Article

On the Recovery of PLP-Molar Mass Distribution at High Laser Frequencies: A Simulation Study

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Abstract: Due to the inherent difficulties in determination of the degree of branching for polymers produced in pulsed laser polymerization (PLP) experiments, the behavior of the degree of branching and backbiting reaction in high laser frequency and relatively high reaction temperatures have not been well-established. Herein, through a simulation study, the validity of different explanations on the recovery of PLP-molar mass distribution at high laser frequencies is discussed. It is shown that the reduction of the backbiting reaction rate at high laser frequency, and consequent decrease in the degree of branching, is not a necessary condition for recovering the PLP-molar mass distribution. The findings of this work provide simulation support to a previous explanation about the possibility of using high laser frequency for reliable determination of the propagation rate coefficient for acrylic monomers.

Keywords: PLP-SEC; *n*-butyl acrylate; degree of branching

1. Introduction

Having accurate rate coefficients of polymerization reactions is crucial to obtaining basic knowledge about complex polymerization reactions, modeling and better controlling the industrial processes. Pulsed laser polymerization (PLP) has been used to measure the rate coefficients of polymerization reactions of different monomers [1–5]. In particular, PLP together with size exclusion chromatography (PLP-SEC), has been recommended by International Union of Pure and Applied Chemistry (IUPAC) and successfully applied to calculate the propagation rate coefficient of several academically and industrially relevant monomers. A PLP-SEC experiment can be carried out as a function of temperature, and hence it is possible to calculate Arrhenius' parameters, pre-exponential factor, and activation energy [6]. In a PLP-SEC experiment, a reacting mixture containing monomer (optionally a solvent) and a photoinitiator is initially irradiated with a laser pulse at t_0, generating radicals, $[R_0]$, in the order of 10^{-5} mol L^{-1} [7]. These radicals initiate the polymer chains that grow altogether during the so called dark period, i.e., when the mixture is not irradiated by the laser and therefore, there is not any new radical. At a later time, t_1, another laser pulse hits the reacting mixture and the new radicals terminate a large fraction of the growing chains (those who did not undergo termination during the dark period) or initiate new chains. In a posterior multiple of $t_1 - t_0$, i.e., t_d, another laser pulse hits the sample and this continues; t_d is controlled by the laser frequency or laser repetition rate. Obviously, some chains grow during more than one dark period. Once the polymerization finishes, either at a fixed time or after a number of laser pulses, the molar mass distribution (MMD) is measured by size

exclusion chromatography (SEC), and the MMD or the chain length distribution (CLD) should show distinctive peaks at defined chain lengths according to the following equation:

$$L_n = n k_p [M] t_d \ n \geq 1 \tag{1}$$

where L_n is the chain length at which the CLD shows a critical point (calculated by the maximum of the first derivative), n is an integer number related to the number of dark periods that the chains were able to grow (i.e., $L_1 = 1L_0$, $L_2 = 2L_0$ and so forth); $[M]$ is the monomer concentration; and k_p is the propagation rate coefficient, as the unknown parameter. To provide reliable results in a PLP-SEC experiment, several consistency criteria must be fulfilled. First, at least two peaks should be present in the CLD, which are multiples of L_0; second, it is desirable to reach conditions for the independence of k_p on initiator concentration, laser power, laser frequency, and monomer concentration [1,8]. The PLP-SEC method has provided good results within a broad temperature range for some widely used monomers, such as styrene [2], methyl, and alkyl methacrylates [1,3], among others. Laser frequencies up to 100 Hz were used in most of the above-mentioned PLP-SEC experiments. Nevertheless, accurate estimation of k_p from a PLP experiment is still a challenge [9].

However, the PLP-shape of the MMD (distributions with clearly defined critical points) was not obtained for acrylic monomers, specifically for *n*-butyl acrylate at temperatures ≥30 °C. Although it was found that by carrying out the PLP reaction at sufficient low temperatures the PLP-MMD was recovered, the origin of this phenomena was not known initially [10,11]. It is well known now that in addition to the common reactions of a free radical polymerization (initiation, propagation, and termination), acrylic monomers undergo significant intramolecular chain transfer to polymer or backbiting. Intermolecular chain transfer reaction is present as well, which is important at high polymer concentration. However, this is not the case in a standard PLP-SEC experiment due to the low monomer-to-polymer conversion. In the backbiting reaction, a growing chain-end radical wraps around itself to abstract a hydrogen atom from a monomer unit on its own backbone via the formation of a six-membered ring [4,12]. The stability of the resulting mid-chain radical (MCR) has a significant effect on the polymerization kinetic and the microstructure of the polymer chains, leading to a featureless MMD, which in turn invalidates the k_p determination by PLP-SEC above c.a. 30 °C [13,14]. As the activation energy of backbiting is higher than the activation energy of the propagation of the chain-end radicals, the k_p of *n*-butyl acrylate (BA) could be determined accurately between −65 °C and 20 °C using frequencies up to 100 Hz [4].

It is worth noting that simulation studies dealing with the polymerization of acrylic monomers have been very important for better understanding of this phenomenon and better estimation of the propagation rate coefficient [15], and even later used to estimate the rate coefficients of the secondary reactions in acrylic radical polymerization [16,17]. Using a simulation approach, it was demonstrated that the increment of the laser frequency in a PLP-SEC experiment could lead to a better determination of the k_p of the chain-end radicals. For BA, at frequency around 300–500 Hz and temperature of 20 °C, the PLP-MMD is recovered and makes the average propagation coefficient (considering both MCR and chain-end radicals) independent from the laser frequency [14]. With the development of the laser technology, this simulation finding was experimentally confirmed. With a laser frequency of 500 Hz, it was possible to calculate the k_p of BA up to 70 °C. This temperature was 50 °C higher than the previously reported experiments, meeting the consistency criteria, showing up to three inflection points in the derivative of the CLD, providing a very good agreement of Arrhenius' parameters between the two data sets [18]. It was logical to carry out the PLP-SEC experiment at such frequency and higher temperature than in previous experiments for other acrylic monomers: up to 80 °C for isobornyl acrylate, tert-butyl acrylate and 1-ethoxyethyl acrylate [19], and for methyl acrylate and 2-ehtylhexyl acrylate [20,21]. Nevertheless, as an MCR can undergo β-scission at high temperatures, the MMD can be even more complex to analyze.

As in a PLP-SEC experiment, the conversion of monomer to polymer remains rather low, and it is difficult to measure the degree of branching directly (defined as the ratio of the quaternary carbons to

the total polymerization events). Generally, the cumulative determination of the degree of branching is carried out by ^{13}C-NMR spectroscopy [22–25], which requires some milligrams of polymer, which is not easy to obtain in a standard PLP-SEC experiment; otherwise, the error in the ^{13}C-NMR determination invalidates such a measurement. Plessis et al. were able to measure experimentally the branching density in a PLP experiment using a reactor with larger volumes of reactants than in conventional PLP set-ups [26]. They studied the effect of temperature and monomer concentration on branching density in a PLP experiment. To the best of our knowledge, no experimental study has been done to investigate the effect of frequency on the branching level.

Now the question is why do reaction temperatures close to 70 °C, using a laser frequency of 500 Hz, lead to a PLP-MMD, allowing an adequate k_p determination for *n*-butyl acrylate? It is reported in the literature: "Diminishing the effects from the MCRs is hence a prerequisite for a successful PLP-SEC experiment" [18,27]. Nikitin et al. [7] stated that the fraction of radicals that are not subjected to backbiting is proportional to $\exp(-k_{bb}t)$, where k_{bb} is the backbiting rate coefficient and *t* is the time after generation of these radicals by a laser pulse. Therefore, as the laser frequency increases, the fraction of growing chains that undergoes backbiting decreases. Such explanation has been used to explain the PLP-MMD-recovering of other acrylic monomers at higher temperatures than previous experiments [21]. On the other hand, in a PLP Monte Carlo simulation, the concept of competitive processes was used to explain the recovery of PLP-MMD at high laser frequencies [28]. In this simulation, the events that each of the radicals undergo were selected based on the probability of the corresponding reaction mechanism, with the condition that the time needed to undergo the chosen reaction could not exceed the life expectancy of the radical. This assumption led to a decrease in the degree of branching and recovery of PLP-MMD distributions at high temperatures and laser frequencies [28]. Additionally, in a deeper study of reversible addition-fragmentation chain transfer polymerization (RAFT), the concept of competitive processes was used to explain the decrease in the degree of branching in such a controlled radical polymerization. In this process, the deactivation time of growing radicals (adjusted by changing the amount of the RAFT agent) is typically faster than the characteristic time for backbiting. Following the same idea, the authors explained that the reduction of the radical lifetime to chain termination induced by fast laser pulse can result in a decrease in backbiting rate and, hence, the branching level in the PLP process, allowing the recovery of the PLP-MMD [29]. In summary, there are two possible explanations for the recovering of the PLP-MMD as the laser frequency increases. According to the latest explanation, reduction in the backbiting rate and, hence, the branching level is a crucial requisite for recovery of the PLP-MMD. However, in the first explanation, only decreasing the fraction of the radicals that undergo backbiting while maintaining the same backbiting rate leads to recovery of PLP-MMD.

In this study, PLP-SEC experiments are simulated using the polymerization kinetics of BA (the most studied acrylic monomer); the behavior of backbiting and the degree of branching are analyzed during PLP-SEC experiments carried out at different temperatures, laser frequencies, and concentration of radicals generated in the laser pulse. The degree of branching of the polymer obtained in a PLP is studied and discussed under different experimental conditions; and finally, the simulation results are used to study the validity of different explanations for the recovery of PLP-MMD at high laser frequency. It is shown whether reduction of the backbiting rate/branching level is an essential requisite for recovery of the PLP-MMD.

2. Simulation Details

BA PLP experiments at different reaction conditions were simulated in the present study. The detailed kinetic scheme used in these simulations, and relevant kinetic parameters which were taken from the literature, are presented in Supporting Information. It includes all relevant reactions in homopolymerization of acrylates, such as inter/intra molecular transfer to polymer. β-scission was not included in the kinetic scheme due to its negligible effect at the simulated temperatures (maximum 60 °C) [30]. The simulated PLP experiments were implemented in Predici commercial

software package [31]. To simulate the PLP polymerization by using an isothermal process at a given time (that is fixed by the laser frequency), the concentration of new radicals generated by the laser pulse ($[R_0]$) sharply increased to 10^{-5} moL L^{-1}. The total time of the simulation was 1 s in these simulations. Three different temperatures (20, 40, and 60 °C) and four laser frequencies (50, 100, 250, and 500 Hz) were employed. The monomer concentration was 7 moL/L. Also, in order to analyze the effect of radical concentration generated in the laser pulse on the CLD and on the degree of branching, PLP-SEC experiments at 20 °C with frequencies of 100 and 500 Hz and at two additional $[R_0]$, 10^{-4} moL L^{-1} and 10^{-6} moL L^{-1}, were simulated.

Instead of using the MMD of the polymer chains and polymeric radicals, the analysis was done using the CLD calculated by Predici in the Gel Permeation Chromatography (GPC) mode, size exclusion chromatography-chain length distribution (SEC-CLD). This simplified the analysis of the results, and the transformation process to the MMD was straightforward. Moreover, it should be pointed out that measuring the absolute molar mass of branched polymer chains by SEC is not trivial [20], and the calibration might introduce some error in the experimental measurements; such analysis is beyond the scope of the present study.

In addition to SEC-CLD of the inactive polymer chains, the simulation allows the calculation of the SEC-CLD of the chain-end radicals and of the MCR, the degree of branching, the fraction of MCRs that terminates with radicals generated by the laser pulse, and the ratio of the formed MCRs to the total propagation steps, among others.

3. Results and Discussion

In Figure 1 (left side), the final SEC-CLD of the polymer chains is presented for the simulations with $[R_0] = 10^{-5}$ moL L^{-1}. Each row of Figure 1 shows a different temperature. In the same figure (right side), the first derivative of each SEC-CLD is presented; the derivate was calculated by averaging the slopes of two adjacent points for each data point using the raw data, i.e., no smoothing was applied. At 20 °C and 50 Hz, it can be seen that there is a single peak in the CLD. The presence of this peak was confirmed in its corresponding derivative, which showed a sharp peak that resembles a PLP polymerization; however, a second peak was not observed. By increasing the frequency to 100 Hz, the peak at short chain-length became more visible and it shifted to nearly half of the value of chain-length of the previous condition; in the corresponding derivative, one can see that there is another small peak at larger chain-length, and this last peak is at the chain-length of the previous experiment at 50 Hz. In the SEC-CLD of the simulation at 250 Hz, two defined peaks can be seen in the CLD that were also present in the corresponding derivative. At the highest frequency, 500 Hz, two peaks at shorter chain-length were clearly observed, and in the derivative there were up to three peaks. For this temperature, the PLP-shape of the CLD was obtained at frequencies higher than, or equal to, 100 Hz. The higher the frequency of the laser pulse, the shorter the chains (shorter dark period) and the more defined the peaks in the SEC-CLD and in the correspondent derivative. From an experimental point of view, the acceptable k_p calculations were carried out up to this temperature at 100 Hz due to the presence of more than one peak in the derivative of the SEC-CLD [4], which was observed in the present results as well.

Next, we analyzed the results at 40 °C; it should be recalled here that at such temperature, it was not possible to obtain reliable experimental PLP-MMDs to properly calculate the k_p using frequencies up to 100 Hz. At 50 Hz, there were no defined peaks in the SEC-CLD or in its derivative, and a broad, featureless distribution was obtained. At 100 Hz, although the SEC-CLD was broad, there was a rather small peak in the SEC-CLD that was also observable in its derivative. The peak in the derivative resembles a PLP polymerization. In principle, this peak could be used to determine the k_p [7], but for the reliability of the results, the presence of at least a second peak at larger chain lengths is desired. Such second peak in the derivative of the SEC-CLD appeared when the frequency was 250 Hz, along with the formation of a broad peak at even larger chain lengths. For the simulation with 500 Hz, a PLP-shape of the CLD was totally recovered, and in the derivative it was possible to observe the

presence of three peaks. Therefore, the information of the experiment with 500 Hz could be used to calculate k_p.

The highest temperature considered in the simulations was 60 °C (third row in Figure 1). For this temperature, the SEC-CLD at 50 and 100 Hz did not have the shape of a PLP experiment, i.e., there were no peaks in the SEC-CLD nor in the corresponding derivatives. At 250 Hz, only one peak in both graphs was formed, therefore, the use of such information to calculate the k_p would not be recommended. However, at 500 Hz, the SEC-CLD recovered the PLP-shape and in the derivative two peaks were present. Therefore, it was possible to use this information to calculate the k_p at such a temperature.
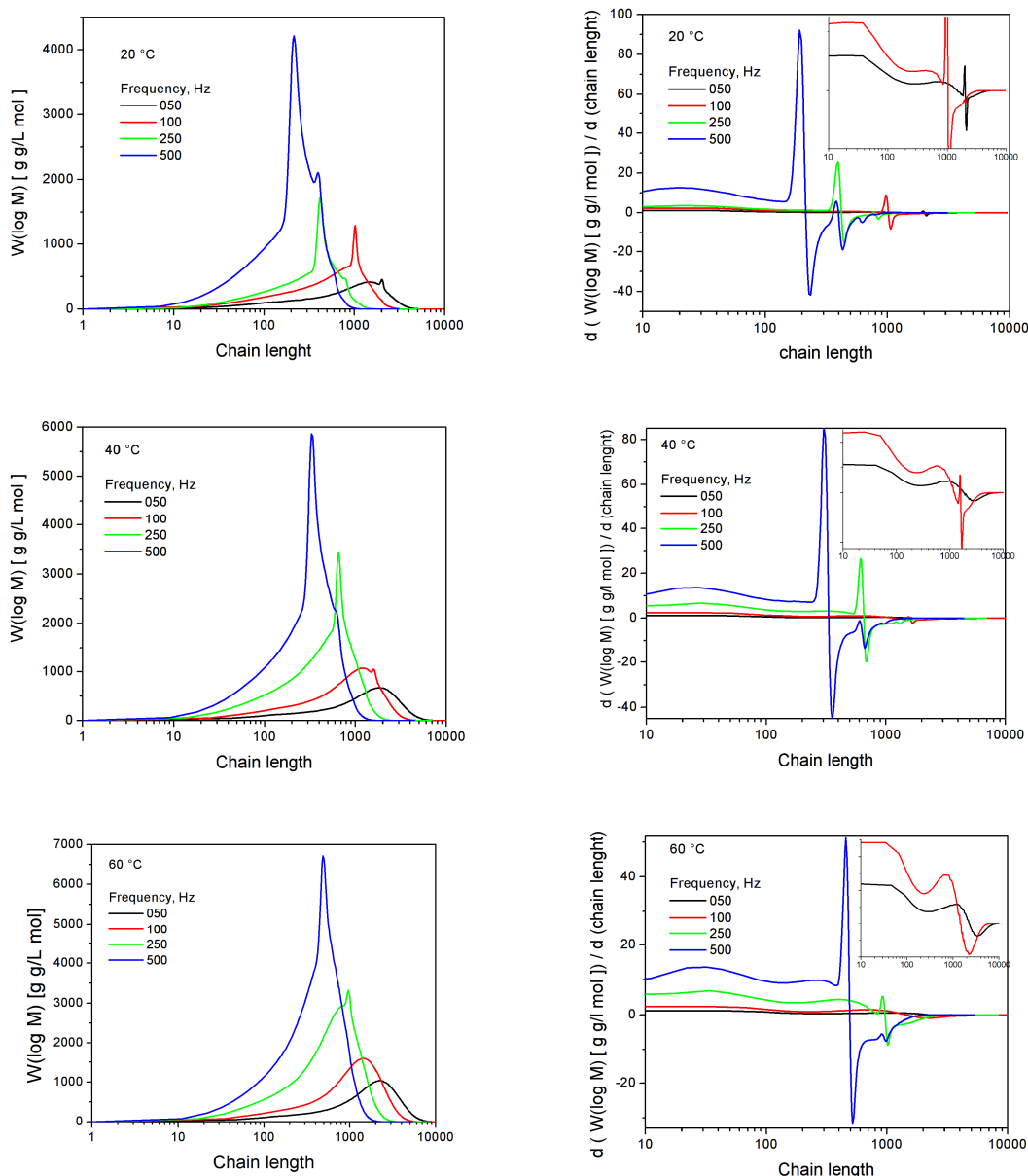

Figure 1. (**left**) Final size exclusion chromatography-chain length distributions (SEC-CLDs), and (**right**) the correspondent derivatives of the polymer chains for different temperatures and laser frequencies. Take into account that the conversion is not the same in each experiment, leading to different area under the curve.

The most relevant information presented in Figure 1 is summarized in Table 1. The chain lengths reported in this table were obtained by reading the maximum of each peak in the derivative of the SEC-CLD (if observable); the first peak is the one at the shortest chain length. In the same table, the k_p was calculated by using the chain length of each peak (k_{p1} corresponds to the peak L_1, and so on) and Equation (1). The concentration of monomer was 7 moL L^{-1}. The last column of Table 1 reports the k_p used as an input in the simulation at the given temperature (calculated with Arrhenius' parameters of Table S1). In all cases, the error between the calculated value of k_p using the data reported in Table 1, along with Equation (1), and the k_p calculated through Arrhenius' parameters was less than 7%. Additionally, the ratio k_{pi}/k_{pi+1} was rather close to 1 in all cases.

Table 1. Chain lengths at which the chain length distribution (CLD) shows critical points, L_i, determined at the maximum of the derivatives of the CLD of Figure 1. k_{pi} calculated with this information and Equation (1) and k_p the input at the given temperature.

T, °C	F, Hz	t_d, s	L_1	L_2	L_3	k_{p1}, L moL^{-1} s^{-1}	k_{p2}, L moL^{-1} s^{-1}	k_{p3}, L moL^{-1} s^{-1}	k_p, L moL^{-1} s^{-1}
20	50	0.020	1968	—	—	14,000	—-	——	14,200
20	100	0.010	971	1942	—	13,800	13,800	——	——
20	250	0.004	395	779	1163	14,100	13,900	13,800	——
20	500	0.002	191	382	573	13,600	13,600	13,600	——
40	50	0.020	—	—	—	—-	—-	——	22,800
40	100	0.010	1542	—	—	22,000	——	——	——
40	250	0.004	612	1223	—	21,800	21,800	——	——
40	500	0.002	303	606	917	21,600	21,600	21,800	——
60	50	0.020	—	—	—	—-	—-	——	34,400
60	100	0.010	—	—	—	—-	—-	——	——
60	250	0.004	932	—	—	33,200	—-	——	——
60	500	0.002	457	903	—	32,600	32,200	——	——

Figure 2 shows the degree of branching, which was calculated as the cumulative fraction of polymerized acrylic units that have a quaternary carbon for different temperatures and laser frequencies. The quaternary carbons are mainly formed by the MCR propagation (termination by combination also contributes to the formation of quaternary carbons). It is worth mentioning that in order to separate the effect of the patching reaction from the branching level, the quaternary carbons created in the patching reaction were not considered in the degree of branching. In all cases, once the polymerization begins, the degree of branching increases and, after some time, a plateau with positive slope is observed. The degree of branching increases as the temperature becomes higher, which is a reasonable result due to the higher activation energy of the backbiting reaction compared to propagation of the chain-end radicals. By a totally different simulation approach of the PLP of BA at 500 Hz (kinetic Monte Carlo), it has been determined that the degree of branching reaches a value of 0.14% at 32.85 °C and 0.21% at 51.85 °C after 100 pulses [32]. At 51.85 °C and monomer concentration of 6.76 moL L^{-1}, the simulation used in this work reached 0.18% after 1 s, showing a good agreement between both simulation approaches. The differences between both simulation approaches were due to the different kinetic scheme used in the kinetic Monte Carlo simulations (two types of initiator radicals and time dependent initiator concentration). As observed in Figure 2, although slightly lower values of the degree of branching were calculated as the laser frequency increased at constant temperature, there was not a significant decrease of the degree of branching at a fixed temperature. At 20 °C, degree of branching was between 0.10 and 0.08% at 50 and 500 Hz, respectively; at 60 °C, the variation was between 0.22 and 0.21% at 50 and 500 Hz, respectively. From these results, it can be concluded that the degree of branching at a constant temperature does not depend on the laser frequency. In the same figure, for each temperature, the instantaneous probability of backbiting, calculated by $k_{bb}/(k_p[M] + k_{bb})$, is plotted as a solid line, where $[M]$ is the monomer concentration. The ratio of backbiting events to the total propagation events obtained during the simulations at 500 Hz was plotted as a dashed gray line (both values were

multiplied by a factor of 100). The instantaneous probability of backbiting under the quasi-steady-state conditions is related to the degree of branching, that is why these calculations were plotted in the same figure. As observed, the degree of branching has approached the instantaneous probability of backbiting at 500 Hz, but within the simulation time they never touched each other; the same behavior was observed with the kinetic Monte Carlo simulation [32]. Regarding these results, the reason for such a difference is that an MCR can terminate with the radicals generated in the laser pulse; the faster the laser pulse, the larger the MCRs that are terminated by this reaction, as discussed below.
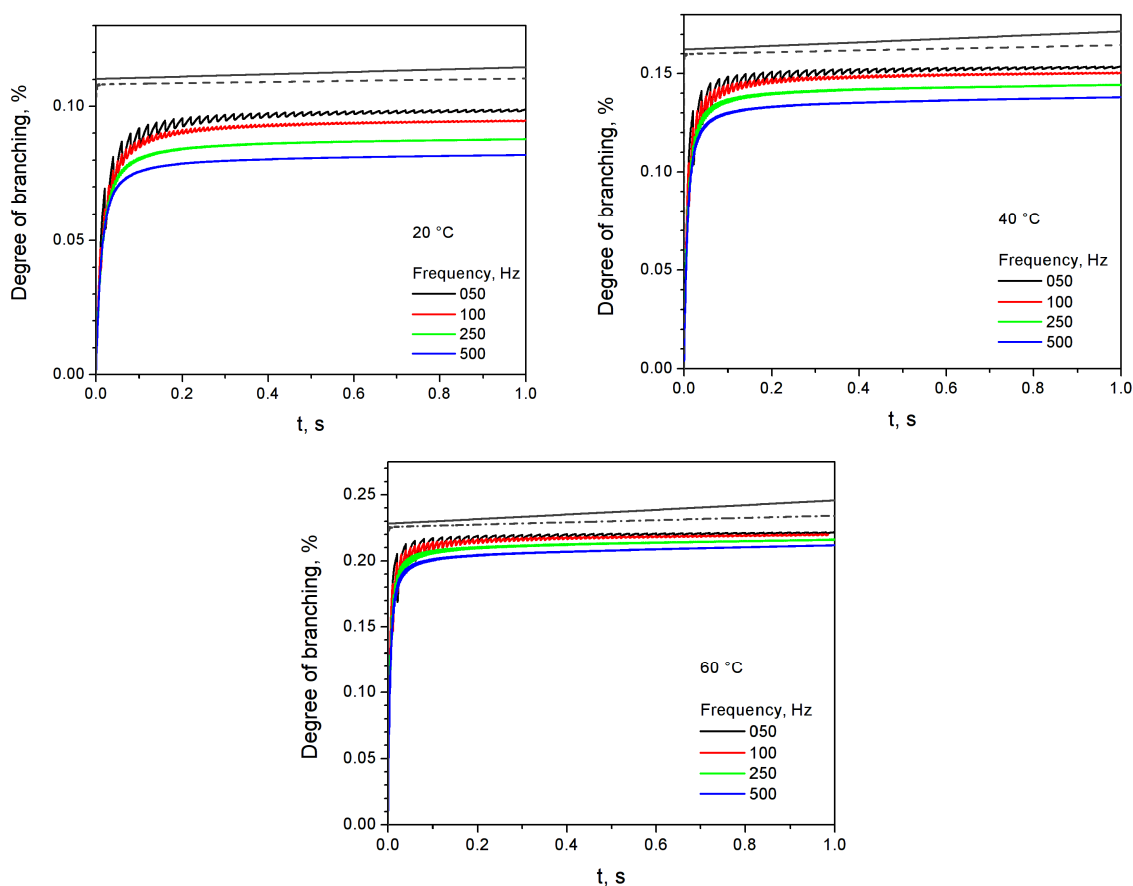
Figure 2. Degree of branching as a function time obtained during the simulation at different temperature and laser frequencies. The solid gray line is the instantaneous probability of backbiting and the dashed line is the ratio of the backbiting events to the total propagation events during the simulation; both calculations multiplied by a factor of 100.

Additionally to MCR's propagation and (cross) termination with another polymeric radical, it might be possible for an MCR to react with the radicals generated during the laser pulse (see Kinetic Scheme S1). It is worth mentioning that in the simulations, initiation rate coefficient was assumed equal to the propagation rate coefficient. Therefore, the difference between the calculated degree of branching in the simulations and the instantaneous probability of backbiting could be explained by the fraction of MCRs that react with the radicals generated in the pulse, giving place to patched MCRs. As the laser frequency increases, the number of radicals at the same interval of time also increases, leading to a larger fraction of patched MCRs. Figure 3 shows the percentage of patched MCRs at different temperatures and laser frequencies. As explained above, it can be seen that increasing laser frequency leads to a larger fraction of patched MCRs. On the other hand, the fraction of patched MCRs decreases by increasing temperature.
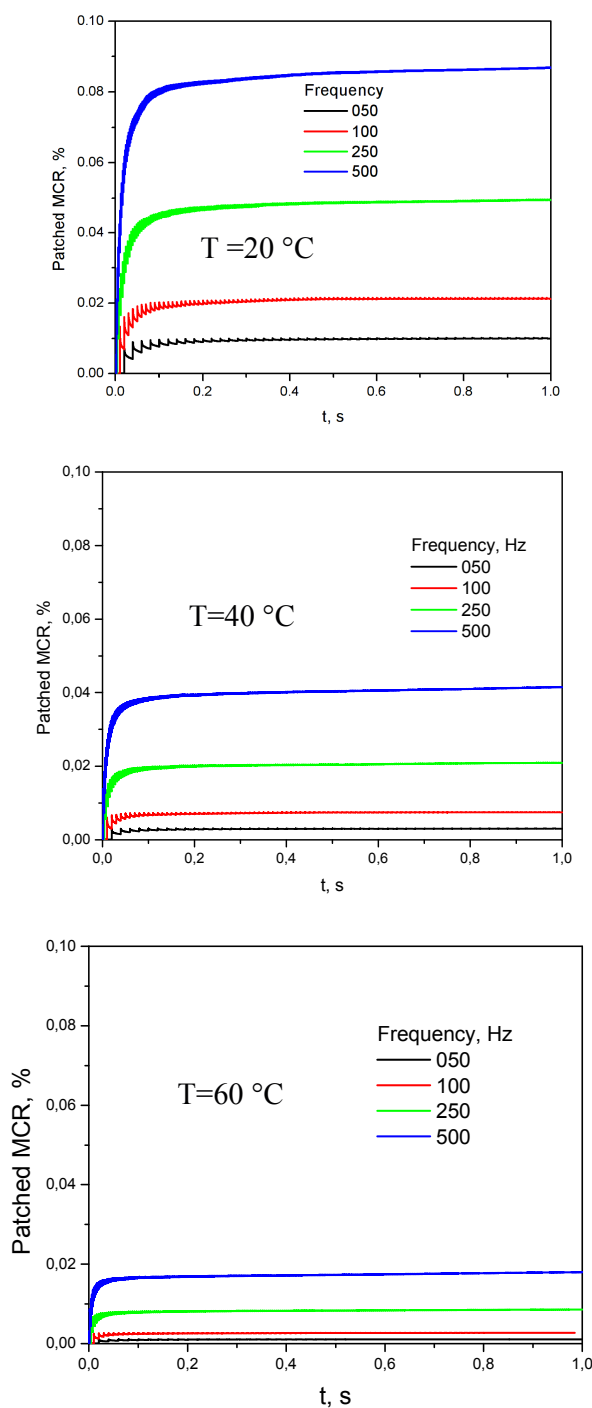
Figure 3. Percentage of mid-chain radicals (MCRs) that are patched by the radicals generated in the laser pulse.

As it was shown in Figure 2, increasing the laser frequency does not significantly change the degree of branching at a constant temperature, and the slight difference can be explained by patching of the MCRs as discussed above. However, the PLP-CLD is recovered by increasing the laser pulse frequency. Nikitin et al. claimed that there is a minimum fraction of chain-end radicals, with respect to total radical concentration, at a constant temperature and time that still allows the observation of the peaks in the CLD [7]. This fraction is proportional to the $\exp(-k_{bb}/f)$, where f is the laser frequency. They also showed that this minimum fraction is independent of polymerization conditions at constant temperature. As a consequence, if the reaction temperature increases, the backbiting rate coefficient

will also increase and, therefore, to have a significant fraction of secondary radicals that do not undergo backbiting the laser frequency should increase.

It is worth mentioning here that all the simulations have the same duration (1 s) and monomer concentration. Thus, the number of polymer chains is lower at low frequencies than at high ones. On the other hand, the ratio of backbiting events to propagation is nearly independent of the laser frequency. Therefore, at low laser frequency a larger fraction of chains undergoes backbiting, creating MCRs that could distort the CLD by breaking the time correlation of Equation (1) due to the stability of the MCRs. When the number of polymer chains increases (as in a high frequency experiment with the same duration), nearly the same number of backbiting to propagation events takes place, but affecting a relatively lower fraction of chains; therefore, the PLP-MMD is recovered. This is supported by the results presented in Figure 4, in which the zeroth moment of the chain-end radical species, or the concentration of the chain-end radicals and MCRs, for 20 and 60 °C and different laser frequencies is shown. In this figure, the concentration of each radical is divided by the concentration of radicals generated in each laser pulse (10^{-5} moL L^{-1}). At 20 °C and 50 Hz, immediately after the laser pulse, the concentration of the chain-end radicals starts to decay during the dark period as they mainly undergo termination reaction. Moreover, a fraction of them undergoes backbiting reaction; the concentration of MCRs increases, and then decreases in the last part of the dark period. Towards the end of the dark period, the concentration of MCRs is greater than that of the chain-end radicals. Nevertheless, since some chains did not undergo backbiting during the dark period, they could be terminated in the next laser pulse, leading to a peak in the SEC-CLD. Increasing the laser frequency to 100 Hz leads to a greater concentration of both types of radicals because, in this case, the dark period has half the duration of the previous simulation. Thus, it can be seen that concentration of chain-end radicals is greater, leading to a well-defined peak in the SEC-CLD. It is true that the MCRs are also in greater number but affecting a relatively lower fraction of chains. At 250 Hz, although the concentration of chain-end radicals decreases during the dark period, the next laser pulse hits the reacting mixture when the concentration of chain-end is enough to produce a PLP-CLD of the polymer chains. Again, because there are more radicals, the MCR concentration also increases, but it seems not to affect a significant fraction of chains. With the highest frequency, the concentration of chain-end is even greater, resulting in a higher concentration of MCRs. For this case, such concentration of chain-end radicals leads to a well-structured PLP-CLD. As the laser frequency increases, the fraction of chain-end radicals close to the next laser pulse also increases. At 60 °C, the behavior is rather similar to the previous description; however, as the temperature is higher, a larger fraction of MCRs is present [26]. Nevertheless, as the dark period diminishes and before the next laser pulse hits the sample, a larger fraction of chain-end radicals is present, leading to the recovery of the PLP-CLD.

Additional information that can be extracted from the simulation is the CLD of chain-end radicals, which of course is not obtained by experimental procedures. The results are presented in Figure 5, which show the final SEC-CLD of the chain-end radicals (at 1 s of integration time, before the last laser pulse is applied). It is worth mentioning that it is a cumulative distribution that contains the information of all of the chain-end radicals that were generated at different times during the reaction, and some of the chains might have multiple branching points. For example, at 20 °C, it is observed that increasing the laser frequency leads to the formation of peaks in the SEC-CLD of the chain-end radicals. As the frequency increases, a multimodal CLD is obtained, i.e., some of the chain-end radicals can grow by more than one dark period. These chains would terminate among them or, preferentially, with the radicals generated in the next laser pulse, leading to a well-defined PLP-CLD of the polymer. By increasing the temperature to 40 °C, the multimodal SEC-CLD of the growing chain-end radicals is obtained with frequencies greater than 250 Hz. Because more chain-end radicals undergo backbiting, it is necessary to have enough chains that are not affected by such reaction to recover the PLP-CLD. Increasing the frequency to 500 Hz leads to well-defined peaks in the CLD, because the accumulation of unaffected chain-end radicals is greater. The same behavior is observed at 60 °C, but in this temperature, the multimodality (actually, bimodality) of the CLD is presented only at

500 Hz, in which the accumulation of growing chain-end radicals that are not affected by backbiting is enough to recover the PLP-CLD of the final polymer.
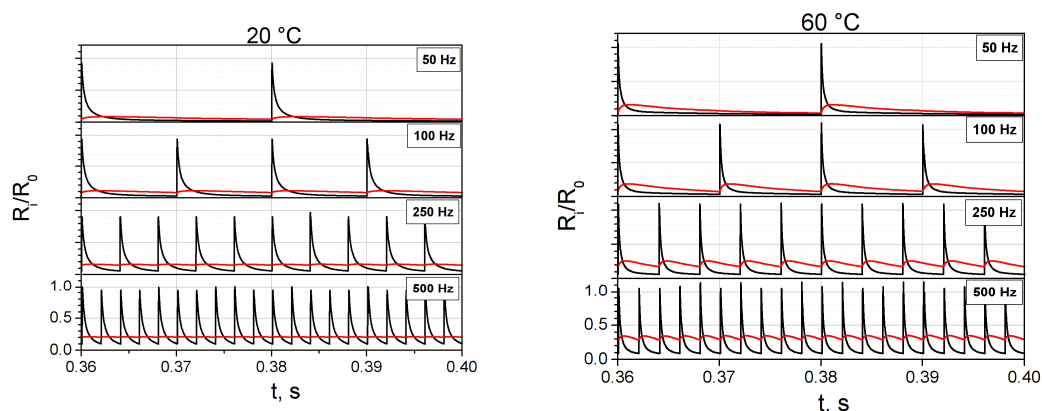

Figure 4. Ratio of the concentration of the radicals i (i: Chain-end radicals in black and MCRs in red), divided by the concentration of the radicals generated in the laser pulse. $[R_0] = 10^{-5}$ moL L^{-1}.

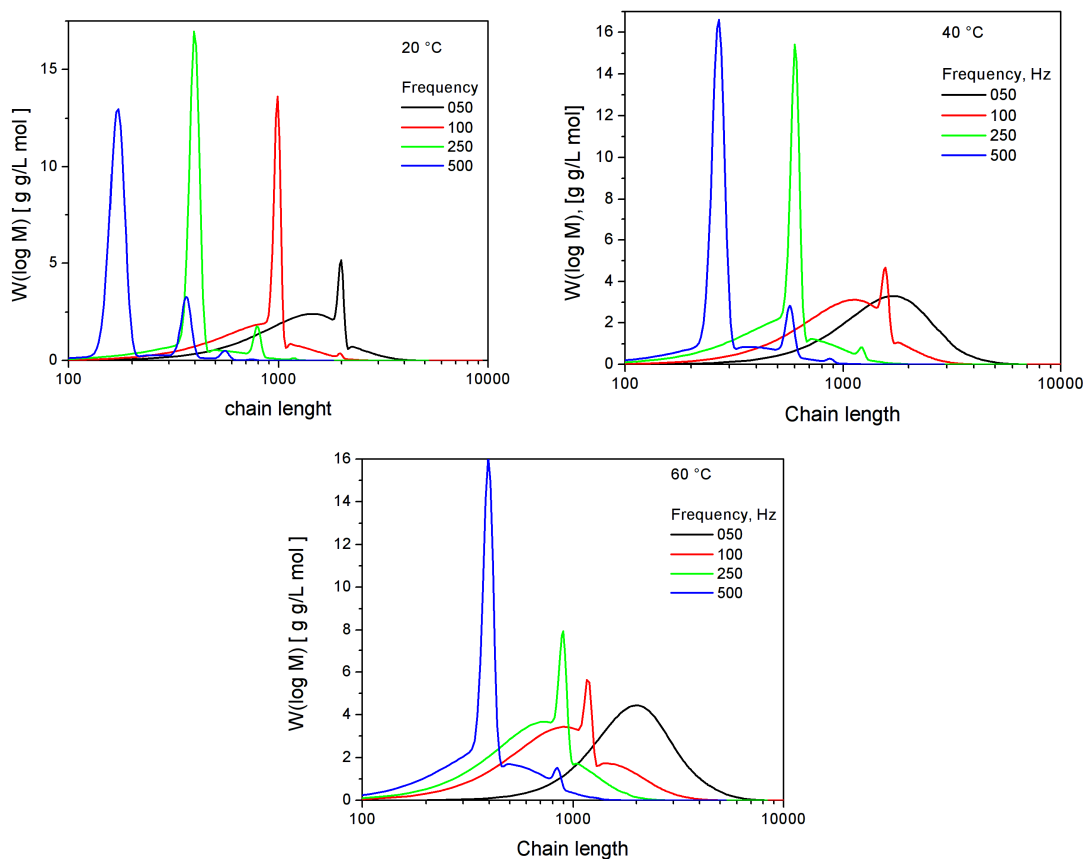**Figure 5.** Final SEC-CLD of the chain-end radicals at different temperatures and laser frequencies.

The last part of the results is shown in Figure 6. This figure summarizes the results at 20 °C for laser frequencies of 100 and 500 Hz, but the radical concentration produced in the laser pulse $[R_0]$ is changing. In all cases, a PLP-CLD is obtained, meeting the IUPAC criteria for a good k_p determination (more than one peak in the CLD and its derivative, and k_{pi}/k_{pi+1} close to 1). Moreover, the deviation with respect to the k_p used as input at 500 Hz and $[R_0] = 1 \times 10^{-4}$ moL L^{-1} is around 15%; at 100 Hz and the same $[R_0]$, the deviation is around 7%. In the other cases, such deviation is smaller, with the smallest being at $[R_0] = 1 \times 10^{-6}$ moL L^{-1} and 500 Hz. Actually, many peaks can be seen at the CLD and

its derivative. These results are in agreement with the simulation results of Nikitin et al. [7], in which they demonstrated that at a minimum laser frequency and constant temperature, there is sufficient population of chain-end radicals to produce sharp peak(s) in the CLD, that is indeed independent of $[R_0]$. Also, in the CLD obtained with the largest concentration of radicals, $[R_0] = 1 \times 10^{-4}$ moL L^{-1}, one can see the formation of polymer chains with low molecular mass. The concentration of chains with such low molar mass decreases as $[R_0]$ becomes lower. The reason is that due to the high concentration of growing radicals (chain-end and MCR), the cross termination of these radicals is enhanced during the dark period, still having a fraction of radicals that are terminated at the next laser pulse.
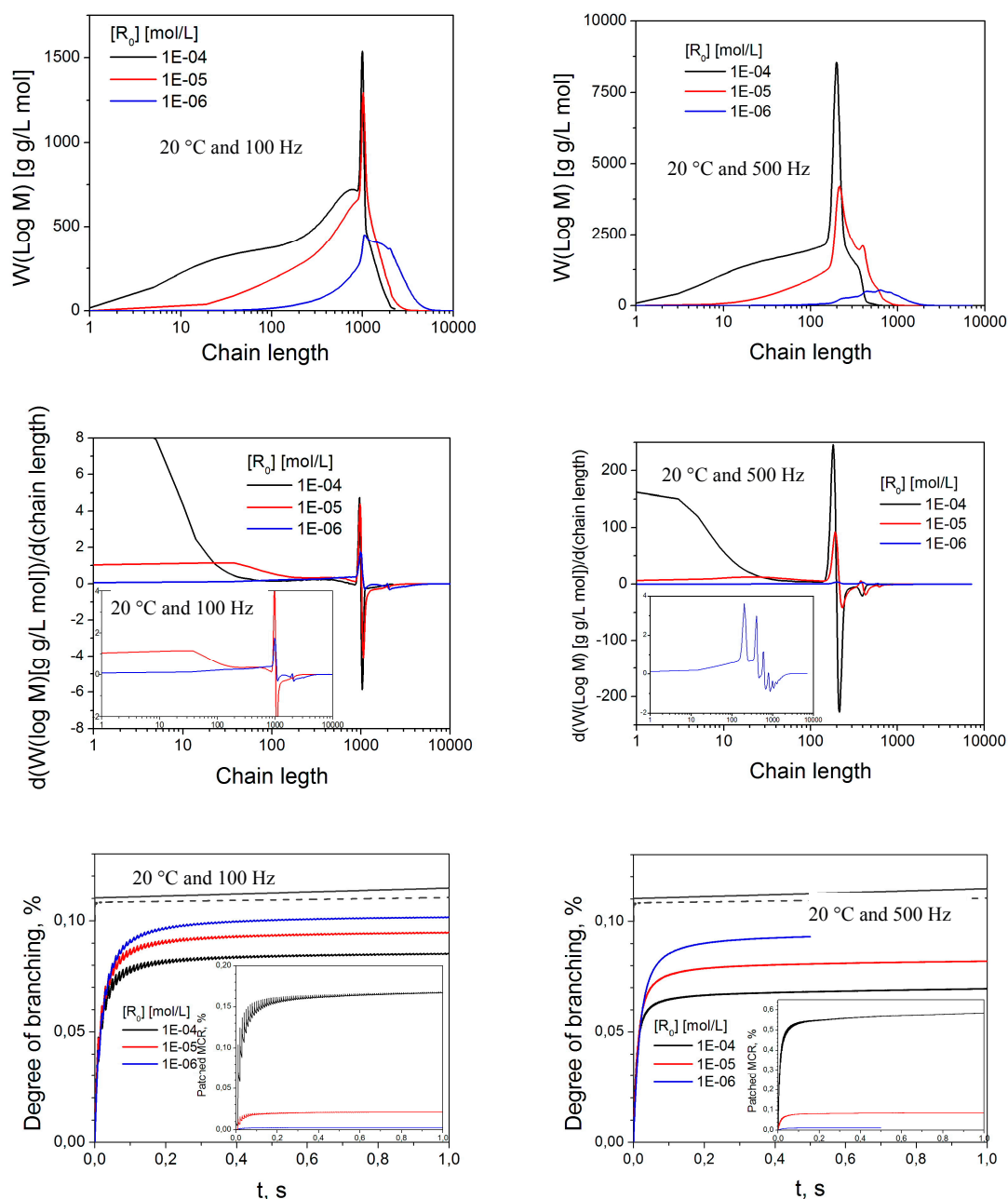

Figure 6. Effect of $[R_0]$ on different parameters. Left side column is at 20 °C and 100 Hz, whereas left side is at 20 °C and 500 Hz. First row, final SEC-CLDs; second row, the correspondent derivatives; third row, the degree of branching (and patched MCR in the inset) at 20 °C, 100 Hz (left side column) and 500 Hz (right side column). At 500 Hz and $[R_0] = 1 \times 10^{-6}$ mol L^{-1}, the simulation was stopped at 0.5 s due to computer memory limitations. Inserts in each graph is a zoom in a desired area.

Regarding the backbiting-to-propagation ratio, the results show that this ratio is not significantly affected. However, the degree of branching decreases as [R_0] increases. Such a decrease is larger at high laser frequency of 500 Hz. In this case, the reduction of the degree of branching is due to the larger fraction of pathed MCR as [R_0] increases. From these results, in order to have reliable k_p determinations, it could be recommended to produce a low concentration of radicals in the laser pulse (by lowering the laser power and/or using a low initiator concentration), but having in mind the necessity of producing enough polymer chains for an adequate SEC measurement.

4. Conclusions

PLP-SEC experiments of *n*-butyl acrylate were simulated at different temperatures, laser frequencies, and radical concentrations produced at laser pulses. At all temperatures, the PLP-CLD was recovered as the laser frequency increased. It was shown that the recovery of PLP-CLD by increasing laser frequency is a consequence of increasing the fraction of chain-end radicals that does not undergo backbiting, which is in line with the explanation given by Nikitin et al. [7]; therefore, the degree of branching does not significantly decrease as the laser frequency increases at a fixed temperature. According to the simulation results, the ratio of backbiting to propagation reaction was not affected by the increment of the laser frequency; the ratio of quaternary carbons to the total propagation steps was rather close to the instantaneous degree of branching in all conditions. These results did not give support to other explanations given in the literature, which related the recovery of the PLP-MMD only with the decrease in the backbiting rate and, consequently, the decrease of branching density. The difference between the degree of branching with respect to the instantaneous probability of backbiting was explained by the patching of MCRs (termination reaction of the MCRs with the radicals generated in the laser pulse). By increasing laser frequency or the radical concentration at laser pulses, the patched MCRs' percentage increased, which consequently led to a lower degree of branching.

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