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Nominal vs Real Reaction Temperature in PLP Experiments. A Likely Explanation of the Observed Variation in the Propagation Rate Coefficients with Pulse Repetition Rate

Nuria García,* Pilar Tiemblo, and Julio Guzmán

Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: Pulsed laser polymerization experiments with methyl and dodecyl methacrylate were carried out at various frequencies and temperatures. In addition, the temperature inside the polymerization cell was continuous and automatically registered all along the polymerization time by means of a temperature probe of rapid response time. A significant increase in the reaction temperature was observed for most of the experiments. The temperature profile during the experiments was dependent on the chemical structure of the monomer and on the pulse repetition rate (the higher increase in temperature, the shorter the time between successive laser pulses). The analysis of the well-structured molecular weight distributions of the resulting polymers by size exclusion chromatography (SEC) allowed the determination of the propagation rate coefficients, k_p. The k_p values showed a decreasing trend when the pulse repetition rate did so. This effect is nowadays being discussed in terms of a long-range chain length dependence of k_p (molecular weights at the first inflection points in the SEC traces were always higher than 100 monomeric units). However, the changes in k_p for different pulse repetition rates could be adequately explained by considering the increase in temperature in every PLP experiment.

Introduction

The pulsed laser polymerization (PLP) in conjunction with the analysis of the resulting polymers by size exclusion chromatography (SEC), the so-called PLP−SEC technique pioneered by Olaj et al.,[1] provides the propagation rate coefficients, k_p, for a wide range of monomers under multiple experimental conditions.[2] A common experimental observation when applying this technique is being now a matter of debate, namely the chain-length dependence of k_p over the first few propagation steps. Although most of the k_p values derived from PLP show an increasing trend at higher pulse repetition rate, this experimental observation was quite recently ascribed to a chain-length dependency by Olaj et al.[3,4] Since then, other authors have proposed alternative explanations to this effect, such as the incorrect selection of experimental conditions and the SEC broadening of the molecular weight distributions (MWD).[5,6] Willemse et al.[6] analyzing PLP samples by means of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-Tof-MS) found no chain-length dependency of k_p above chain length of 100 monomeric units. On the basis of these analyses, the authors explained the above-mentioned effect appealing to the calibration and band broadening in SEC analysis. Later on, Olaj et al.[7] proved that a substantial long-range chain length dependence of k_p persisted even after having corrected the distortions caused by the SEC analysis. Consequently, Olaj et al.[7] attributed the disagreement found between SEC and MALDI-Tof-MS to a “mass discrimination” of the latter technique when analyzing polymer samples. Finally, recent works by Heuts and Russell[8,9] present a model that interprets the observed variation of k_p values in PLP experiments in terms of a chain-length dependent k_p for the very first monomer units. Therefore, the average k_p determined by PLP will be strongly affected by this dependence when the experiments yield low molecular weight materials, i.e., at high laser pulse repetition rate.

The discrepancies found in the experimental results, the controversy on this topic, and its practical and academic relevance invite to explore other potential reasons to explain the variation of k_p with the laser pulse repetition rate in PLP experiments. For example, given the high energy supplied by the laser initiation, the question arises as to whether the absorption of this energy produces not only the decomposition of the initiator but also an increase in the reaction temperature.

The temperature in the polymerization medium during the time of pulsing in a PLP experiment has been rarely monitored, and temperature data as a function of time of pulsing have never been reported in the literature. In addition, these previous works did not report the response time of the probes used to measure the temperature inside the polymerization cell. Van Herk’s group used a Pt-100 resistance element inside the polymerization cell to control the temperature during the experiment.[6,10−14] They found only small variations in the temperature of the reaction medium (±0.1,[14] ±0.2,[12] and ± 1 °C[13]) being the resistance element sometimes protected from direct irradiation by the laser beam.[10,11] Lyons et al.[15] also measured the temperature of the pulsed laser polymerization of butyl acrylate in tetrahydrofuran with the aid of a thermocouple. They reported an increase of less than 3 °C due to the polymerization reaction. The exotherm measured for the same conditions in the absence of monomer was 1.7 °C. Couvreur et al.[16] reported an overall temperature increase lower than 2 °C in PLP experiments with different alkyl acrylates. These authors mentioned that the conversions reached in their experiments were adjusted to be low in order to preclude a further increase in temperature due to the heat of polymerization. The results in the temperature registered during PLP experiments indicate that these reactions seem to proceed in almost isothermal conditions. However, these authors are among those who have not found a clear increasing trend of k_p when the laser repetition rate augments.[6,10−16] Hence, those researchers who have seen k_p increase when the laser repetition rate

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* Corresponding author: e-mail ngarcia@ictp.csic.es, Tel +34 91 562 29 00, Fax +34 91 564 48 53.

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augments do not report the temperature of their experiments, and those that report quasi-isothermal conditions see no changes in k_p with laser repetition rate.

The monomer molecules may absorb the photon energy of the laser and be promoted to electronic excited states. Depending on the frequency and total absorbed energy, the molecules can ionize, dissociate to form new species in the liquid, or simply relax nonradiatively or radiatively to the initial ground state.[17] In the case of nonradiative relaxations, the absorbed photon energy will finally be converted into thermal energy. Under adiabatic conditions and assuming the contribution of both the heat of polymerization (ΔH_v) and the thermal energy due to light absorption (Q) per volume unit, the increase in temperature (ΔT) which can be reached in the reaction medium will be given by eq 1:

$$\Delta T = \frac{Q + \Delta H_v}{\rho c_m} \tag{1}$$

where ρ is the monomer density and c_m the specific heat of the monomer. If only the heat of polymerization is considered, the energy liberated for a monomer such as methyl methacrylate (MMA) will be 560 J per gram of monomer converted into polymer. Equation 1 would thereby result in a temperature increase of 15 °C for the polymerization of 1 g of MMA up to a monomer conversion of 5% (recommended limit in PLP experiments). Consequently, isothermal conditions during the experiment will only be achieved if the thermostatic setup is able to dissipate the external heat due to the laser beam (if existing) and the internal heat of polymerization in a period of time short enough, the duration of this time period being dependent on the laser energy and pulse repetition rate, the polymerization rate, and the monomer conversion.

Therefore, it seems to be of great importance to know the real polymerization temperature when performing PLP experiments, especially so when dealing with high pulse repetition rates.

In this work, we have determined the k_p values for the polymerization of MMA and dodecyl methacrylate (DMA) by using the PLP−SEC technique at different laser pulse repetition rates. The temperature inside the polymerization cell has been monitored all along the time of laser pulsing. The aim of these measurements is to look for a connection between the changes in temperature and the increase in k_p values when performing experiments at high pulse repetition rates which yield low molecular weight materials.

Experimental Section

Materials. Methacrylic monomers, MMA (Aldrich, 99%) and DMA (Fluka, 97%), were distilled under high vacuum before use. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), was used as received.

Pulsed-Laser-Initiated Polymerizations. The k_p values for MMA and DMA were measured using the PLP−SEC technique. A series of pulsed-laser-initiated bulk polymerizations were carried out at different temperatures and pulse repetition rate inside a jacketed cylindrical quartz cell (HELLMA 165-QS, 0.86 mL of volume, path length 10 mm). The cell was connected to a thermostatic bath with a recirculating mixture of water and ethylene glycol regulated at the desired initial temperature of the experiment. The cell containing the monomer and initiator solution was thermostated for 10 min prior to pulsing. The temperature was controlled before, during, and after the polymerization reaction by a digital thermometer (Testo 735-2) equipped with a 1 mm diameter external probe placed inside the cell and located at the center of the laser beam pathway. The response time and precision of this temperature probe are 1 s and ± 0.1 °C, respectively. The temperature data were thus automatically registered in short sequences of time. For all the experiments, the nominal temperature, T_0, represents the initial and constant temperature registered before laser pulsing, whereas the final temperature, T_f, is the last temperature value detected just before stopping the laser source. As a representative reaction temperature, the arithmetic mean value of the sequentially registered temperatures has been considered, and called hereafter $T_{ave,}$ the average reaction temperature during the experiment. To check the possible effect of the probe inside the cell, additional experiments were also undertaken in the absence of the probe and registering the temperature after pulsing.

Monomer solutions (10 mL) with different DMPA concentrations ranging between 3×10^{-3} mol L^{-1} (7.7×10^{-3} g in 10 mL) and 8×10^{-3} mol L^{-1} (20.5×10^{-3} g in 10 mL) were prepared. DMPA decomposition was induced by a Quanta-Ray Nd:YAG laser (Spectra-Physics) operating at 355 nm with an energy of 50 mJ/pulse. A Stanford DG 535 pulse delay generator enables to tune the time between laser pulses ranging from 0.1 to 1 s. The samples were subjected to laser pulsing for the time needed to reach a conversion of monomer into polymer ranging from 1 to 5%. This conversion was monitored by FT-IR spectroscopy[18] and also gravimetrically checked. The polymer was precipitated in methanol containing traces of hydroquinone in order to prevent further polymerization and was isolated prior to SEC analysis.

Size-Exclusion Chromatography Analysis. MWD were obtained by means of size exclusion chromatography using a Waters 1515 HPLC pump, a Waters 2414 refractive index detector, and a set of three Waters columns with nominal pore sizes of 10^2, 10^4, and 10^6 Å. The eluent was tetrahydrofuran at 35 °C, pumped at 1 mL min^{-1}. The SEC setup was calibrated against polystyrene (PS) standards of narrow polydispersity (MW between 580 and 5×10^6 g mol^{-1}, Polymer Standards). Absolute molecular weights of the polymer samples were estimated via the principle of universal calibration using the Mark−Houwink parameters for MMA and DMA taken from the literature.[19]

Results and Discussion

Figure 1 shows some representative MWD and the corresponding first-derivative curves of the pMMA (left) and pDMA (right) resulting from the pulsed-laser-initiated experiments. For all the experimental conditions used, well-structured SEC traces with at least two inflection points in the derivative curve were obtained. The PLP structures obtained for the experiments where large times between successive pulses were used show the usual pattern observed under such reaction conditions.[20] The experimental details as well as the resulting molecular weights of the first (M_1) and second (M_2) inflection points for each experiment are compiled in Tables 1 and 2 for MMA and DMA, respectively. As can be directly deduced from these data, the values of the ratio M_1/M_2 are in both data sets about an average value of 0.50, fulfilling the PLP consistency criterion. According to eq 2,[1] where c_M is the monomer concentration and t_0 the time between successive laser pulses, the k_p values were derived from the degree of polymerization of the inflection points, L_1, located in the low molecular weight region.

$$L_1 = k_p c_M t_0 \tag{2}$$

The equations that account for the variation of c_M with temperature have been applied to calculate the k_p values.[19] The as-determined k_p values are gathered in Tables 1 and 2 for MMA and DMA, respectively. Moreover, the Arrhenius graphs in Figure 2 show these k_p values plotted as a function of T_0, i.e., the temperature value of the monomer−initiator solution before pulsing. It must be pointed out that neither the PLP structures

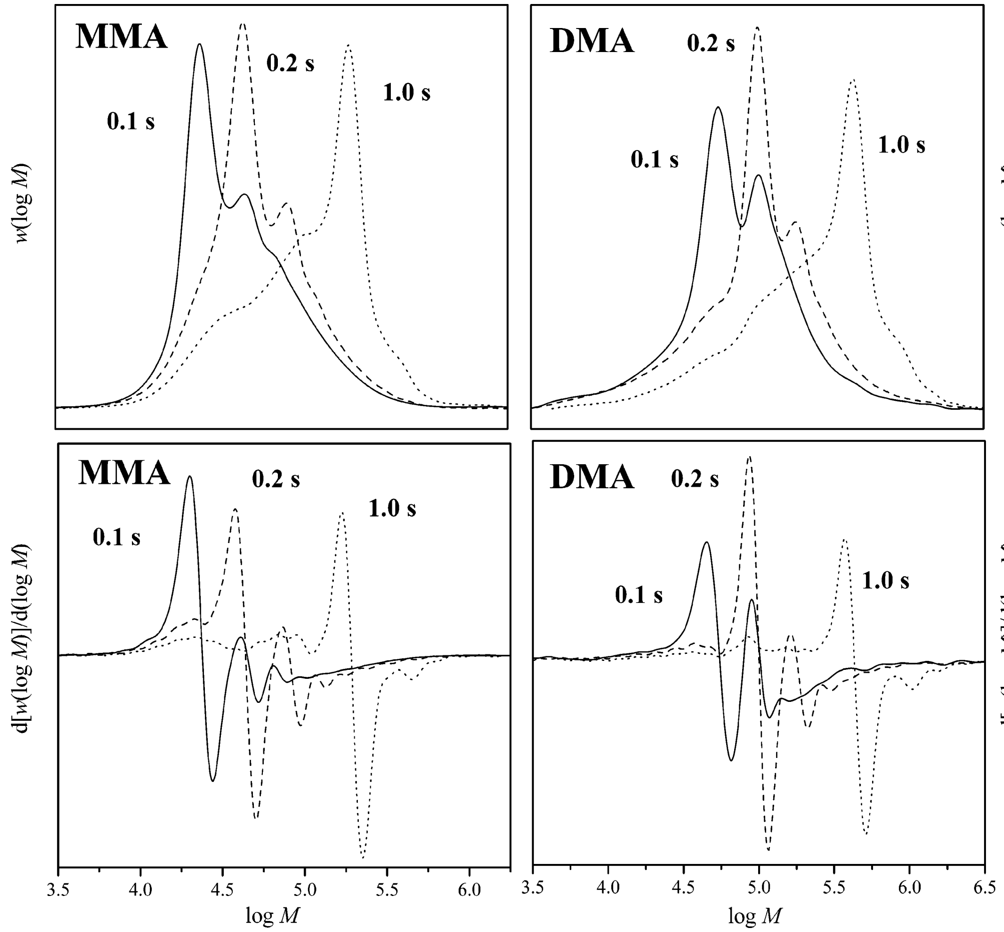

Figure 1. Molecular weight distributions and corresponding first-derivative curves of the polymers obtained from laser initiated experiments of methyl methacrylate (left) at nominal temperature, $T_0 = 10$ °C and dodecyl methacrylate (right) at $T_0 = 22$ °C with different times between laser pulses.

Table 1. Experimental Conditions and Results from the Pulsed Laser Free-Radical Polymerization of Methyl Methacrylate[a]

T_0/°C	T_f/°C	T_{ave}/°C	t_0/s	N laser pulses	α	M_1/g mol^{-1}	M_2/g mol^{-1}	k_p/L mol^{-1} s^{-1}
58.8	65.4	64.0	0.1	1900	2.1	79 300	160 000	889
58.8	65.5	64.0	0.1	1800	2.0	81 100	161 800	908
58.8	61.0	60.3	0.2	900	1.4	152 900	314 500	852
58.8	59.4	59.2	1.0	240	1.0	735 500	1400100	819
48.4	56.2	55.6	0.1	2100	1.9	63 800	123 300	708
40.0	45.2	44.6	0.1	2400	1.5	49 800	95 500	545
40.1	42.1	41.4	0.2	900	1.3	89 400	183 700	487
39.9	40.5	40.2	1.0	180	0.9	409 300	811 400	445
25.2	30.9	29.9	0.1	3000	1.4	31 800	63 800	341
20.7	28.9	28.3	0.1	3000	1.2	27 900	57 300	299
20.7	28.9	28.2	0.1	3000	1.3	28 200	57 900	303
25.3	26.8	26.4	0.2	1800	1.2	63 100	123 300	338
25.0	26.7	26.2	0.3	1200	1.1	89 400	179 500	319
10.0	16.9	15.5	0.1	5400	1.3	20 000	40 600	211
10.0	12.6	11.9	0.2	3300	1.2	37 700	73 500	198
9.8	10.5	10.3	1.0	840	0.9	167 500	351 700	176

[a] Nominal temperature before pulsing = T_0, final temperature at the end of the laser irradiation = T_f, average temperature during the reaction time = T_{ave}, time between successive laser pulses = t_0, number of laser pulses = N, percentage of monomer conversion = α, molar masses of the first and second inflection points from the derivative curve of the weight log MWD = M_1 and M_2, and propagation rate coefficient = k_p obtained from the first inflection point.

nor the calculated k_p values were altered by the presence of the probe inside cell, obtaining practically identical results for the experiments without online temperature monitoring.

For the same nominal temperature, Figure 2 shows a systematic decrease in the k_p values as the time between laser pulses is enlarged and, therefore, as the degree of polymerization increases. The decrease in k_p is slightly more pronounced for DMA than for MMA. In the case of the latter, a similar variation of k_p with chain length has been previously reported.[4] If attention is not drawn on this variation of k_p with pulse repetition rate, the results shown in Figure 2 could be considered to be in good agreement with the IUPAC benchmark fits (dashed curves in Figure 2).[21,22] This agreement is more conspicuous if only short times between laser pulses are considered, which is not surprising since the average times between laser pulses of the experiments considered to obtain the benchmark fits were 0.1 s for MMA[21] and 0.06 s for DMA,[22] whereas in this work, these average times are 0.31 and 0.41 s, respectively.

Table 2. Experimental Conditions and Results from the Pulsed Laser Free-Radical Polymerization of Dodecyl Methacrylate[a]

T_0/°C	T_f/°C	T_{ave}/°C	t_0/s	N laser pulses	α	M_1/g mol^{-1}	M_2/g mol^{-1}	k_p/L mol^{-1} s^{-1}
59.4	74.9	68.9	0.1	450	4.5	114 100	225 200	1366
59.0	74.1	67.6	0.1	400	4.4	117 900	230 500	1409
59.2	69.6	65.0	0.2	225	3	217 600	448 000	1297
59.1	62.9	61.3	1.0	90	1.4	1 063 700	1 999 000	1264
59.2	62.6	61.1	1.0	90	1.2	1 078 700	2 061 800	1282
48.5	60.8	54.6	0.1	300	2.0	89 900	171 700	1062
39.8	54.3	51.5	0.1	900	4.8	70 200	130 200	827
39.6	53.7	50.8	0.1	600	4.1	71 700	133 100	844
48.3	51.3	50.3	1.0	90	1.1	787 700	1 569 100	927
39.7	49.7	46.7	0.2	450	4.8	131 600	258 600	772
33.0	45.5	43.0	0.1	1200	4.7	60 400	110 500	706
39.7	43.1	42.0	1.0	90	1.3	590 800	1 207 700	690
33.1	43.7	38.1	0.2	450	2.2	108 100	210 300	629
33.0	36.2	34.2	1.0	60	1.1	482 600	1 063 700	560
22.1	36.6	30.8	0.1	600	4.1	42 900	87 000	496
23.6	36.2	30.7	0.1	400	2.6	45 200	89 900	523
20.1	35.0	30.4	0.1	600	3.7	39 300	79 000	455
22.2	35.9	29.5	0.1	450	2.2	44 700	89 900	517
22.1	30.8	27.0	0.2	300	4.0	86 100	162 400	496
23.6	26.6	25.3	1.0	120	2.3	391 600	842 400	451
22.1	25.4	23.7	1.0	150	2.2	355 500	767 000	409
22.1	25.0	23.4	1.0	120	1.7	373 100	809 100	429
14.7	28.3	22.6	0.1	450	2.8	34 600	70 200	397
14.7	28.1	22.5	0.1	450	2.2	34 600	69 400	397
9.3	23.8	19.8	0.1	750	4.1	27 900	56 000	320
10.7	23.7	19.8	0.1	600	4.0	28 800	58 500	330
9.3	15.0	13.5	0.2	600	4.8	54 300	101 300	309
9.7	12.2	11.2	1.0	150	2.1	225 200	465 000	256

[a] Nominal temperature before pulsing = T_0, final temperature at the end of the laser irradiation = T_f, average temperature during the reaction time = T_{ave}, time between successive laser pulses = t_0, number of laser pulses = N, percentage of monomer conversion = α, molar masses of the first and second inflection points from the derivative curve of the weight log MWD = M_1 and M_2, and propagation rate coefficient = k_p obtained from the first inflection point.

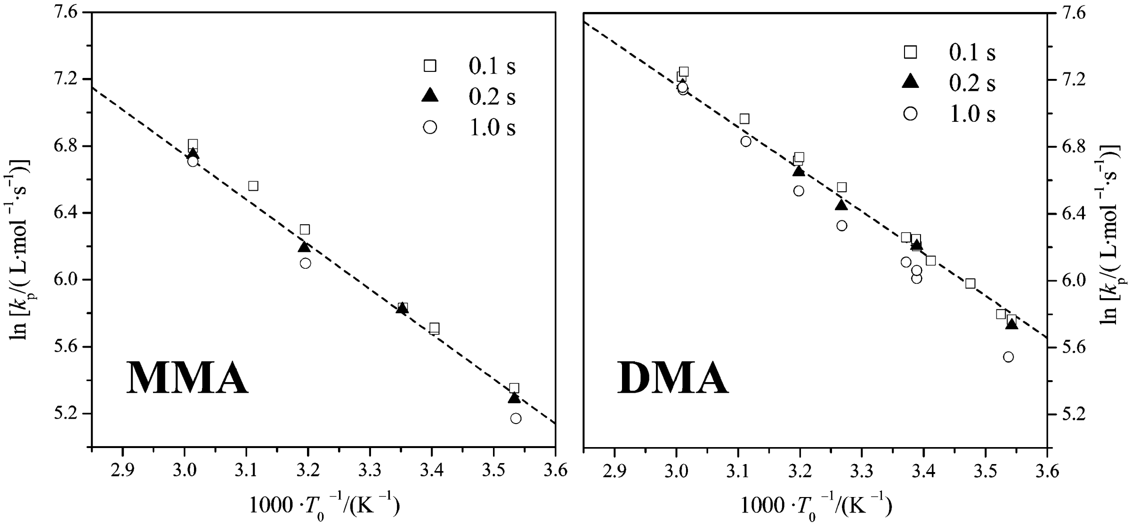

Figure 2. Arrhenius graphs showing the obtained k_p values as a function of the inverse nominal temperature, T_0 (temperature value of the solution before pulsing). IUPAC benchmark fits[21,22] are represented by the dashed curves.

The temperature inside the cell containing the irradiated solution was monitored during the PLP experiments all along the reaction time. Some examples of the variation of the inside temperature with the reaction time are shown in Figure 3.

It can be seen at first glance that the temperature of the reaction medium is over the nominal temperature, T_0, in all the experiments performed, at all pulse repetition rates, and in both monomers. It is also observed that the shorter the time between laser pulses, the larger the registered increase in temperature is and that, at large irradiation times, a plateau in the reaction temperature is attained. Although the temperature plateau is only vaguely suspected in the DMA data plotted in Figure 3, this happens also for this monomer as can be deduced from the temperature data gathered in Table 2 which referred to PLP experiments under similar conditions but different reaction times (note the small variation in the final temperature registered value, T_f, in experiments at similar or identical T_0 and different number of pulses). These observations indicate that during the experiments there is a temperature increase caused by the laser irradiation that is partly counterbalanced by the cooling device.

The increase in temperature is more outstanding for DMA than for MMA. This difference in behavior of both monomers must mainly be ascribed to the higher polymerization rate of DMA. Let us consider the experiments with 0.1 s of pulse repetition rate in Figure 3; the DMA monomer conversion is almost twice that of MMA, whereas the polymerization time is over 10-fold longer for the latter. This means that the DMA polymerization reaction generates a larger amount of heat in

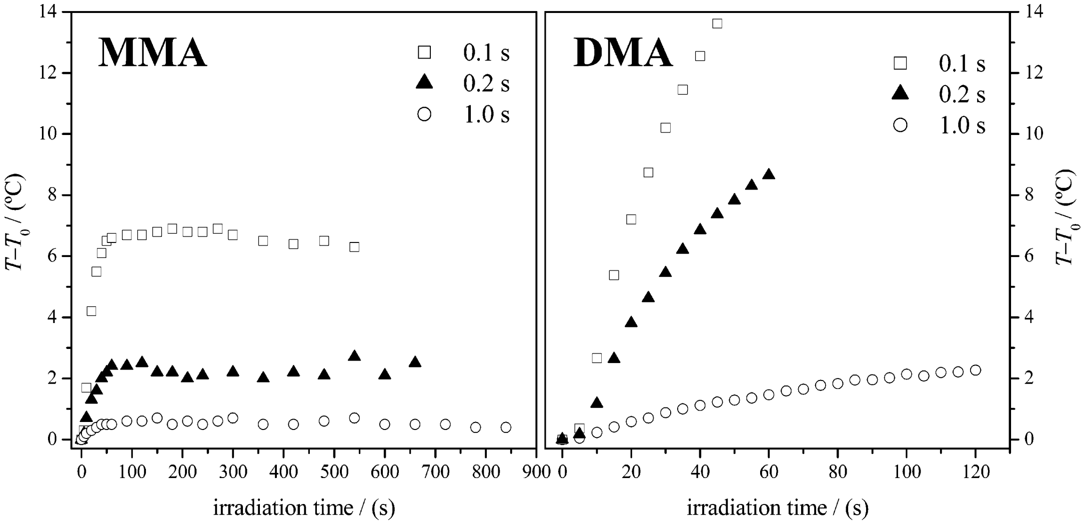

Figure 3. Temperature evolution as a function of overall laser pulsing time during the bulk polymerization of methyl methacrylate (left) at $T_0 = 10$ °C and dodecyl methacrylate (right) at $T_0 = 22$ °C with time intervals 0.1, 0.2, and 1 s between laser pulses.

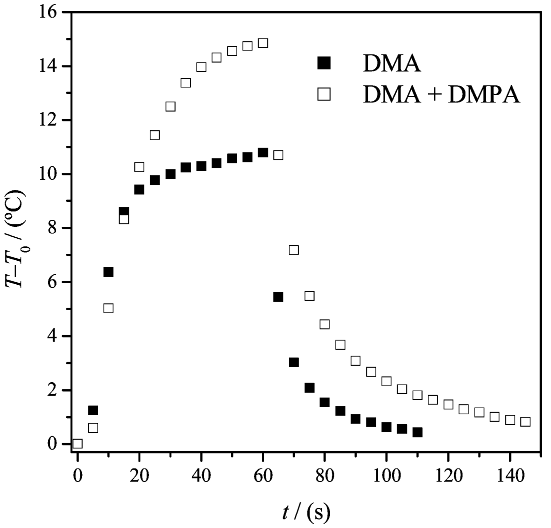

Figure 4. Temperature changes during and after a pulsed laser polymerization experiment with dodecyl methacrylate at $T_0 = 20$ °C and 0.1 s of time between laser pulses. Identical conditions were applied to reproduce the experiment in the absence of the DMPA photoinitiator. Irradiation time for both experiments was 60 s.

very short periods of time compared to the MMA reaction. Therefore, the larger temperature increase for DMA experiments is fully understandable. In addition, there is another contribution to differentiate the behavior of both monomers, and that is the light absorption. The absorbance of both monomers at 355 nm (laser emission) is really low (around 0.01 absorbance units for MMA and 0.02 for DMA) but higher for DMA. Moreover, the strong UV absorption associated with the monomer starts roughly at 350 nm in DMA whereas is shifted down to 315 nm in MMA. These indications lead to expect a higher temperature increase due to nonradiative relaxations in the case of the DMA molecules.

Figure 4 shows the temperature changes during and after a 60 s long PLP experiment for DMA at $T_0 = 20$ °C and with 0.1 s of time between laser pulses. For comparison, an experiment under identical reaction conditions but in the absence of DMPA is included. As can be seen in this figure, on irradiation the monomer by itself undergoes an important increase in temperature with the time of pulsing. It has been checked that no polymerization occurs under these experimental conditions: no changes are observed in the FT-IR spectrum before and after pulsing and no presence of polymer after pouring the sample in methanol. This temperature increase must be mainly caused by the energy absorption as above explained, though other undesirable contributions to the sample heating, such as the heating of the quartz cell, especially the face directly irradiated, or laser emissions in the IR wavelength range (described for Nd:YAG laser, a common equipment used in k_p measurements by PLP experiments) cannot be ruled out.

On the other hand, the difference in temperature between the experiments with and without DMPA is clearly detected in the data depicted in Figure 4. It goes without saying that this temperature increment should be related to the heat of polymerization evolved during the polymerization. Knowing the increases in the temperature during the experiment with (ΔT_p) and without (ΔT_m) photoinitiator, the final conversion, and the specific heat of the monomer (c_m), the heat of polymerization (ΔH) can be calculated by applying eq 3

$$q = mc_m(\Delta T_p - \Delta T_m) = -n\Delta H \tag{3}$$

where q is the heat liberated during the polymerization reaction, m the mass of monomer in the reaction cell, and n the number of moles of monomer converted into polymer. Assuming a c_m value of 1.96 J g^{-1} °C^{-1} and 3.7% of conversion during the experiment, the resulting ΔH value was -55.8 kJ mol^{-1}. This value is consistent with literature data derived by other experimental procedures.[23]

On the other hand, Figure 4 shows also the cooling step after switching off the laser source for both samples. A few seconds after stopping the laser irradiation, the temperature inside the cell is dramatically reduced by the action of the cooling device. This might be the reason why the researchers who measured the temperature before and after pulsing stated that the changes in temperature during the PLP reactions were negligible or not detectable.[24] Temperature probes of slow response time (30 s)[24] may fail to detect the rapid decrease in the temperature. In addition, being the cooling step extremely fast during the first 10 s after stopping laser irradiation, it slowed down afterward. Actually, the original nominal temperature was not reached until over 1 min after switching off the laser source. Given the rapid response of the temperature probe (1 s), this gradual cooling step is also a proof which supports the increase in temperature not being an artifact caused by the direct irradiation of the probe.

The temperature of the solution after pulsing in the experiments which were carried out in the absence of the temperature

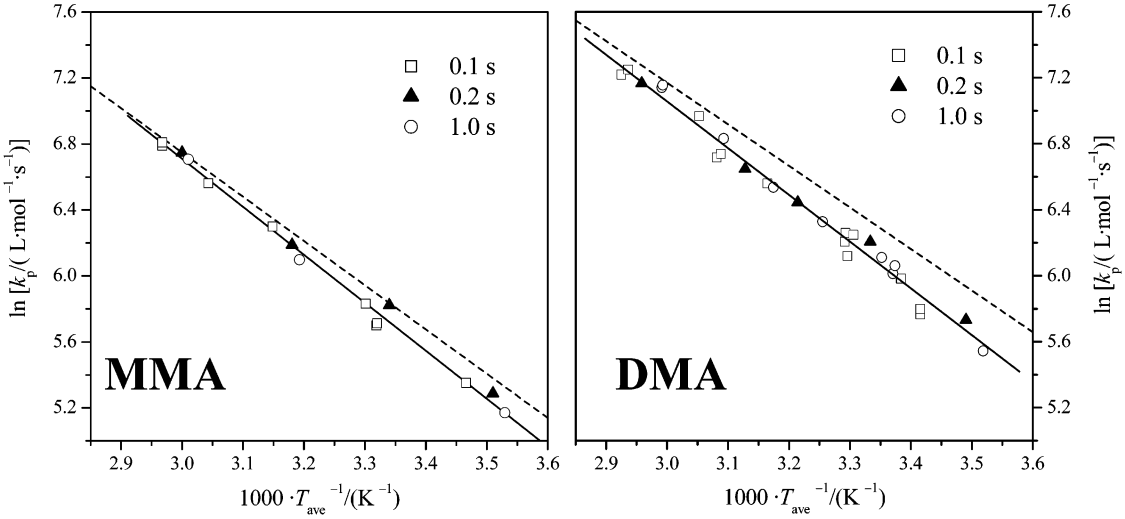

Figure 5. Arrhenius graphs of the k_p values obtained for the polymerization of methyl methacrylate (left) and dodecyl methacrylate (right) and using the average reaction temperatures, T_{ave}. The dashed curves represent the IUPAC benchmark fits for these monomers,[21,22] whereas the solid ones show the linear fits of the resulting k_p as a function of inverse T_{ave}.

probe was also checked. The increases in temperature were not so pronounced as when the temperature was online monitored but by no means negligible (5 °C in an experiment reproducing the polymerization conditions shown in Figure 4 for DMA + DMPA). The detection of a lower increase in the temperature is ascribed to the time consumed in placing the probe inside the cell, the response time of the probe, and the opening of the cell which also contributes to a quicker decrease in the temperature of the solution.

At this point, it is useful to recall that the probe which registered the temperature was located at the center of the cell, i.e., at the farthest position from the cooling source. Therefore, the temperature records shown in Figures 3 and 4 will represent the highest expectable variation, and besides the variation of the temperature with irradiation time, a spatial temperature profile caused by the cylindrical shape of the cell is presumed to occur in the reaction medium. As a consequence of these nonisothermal conditions, a representative reaction temperature value must be chosen. The criterion applied in this work has been to consider the arithmetic mean value of the sequentially registered temperatures, T_{ave}. These values are listed in Tables 1 and 2 for MMA and DMA experiments, respectively.

Once the temperature effect has been evaluated, the calculated k_p values can be replotted taking into account the variation of the temperature all along the PLP experiment.

The Arrhenius graphs in Figure 5 show the same k_p values as in Figure 2 but now plotted as a function of the average reaction temperature, T_{ave}. The pulse repetition rate influence on k_p is not detected in these graphs. The data for both monomers MMA (left) and DMA (right) draw a linear trend placed below the benchmark fits (dashed curves). The linear fits have also been included in the graphs as solid lines. Though only tentative activation parameters can be provided, given the somewhat narrow temperature range used for these experiments, the increase in activation energy, E_A, compared to the benchmark fits (22.4 kJ mol^{-1}for MMA[21] and 21.0 kJ mol^{-1} for DMA[22]) is, nevertheless, noteworthy. Even more remarkable is the coincidence between both E_A values derived from the solid lines in Figure 5, 24.2 kJ mol^{-1}for MMA and 23.6 kJ mol^{-1} for DMA. These results are consistent with the assignment of the rise in k_p on increasing the alkyl ester group size in the methacrylate family solely to a variation of the Arrhenius preexponentional factor.[25,26]

On the other hand, although the E_A values reported above are higher than the IUPAC benchmark values, it is possible to find similar values in the literature. Willemse et al.[6] estimated values for $k_p(\infty)$, a constant propagation rate coefficient for a long-chain limit not affected by the higher k_p values for the very short radicals. The E_A of the $k_p(\infty)$ values for the polymerization of MMA is practically identical (24.4 kJ mol^{-1}) to the value reported in this work. Bergert et al.[27] reported a E_A value of 23.9 kJ mol^{-1}for the bulk polymerization of MMA. It is worthy to mention that the PLP experiments performed to determine k_p in this latter work were carried out at pulse repetition rates not higher than 7.2 Hz and with a low-energy per pulse (4 mJ). On the basis of the results reported in this work, these experimental conditions would be the most suitable to minimize the increase in the temperature during the PLP experiment. This fact could explain the good experimental agreement between our E_A values obtained after correcting the reaction temperature and those found by Bergert et al.[27]

Conclusions

Pulsed laser polymerization experiments were carried out to determine propagation rate coefficients, k_p, for the bulk polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DMA) at different temperatures and pulse repetition rates. The results showed a systematic increase in k_p values when shortening the time between successive pulses. This variation could be interpreted in terms of a long-range chain-length dependency of k_p, a topic which has recently become a controversial debate. However, a temperature register with a rapid-response-time probe placed inside the polymerization cell during the time of pulsing showed that the temperature increased significantly with the first laser pulses. The extent of this temperature increase has proved to be dependent on the laser pulse repetition rate, being larger when shorter time intervals between pulses were applied. In addition, there were differences between the temperature effects on both monomers. The increase in temperature detected during the polymerization was more pronounced for DMA, which is ascribed to the higher polymerization rate of this monomer compared to MMA.

The temperature effect can explain the increase in k_p at high laser pulse repetition rates, if an average polymerization temperature, higher than the nominal or initial one, is considered.

These results can contribute to explain the discrepancies found in the experimental data when different laboratories analyze the influence of the pulse repetition rate on k_p, since the experimental setups and reaction conditions such as pulse energy, cell volume, or monomer conversion can significantly affect the calculated k_p values.

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