Figure 5. The k_p values of Buback and Degener given in Figure 7 are shown with the

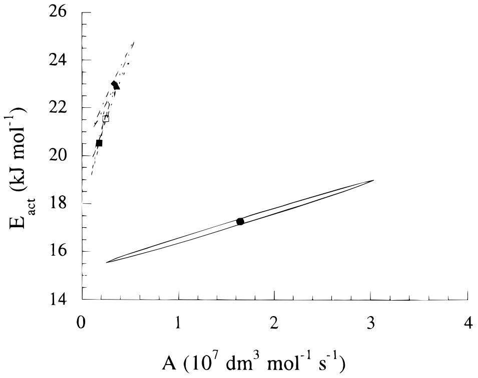

Figure 8. Confidence ellipses for the methacrylate data of refs 15 and 41, compared with that for the present data on butyl acrylate.

uncertainties quoted by the authors. The data of Buback and Degener, which are for higher temperatures than those of the present results, were obtained by three techniques: rotating sector, time-dependent pulsed-laser polymerization, and PLP (although as stated no GPC traces were reported for the single PLP result of these authors). In Figure 7 we have also indicated the uncertainties for the data of Buback and Degener. The two sets of data cannot be said to be within each others' experimental uncertainty; the reasons for this discrepancy are not apparent.

5. Interpretation of Arrhenius Parameters

Although theoretical understanding of the properties of the transition states for free-radical polymerization is still in its infancy, certain inferences can be extracted from the Arrhenius parameters from the present results. The Arrhenius parameters from the present data are compared in Figure 8 with those from corresponding PLP results for methyl, ethyl, butyl, and isobutyl methacrylate.[15,41] In each case, we have calculated confidence ellipses as described above from the rate data given in refs 15 and 41.

The data of Figure 8 also suggest that the frequency factor for butyl acrylate ($10^{7.2}$ dm^3 mol^{-1} s^{-1}) is significantly greater (by almost an order of magnitude) than that of butyl methacrylate. There are theoretical reasons for suspecting that this possible difference is in fact a real effect. Quantum mechanical studies[30] of the transition state expression for the propagation rate coefficient[47] show that the frequency factor involves major contributions from hindered rotations in the transition state, corresponding for example to a torsional rotation of the adding monomer unit. Comparing methacrylates and acrylates, the methyl side chain in the methacrylates is expected to result in increased hindrance in the transition state, and hence one would expect a methacrylate to have a significantly smaller frequency factor than the corresponding acrylate.

Another noticeable result is that activation energy for butyl acrylate (17.3 kJ mol^{-1}) is significantly lower than any of those for the methacrylates (21−23 kJ mol^{-1}); this difference is statistically meaningful. It is likely that the presence of the methyl next to the $C^{\bullet}$ in methacrylates stabilizes the parent radical relative to the transition state; there might possibly be some contributions to this stabilization from polar or hindrance effects.

6. Conclusions

The PLP results for the propagation rate coefficient for butyl acrylate are summarized in eq 3 and Figure 5. The data used for this analysis were subjected to rigorous consistency checks and error analysis, such as PLP affords, to screen the results for validity of the precepts for the applicability of PLP, i.e., so that the low molecular weight point of inflection on the molecular weight distribution corresponds to chains terminated instantly by straight-chain radicals formed by photoinitiation in the pulse immediately subsequent to the initiating pulse. The work given here suggests that pulsed photo-initiation of butyl acrylate leads to a situation so that the PLP precepts do not hold under "ordinary" conditions. The present work did not give definitive information as to the origin of this. However, it has been shown that this process can be minimized by carrying out PLP at sufficiently low temperatures and fast laser pulses, techniques which are probably widely applicable.

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