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Long-Lived Radicals in the Postpolymerization of Methacrylic Monomers at Low Conversions

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ABSTRACT: The bulk radical polymerization of three methacrylic monomers, butyl, dodecyl, and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate, were studied in the dark period after previous illumination by ultraviolet light at $\lambda = 365$ nm. An important postpolymerization process took place in all the polymerization reactions. This indicates that, even at low monomer conversions, a certain and nonnegligible radical concentration remains after switching off radical production. Monomer concentration measurements by FT-IR spectroscopy in the dark period showed that long-lived radicals continued the polymerization up to conversions that, in some cases, were higher than 70%. The half-lifetimes of these macroradicals ranged from 300 to 14000 s. Kinetic expressions were developed to determine the fraction of living and dead polymer during the course of the postpolymerization. The SEC traces of the resulting polymers showed bimodal molecular weight distributions and extremely high-molecular-weight polymers obtained in the post-effect period. By means of both kinetic results and molecular weight distribution, the values of the radical concentration in the dark period, the average termination rate coefficient of the macroradicals, and the transfer constant to the monomer were determined for the different polymerizations reactions carried out.

Introduction

One of the most important tasks in free radical polymerization (FRP) is the accurate determination of the propagation (k_p) and termination (k_t) rate coefficients involved in these reactions, as both coefficients control the reaction kinetics and the final polymer properties.

In this sense, obtaining reliable k_p values seemed to be feasible by means of electronic paramagnetic resonance (EPR) or the IUPAC-recommended pulsed-laser polymerization in conjunction with size-exclusion chromatography (PLP-SEC) technique,[1,2] taking into account some previous recommendations to avoid uncertainties in the resulting values. However, the picture has become more complex because of the introduction of the nonobvious but experimentally observed chain-length dependency on k_p. This dependency, which was first proposed by Hayden and Melville,[3] has come to be one of the most controversial FRP topics.[4−7]

On the other hand, the influence of chain length on k_t is generally assumed. Nowadays, the termination reaction is accepted to be diffusion controlled even from the first stages of the polymerization reaction. The diffusion mechanisms involved in polymerization are translational diffusion of the mass center and segmental diffusion. Because of these diffusive processes, the chain length of the growing macroradicals has a strong influence on k_t, and therefore, in principle, it is only possible to determine an average value of this magnitude for conventional steady-state FRP experiments. Many theoretical and experimental researchers have studied this influence by developing new models and experiments that express quantitatively the effects of conversion and chain length on k_t.[8−13]

The shortcomings to studying radical reactivity arise from radical instability and chain-length inhomogeneity of the radicals involved in polymerization reactions. This precludes an appropriate determination of characteristic k_t values corresponding to the reaction between radicals of similar chain length. One way to carry out this study would be the determination of the termination rate coefficients between long-lived radicals. In this sense, long-lived propagating radicals were observed for reactions at high conversion or cross-linked media, where bimolecular termination of polymer radicals is depressed[14] and also for photopolymerization of certain monomers in the gel formed by hydroxystearic acid.[15] In the last case, postpolymerization in the dark of di-2-ethylhexyl itaconate was observed, and the resulting polymers had bimodal molecular weight distributions due to the generation of low-molecular-weight polymer during the photoinduced polymerization and high-molecular-weight polymer during the postpolymerization in the dark.

Karatekin, O'Shaughnessy and Turro[16] theoretically analyzed a reacting radical−macroradical system to determine the exponents for the universal scaling laws for sufficiently high polymerization degrees, which had earlier been predicted by different theories.[17−19] They proposed a polymerization experiment in which short radicals and macroradicals would be simultaneously generated. After a certain time, the short radicals disappear, and by measuring the surviving macroradicals lifetime, it would be possible to determine the exponent in the scaling law that relates k_t and chain length.

Taking into account the aforementioned considerations, in polymerization reactions in which long chain macromolecules are obtained, a certain quantity of radicals with a long average lifetime should exist.

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Therefore, polymerization should proceed in the absence of a source of radicals that initiate the reaction. Thus, very high-molecular-weight polymers can be prepared by conventionally creating a sufficient amount of radicals and then leaving the persistent radicals to continue the reaction.

The aim of our work is to perform an experimental approximation to the ideal scenario proposed by Karatekin et al.[16] We have studied the polymerization of three methacrylic monomers with different average termination rate coefficients: butyl methacrylate (BMA), dodecyl methacrylate (DMA), and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS). After initiating the reaction during different illumination times using 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), the monomer concentration in the dark was monitored by FT-IR. The conversion-time curves in the dark led to determining the k_t values for the reactions in which only macroradicals of approximately the same chain length are involved. Moreover, another goal of the present work is the determination of the transfer constant to the monomer using two different strategies, the chain-length distribution (CLD) method, and by considering only the number-average molecular weights of the macromolecules grown in the dark period.

This work constitutes the first stage of a more extensive research leading to quantitatively evaluating the influence of chain length on termination rate coefficients for different polymerization reactions.

Experimental Section

Materials. Methacrylic monomers, butyl (BMA, Fluka, 99%), dodecyl (DMA, Fluka, 97%) and 3-[tris(trimethylsilyloxy)silyl] propyl (TRIS, Aldrich, 98%), were distilled under high vacuum before use. The photoinitiator, 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich, 99%), was used as received.

Polymerization Reactions. Monomer solutions (5 mL) with different DMPA concentrations of 3×10^{-2} mol·L^{-1} (3.8×10^{-2} gr in 5 mL) and 7×10^{-3} mol·L^{-1} (9×10^{-3} gr in 5 mL) were prepared. The solutions were subjected to several freeze–pump out–thaw cycles to remove dissolved oxygen. The degassed solution (0.8 mL) was placed in a closed temperature-controlled optical cell (path length 0.5 mm) at 25 °C. The photopolymerization of the reaction mixture was performed inside an ultraviolet cross-linker (UPV, model CL-1000L) operating at $\lambda = 365$ nm. The times of exposure to UV light ranged between 30 and 240 s, depending on the monomer, the initiator concentration, and the desired conversion. Thus, the conversion for BMA ([DMPA] = 7×10^{-3} mol·L^{-1}) after 240 s of exposure was 11% and for DMA ([DMPA] = 7×10^{-3} mol·L^{-1}) after 60 s of exposure was 10%. The monomer concentration was monitored by FT-IR spectroscopy (Spectrum One, Perkin-Elmer) in the region of the first overtone of C–H stretching vibrations, at around 6170 cm^{-1}. The first spectrum after UV light exposure, that gave the initial monomer conversion, was recorded in all the reactions 1 min after the illumination period. The sample was kept inside the IR cavity during the dark period, and the monomer concentration was sequentially registered. After a certain conversion was reached, the resulting polymer was precipitated in methanol containing traces of hydroquinone to prevent further polymerization and was isolated prior to SEC analysis.

Additional experiments at 25 °C with monomer solutions at DMPA concentration of 3×10^{-2} mol·L^{-1} were carried out to estimate the radical concentration during the illumination period. The monomer–initiator mixture in the optical cell was subjected to successive illumination periods, and monomer concentration was registered after each one.

Pulsed Laser Initiated Polymerizations. The k_p values for BMA, DMA, and TRIS were measured using the pulsed laser polymerization technique, pioneered by Olaj et al.[20] A series of pulsed laser initiated bulk polymerizations was carried out at 25 °C in a closed temperature-controlled optical cell (path length 0.5 mm). Solutions of monomer (5 mL), with DMPA concentrations ranging between 2.4×10^{-2} and 6×10^{-3} mol·L^{-1} (3.0×10^{-2} gr and 7.7×10^{-3} gr in 5 mL), were prepared. DMPA decomposition was induced by laser pulses (Spectra Physics) at 351 nm with pulse repetition time, t_0, of 0.3 s. The samples were subjected to laser pulsing for a period of time sufficient to convert around 3% of the monomer into polymer (in the case of BMA, [DMPA] = 9×10^{-3} mol·L^{-1}, after pulsing for 3 min, the conversion was 2%). Monomer conversion was monitored by FT-IR spectroscopy. 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. Molecular weight distributions (MWD) were determined by means of size-exclusion chromatography using a Waters 1515 HPLC pump, 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 THF at 35 °C, pumped at 1 mL·min^{-1}. The SEC setup was calibrated against polystyrene (PS) standards of narrow polydispersity (MW = 580 to 5×10^6 g·mol^{-1}, Polymer Standards). Absolute molecular weights of the polymer samples were estimated via the principle of universal calibration[21] using the Mark–Houwink parameters $K = 11.4 \times 10^{-5}$ dL·g^{-1}, $\alpha = 0.716$ for PS, $K = 14.8 \times 10^{-5}$ dL·g^{-1}, and $\alpha = 0.664$ for poly(BMA), $K = 5.18 \times 10^{-5}$ dL·g^{-1}, $\alpha = 0.720$ for poly(DMA), and $K = 1.67 \times 10^{-5}$ dL·g^{-1}, $\alpha = 0.740$ for poly(TRIS) taken from the literature.[22,23]

Electron Paramagnetic Resonance Measurements. Measurements of the radical concentration during the post-polymerization by electron paramagnetic resonance (EPR) were attempted. The polymerization reactions were carried out in 3-mm diameter quartz tubes, reproducing the same conditions as used for the reactions monitorized by FT-IR spectroscopy. The same monomer–initiator solutions were exposed to UV light at 25 °C for identical times as described for the polymerization reactions. The spectra were recorded by using a Bruker ESP 300 spectrometer. To register the spectra, the conditions were: microwave frequency, 9.5 Ghz; modulation frequency, 100 kHz; modulation amplitude, 3 G; conversion time, 40 ms; time constant, 655 ms; sweep time, 42 s; power, 6.32 mW; receiver gain 3×10^5; scan number, 20.

Results and Discussion

Determination of the Propagation Rate Coefficient. A previous determination of k_p values for the monomers studied in this work under the same reaction conditions is necessary to undertake a further kinetic analysis of the polymerization reactions. These values could have been taken from the literature, but an experimental determination was considered to be more convenient. The PLP-SEC technique was used for this purpose, and by applying this technique,[20] the propagation rate coefficient was derived according to eq 1,

$$L_1 = k_p \cdot c_M \cdot t_0 \tag{1}$$

where L_1 and t_0 denote the number of propagation steps and the time interval between two successive laser pulses, respectively, and cM is the monomer concentration. L_1 is generally calculated from the position of the first inflection point of the MWD. The first derivative curves of the MWDs for BMA, DMA, and TRIS polymerization at 25 °C are depicted in Figure 1. The inflection points are located at molecular weights that fulfill the PLP-SEC consistency criteria.[20] According to eq 1, propagation rate coefficients were calculated from the molecular weights $M_1 = L_1 \cdot M_0$ (where M_0 is the monomer molecular weight) at the position of the first

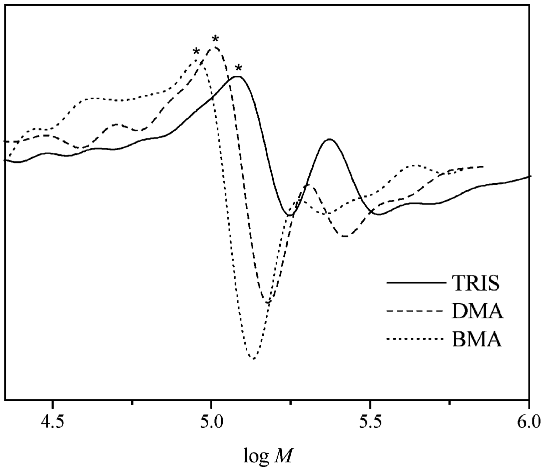

Figure 1. First derivative curves, d(w(log M)/d(log M), of MWDs obtained for pulsed-laser-initiated bulk polymerizations of butyl methacrylate (BMA), dodecyl methacrylate (DMA), and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS). Pulse time interval was always 0.3 s and temperature was 25 °C. The asterisks point out the first inflection points that were used to calculate the k_p values by eq 1.

inflection point, which are pointed out as asterisks in Figure 1. The k_p values obtained for bulk polymerizations of BMA, DMA, and TRIS are gathered in Table 1, and for comparison, k_p values from literature are also included in this table. Our k_p values agree fairly well with literature data for TRIS and BMA polymerizations at 25 °C.[23,24] In the case of DMA, critically evaluated k_p values for this monomer[24] are higher than those obtained in this work. A careful revision of literature data reveals that, for DMA,[24] k_p values were derived from PLP experiments at t_0 values, which were significantly lower than those used in our experiments, whereas for BMA[24] and TRIS,[23] the differences in the applied t_0 are not so pronounced (the range of applied t_0 for literature data is listed in Table 1). The problems associated with the broadening in SEC traces for PLP experiments at high t_0 are well-known, and the discrepancy with literature data might be attributed to this fact. However, it goes without saying that the t_0 values used for PLP experiments are directly related to the chain length reached by the resulting polymer, in such a way that the higher the t_0, the larger the polymer chain length. Therefore, a chain-length dependency of k_p cannot be ruled out, but the discussion of this event is beyond of the scope of this work.

Kinetics During the Photoinduced Polymerization. The stationary radical concentration, $[R]_{ph}$, during the photoinduced FRP can be estimated by plotting the changes in monomer concentration with illumination time according to eq 2, given that k_p is known

$$\ln\frac{[M]_{0,ph}}{[M]_{ph}} = k_p[R]_{ph}t \tag{2}$$

where $[M]_{0,ph}$ and $[M]_{ph}$ are the initial and instantaneous monomer concentrations during the photoinduced polymerization period, respectively. The conversion-time data for bulk photopolymerizations of BMA, DMA, and TRIS at the same temperature and initiator concentration are plotted in Figure 2.

Table 1. Propagation Rate Coefficients, k_p, Derived from PLP–SEC Experiments at 25 °C (t_0 = 0.3 s) for Butyl Methacrylate (BMA), Dodecyl Methacrylate (DMA), and 3-[Tris(trimethylsilyloxy)Silyl] Propyl Methacrylate (TRIS)[a]

monomer	k_p/ (L·mol^{-1}·s^{-1})	$k_{p\ (literature)}$[b]/ (L·mol^{-1}·s^{-1})	$t_{0\ (literature)}$[c]/ (s)	ref
BMA	334	367	0.040–0.4	24
DMA	392	515	0.037–0.222	24
TRIS	433	460	0.1–1.0	25

[a] The resulting values are the average of three experiments (standard deviation was less than 10%). [b] Benchmark k_p values from literature. [c] Range of applied t_0 for literature k_p values.

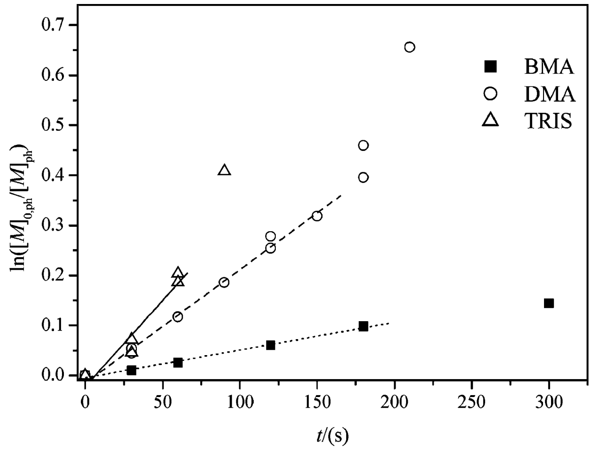

Figure 2. Conversion-time curves for butyl methacrylate (BMA), dodecyl methacrylate (DMA), and3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS) photoinitiated polymerizations at 25 °C and DMPA concentration of 3 × 10^{-2} mol·L^{-1}. Straight lines are linear fits for the steady-state region.

In Figure 2, it is possible to distinguish for all the monomers a defined steady-state region, during which radical concentration is constant, and therefore, eq 2 can be applied. $[R]_{ph}$ is directly obtained from the slopes of the straight lines drawn in Figure 2 for the steady-state region. The resulting values for $[R]_{ph}$ are listed in Table 2. These values, which are in agreement with those found for photoinitiated polymerizations under similar reaction conditions,[12] are higher for TRIS and DMA than for BMA. This trend is explained by a higher k_t value for BMA than for DMA and TRIS under steady-state conditions.

Postpolymerization in the Dark. In the postpolymerization experiments performed in this work, the changes with time of the monomer concentration in the dark are measured after the steady-state is interrupted by switching off the primary radical production. The kinetics of the three monomers at different initial conversions during the illumination period are shown in Figures 3–5. The kinetic curves reveal that the monomer conversion in the dark time is considerably high, even at very low initial polymer concentration (less than 5%). This indicates that the concentration of radicals that survive after switching off the light is low but significant. TRIS exhibits the highest conversions at the postpolymerization process. As an example, Figure 6 shows the postpolymerization of TRIS after interrupting the illumination at an initial conversion of 10%. The monomer consumption proceeds in the dark up to 53% of conversion at a reaction time of 63000 s. After that, a sharp increase in the polymerization rate is observed, probably because of the size reached by the macroradical chain length and the high viscosity of the reaction medium.

From the slopes of the kinetic curves at t = 0, it is derived that TRIS and DMA exhibit higher polymeri-

Table 2. Experimental Information and Results for the Polymerization Experiments of Butyl Methacrylate (BMA), Dodecyl Methacrylate (DMA), and 3-[Tris(trimethylsilyloxy)Silyl] Propyl Methacrylate (TRIS) during Photopolymerization and Postpolymerization Times

monomer	[DMPA]/ $(\mathrm{mol{\cdot}L^{-1}})$	x_{ph}[a]	x_{dark}[b]	$10^6\,[R]_{\mathrm{ph}}$[c]/ $(\mathrm{mol{\cdot}L^{-1}})$	$k_p/\langle k_t\rangle$	$\langle k_t\rangle$/ $(\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}})$	$10^7\,[R]_0$[d]/ $(\mathrm{mol{\cdot}L^{-1}})$	τ[e]/ (s)
BMA	0.007	0.11	0.06	1.66	0.058	5740	0.36	4894
DMA	0.03	0.04	0.03	5.79	0.008	45745	0.78	281
DMA	0.007	0.10	0.09		0.236	1661	0.42	14507
DMA	0.03	0.37	0.29	5.79	0.302	1297	1.14	6763
TRIS	0.03	0.05	0.05	7.92	0.021	21030	0.42	1146
TRIS	0.007	0.10	0.74		0.281	1542	0.46	14253
TRIS	0.03	0.18	0.29	7.92	0.168	2573	1.09	3565

[a] Conversion during photopolymerization. [b] Conversion during postpolymerization in the dark. [c] Stationary radical concentration during photopolymerization. [d] Initial radical concentration in the postpolymerization. [e] Half-lifetimes for the surviving radicals during postpolymerization.

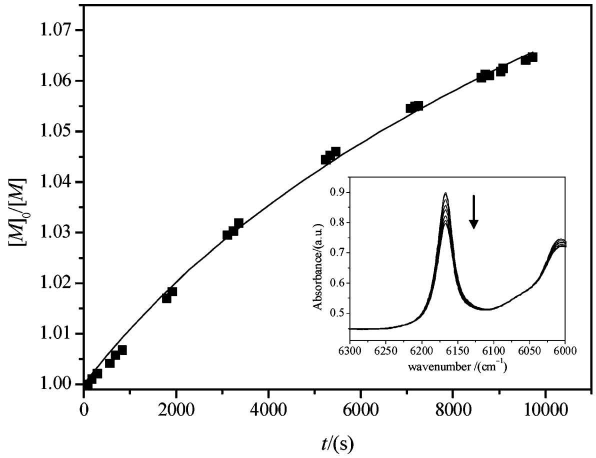

Figure 3. Changes in monomer concentration with time for butyl methacrylate bulk polymerization in the dark after an illumination period in which the monomer conversion was 11%. The solid line represents the best fit for the experimental data according to eq 5. Plotted in the insert is an example of the absorbance spectral series for a 3-[tris(trimethylsilyloxy)-silyl] propyl methacrylate postpolymerization experiment during which a conversion of 29% was reached.

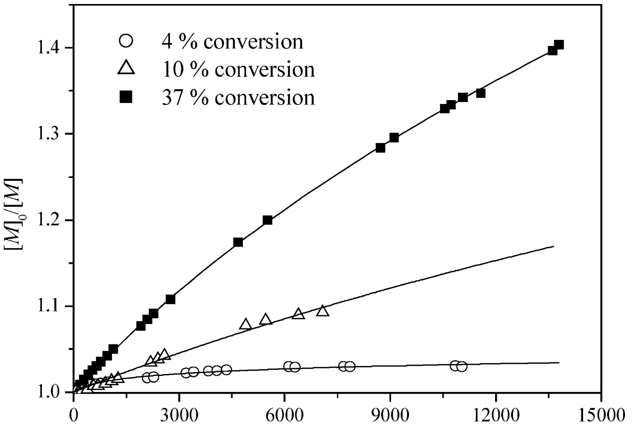

Figure 4. Changes in monomer concentration with time for dodecyl methacrylate bulk polymerizations in the dark after illumination periods in which the monomer conversions were 4, 10, and 37%. The solid lines represent the best fits for the experimental data according to eq 5.

zation rates than BMA at similar initial conversions, though a deeper insight into the kinetics is required.

For the postpolymerization reactions, the polymerization rate is given by eq 3

$$-\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p[R][M] \tag{3}$$

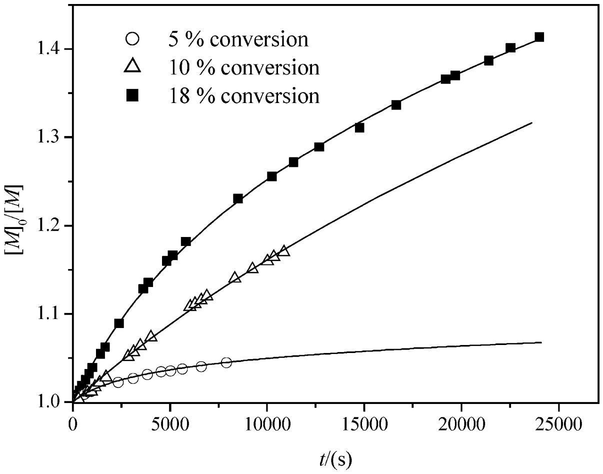

Figure 5. Changes in monomer concentration with time for 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate bulk polymerizations in the dark after illumination periods in which the monomer conversions were 5, 10, and 18%. The solid lines represent the best fits for the experimental data according to eq 5.

where $[M]$ and $[R]$ represent the monomer concentration in the dark period and the radical concentration of living chains, respectively.

Under ideal conditions, the termination rate can be described by eq 4.

$$-\frac{\mathrm{d}[R]}{\mathrm{d}t} = \langle k_t\rangle\,[R]^2 \tag{4}$$

The integrated equation that can be derived from eqs 3 and 4, assuming that k_p and $\langle k_t\rangle$ remain constant is

$$\frac{[M]_0}{[M]} = (1 + \langle k_t\rangle[R]_0 t)^{k_p/\langle k_t\rangle} \tag{5}$$

where $[M]_0$ is the initial monomer concentration after switching off the light, $\langle k_t\rangle$ is the average termination rate coefficient of the surviving macroradicals after the illumination period, and $[R]_0$ is the radical concentration at the beginning of the dark period.

Nonlinear curve fitting of the experimental curves shown in Figures 3−5 using eq 5 leads to determining the $\langle k_t\rangle[R]_0$ and $k_p/\langle k_t\rangle$ values for each postpolymerization experiment. The resulting fitting curves are depicted in these figures. Knowing k_p, previously determined by PLP-SEC, the $\langle k_t\rangle$ and $[R]_0$ values are derived from the ratio $k_p/\langle k_t\rangle$ and from the product $\langle k_t\rangle[R]_0$. The values of the ratio $k_p/\langle k_t\rangle$, of $\langle k_t\rangle$ and of $[R]_0$, thus estimated for each postpolymerization experiment, are shown in Table 2. A first inspection of the results reveals

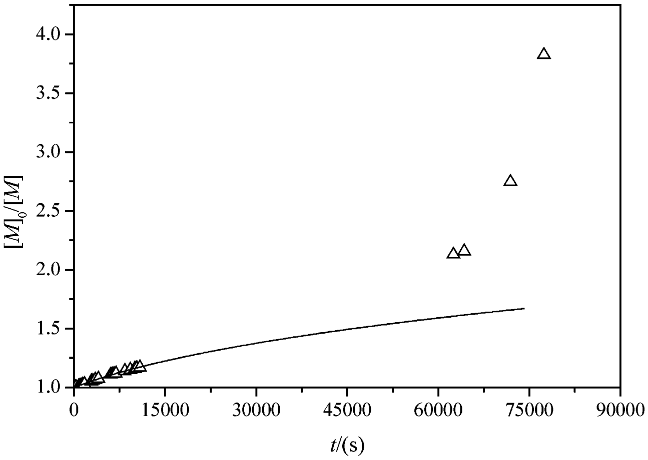

Figure 6. Changes in monomer concentration with time for 3-[tris(trimethylsilyloxy)silyl] propylmethacrylate bulk polymerization in the dark after an illumination period in which the monomer conversion was 10%. The solid line represents the best fit for the experimental data (only fitting up to 10000 s) according to eq 5.

that the $\langle k_t \rangle$ values are extremely low (in some cases lower than 5×10^3 L·mol^{-1}·s^{-1} at initial conversion lower than 10% where viscosity effects should be neglected) in comparison to those reported by others[11,12,25] for polymerizations of these monomers. In addition, the $\langle k_t \rangle$ values decrease as monomer conversion increases during the photopolymerization time. This behavior can be ascribed to an increase of the reaction medium viscosity, which consequently lowers $\langle k_t \rangle$. On the other hand, the estimated $[R]_0$ values range from 1×10^{-7} to 4×10^{-8} mol·L^{-1}. These values are over an order of magnitude lower than those found for the photopolymerization period, $[R]_{ph}$. An interesting finding is that the $[R]_0$ values are not dependent on the monomer nature, as it occurs at the photopolymerization period. The $[R]_0$ values are very similar for the BMA, DMA, and TRIS postpolymerization experiments at the same initial conversion during illumination.

It must be pointed out that trios, k_p, $\langle k_t \rangle$, and $[R]_0$, different from those listed in Table 2, could give rise to identical fitting curves as those shown in Figures 3−5 by applying eq 5 to experimental data. However, both the ratio $k_p/\langle k_t \rangle$ and the product $\langle k_t \rangle [R]_0$ always remain constant. As a consequence, the $[R]_0$ and $\langle k_t \rangle$ values directly derived by using k_p might not be correct. If a variable k_p is assumed for the fitting, both kinetic coefficients, k_p and $\langle k_t \rangle$, diminish with an increase in $[R]_0$. This opens again the matter for debate: the chain-length dependency of k_p.

Notwithstanding this discussion, the product $\langle k_t \rangle [R]_0$ values allow the direct determination, without assumptions, of the radical average half-lifetime, τ, by using the integrated form of eq 4. The τ values, included in Table 2, vary from 300 to 14000 s, which clearly indicates, together with the estimated $\langle k_t \rangle$ and $[R]_0$, that the macroradicals grown during the postpolymerization must yield polymers with very high molecular weight.

The MWDs of pDMA and pTRIS synthesized in the postpolymerization reactions are shown in Figures 7 and 8, respectively. Extremely high molecular weights and bimodal distributions are the shared features of the MWDs depicted. The bimodal pattern must have its origin in a mixture of two different MWDs, one for the polymer synthesized during the photopolymerization period and the other for the polymer obtained during the polymerization in the dark time. To validate this hypothesis, Figure 9 shows the MWDs of the pBMA synthesized by photopolymerization and postpolymerization in the dark, together with a pBMA prepared under the same conditions, but precipitated just after the illumination period. The former presents a bimodal pattern, whereas the latter shows a simple MWD, which coincides with the low-molecular-weight peak of the bimodal distribution. The same occurs with the DMA and TRIS experiments.

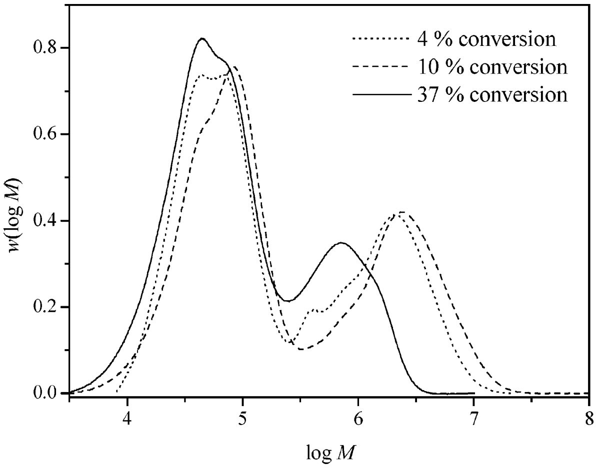

Figure 7. Bimodal molecular weight distributions of the polymers generated in the two-step polymerization reactions, first in photoinitiated polymerization (peak at low molecular weight) and then in dark polymerization (high-molecular-weight region) of dodecyl methacrylate at 25 °C. The monomer conversions in the illumination periods were 4% (dotted line), 10% (dashed line), and 37% (solid line).

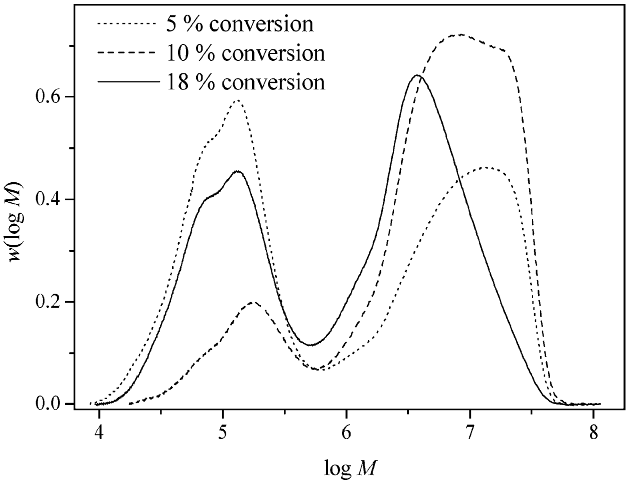

Figure 8. Bimodal molecular weight distributions of the polymers generated in the two-step polymerization reactions, first in photoinitiated polymerization (peak at low molecular weight) and then in dark polymerization (high-molecular-weight region) of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate at 25 °C. The monomer conversions in the illumination periods were 5% (dotted line), 10% (dashed line), and 18% (solid line).

The number-average degrees of polymerization for the polymers synthesized during the illumination and the dark time, $DP_{n,ph}$ and $DP_{n,dark}$, respectively, for each experiment are listed in Table 3.

The polymer synthesized during the first stage (the illumination period) exhibits number-average molecular weights that can be considered in the range of conventional FRP, whereas the polymer obtained during the

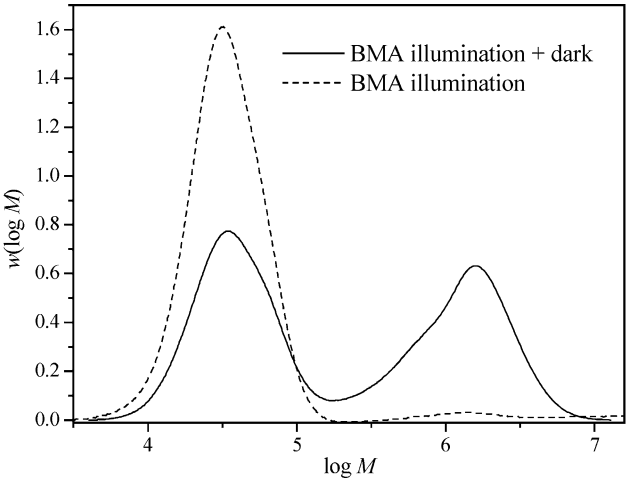

Figure 9. MWDs of poly(butyl methacrylate) prepared by photopolymerization at 25 °C with (solid line) and without (dashed line) postpolymerization in the dark. For both cases, the monomer conversions in the illumination periods were 11%.

second stage (the postpolymerization) has M_n larger than 1×10^6 Da. In addition, the polydispersity index is about 1.6 for the first period and 2.6 for the dark one. The first value can also be considered usual for FRP, but the latter is apparently anomalous given the "quasiliving" nature of the postpolymerization regime. A low polydispersity index should be expected for the polymer yielded during the postpolymerization. Several explanations may be proposed, although perhaps one of the most plausible is that some of the polymer obtained during the first illumination stage is contributing to enlarge the high-molecular-weight peak and, consequently, to increase the polydispersity index. However, this explanation is not consistent with SEC results because the percentage of polymer synthesized in the illumination period is fairly in agreement with the experimental conversion, and as shown in Figure 9 (dashed line), the contribution of high-molecular-weight polymer synthesized during photopolymerization is negligible. Therefore, we believe that the high polydispersity index at the postpolymerization is a consequence of the existence of transfer reactions to the monomer, the initiator, and/or the polymer involved in these radical polymerizations. These events can be estimated by the analysis of the conversion experimental data in the dark and the MWDs.

The kinetic analysis of the reaction and the quantitative values of the polymer molecular weights can provide valuable information on the initial and instantaneous radical concentration during the postpolymerization.

Changes with time in the living polymer concentration can be expressed by eq 6

$$\frac{\mathrm{d}\sum_i R_i i}{\mathrm{d}t} = k_\mathrm{p}[M] \sum_i R_i - \langle k_\mathrm{t}\rangle \sum_i R_i \sum_i R_i i \qquad (6)$$

where R_i denotes the concentration of living radicals of chain length i.

The solution to this first-order differential equation, considering that

$$\sum_i R_i = \frac{[R]_0}{1 + \langle k_\mathrm{t}\rangle [R]_0 t} = [R] \qquad (7)$$

and eq 5, leads to eq 8.

$$\sum_i R_i i = [LivingPolymer] = \frac{k_\mathrm{p}[M]_0}{(\langle k_\mathrm{t}\rangle - k_\mathrm{p})(1 + \langle k_\mathrm{t}\rangle\, [R]_0 t)} [(1 + \langle k_\mathrm{t}\rangle\, [R]_0 t)^{1-(k_\mathrm{p}/\langle k_\mathrm{t}\rangle)} - 1] \qquad (8)$$

It goes without saying that the dead polymer concentration is then given by

$$[DeadPolymer] = ([M]_0 - [M]) - [LivingPolymer] \qquad (9)$$

The contribution of the living and dead polymer concentration to the monomer conversion during a postpolymerization experiment for TRIS is given as an example in Figure 10. As the reaction proceeds and according to eq 8, the living polymer concentration goes through a maximum and then decreases slightly. The time at which the living polymer concentration maximum is reached can be defined by eq 10.

$$t_\mathrm{max} = \frac{\left(\dfrac{\langle k_\mathrm{t}\rangle}{k_\mathrm{p}}\right)^{[\langle k_\mathrm{t}\rangle/(\langle k_\mathrm{t}\rangle - k_\mathrm{p})]} - 1}{\langle k_\mathrm{t}\rangle [R]_0} \qquad (10)$$

The results shown in Figure 10 clearly indicate the existence of a large amount of living polymer during the postpolymerization process, even at long reaction times.

The number-average degree of polymerization $\mathrm{DP}_{n,\mathrm{dark}}$ of living and dead chains in the absence of transfer reactions reads

$$\mathrm{DP}_{n,\mathrm{dark}} = \frac{2([M]_0 - [M])(1 + \langle k_\mathrm{t}\rangle [R]_0 t)}{[R]_0[2 + (2 - \alpha)\langle k_\mathrm{t}\rangle [R]_0 t]} + \mathrm{DP}_{n,\mathrm{initial}} = \frac{2([M]_0 - [M])}{(2 - \alpha)[R]_0 + \alpha[R]} + \mathrm{DP}_{n,\mathrm{initial}} \qquad (11)$$

where α is the fraction of propagating chains that undergoes termination by coupling.

The $\mathrm{DP}_{n,\mathrm{initial}}$ is the number-average degree of polymerization for the living chains surviving immediately after switching off the production of primary radicals from the initiator.

The assignation of a $\mathrm{DP}_{n,\mathrm{initial}}$ value is a very difficult task, but it can be assumed that immediately after switching off the light, there is a certain concentration of living macroradicals in the reaction medium and that these surviving macroradicals have approximately the same chain length. Therefore, $\mathrm{DP}_{n,\mathrm{initial}}$ might be assigned to the molecular weight value located at the intersection point between both MWDs belonging to the bimodal pattern. These values extracted from the SEC traces are listed in Table 3.

By using eq 11, a rough approximation can be made to determine the initial radical concentration in the dark period, $[R]_0$, considering the experimental $\mathrm{DP}_{n,\mathrm{dark}}$ values and the product $\langle k_\mathrm{t}\rangle \cdot [R]_0$, determined by simulation of experimental data according to eq 5.

The $[R]_0$ values calculated in this way by using eq 11 for each polymerization reaction can be compared to

Table 3. Experimental Information and Results for the Polymerization Experiments of Butyl Methacrylate (BMA), Dodecyl Methacrylate (DMA), and 3-[Tris(trimethylsilyloxy)Silyl] Propyl Methacrylate (TRIS) during Photopolymerization and Postpolymerization Times

monomer	x_{ph}[a]	x_{dark}[b]	$\mathrm{DP}_{n,\mathrm{ph}}$[c]	$\mathrm{DP}_{n,\mathrm{dark}}$[d]	$\mathrm{DP}_{n,\mathrm{initial}}$[e]	$10^4\,C_M$[f]	$10^4\,C_M$[g]
BMA	0.107	0.061	220	7470	1207	1.61	1.15
DMA	0.043	0.029	160	5190	986	2.40	1.25
DMA	0.099	0.085	190	7550	1325	1.54	0.88
DMA	0.368	0.287	150	2950	940	5.04	3.38
TRIS	0.045	0.046	180	13530	1564	0.81	0.33
TRIS	0.097	0.739	300	12470	1345	0.88	0.28
TRIS	0.184	0.292	190	7850	1203	1.51	0.59

[a] Conversion during photopolymerization. [b] Conversion during postpolymerization in the dark. [c] Number average degree of polymerization during photopolymerization (determined from the bimodal MWD). [d] Number average degree of polymerization during postpolymerization (determined from the bimodal MWD). [e] Number average degree of polymerization at the beginning of the dark period (determined from the bimodal MWD). [f] Transfer constant to monomer determined according to eq 16. [g] Transfer constant to monomer determined by CLD method.

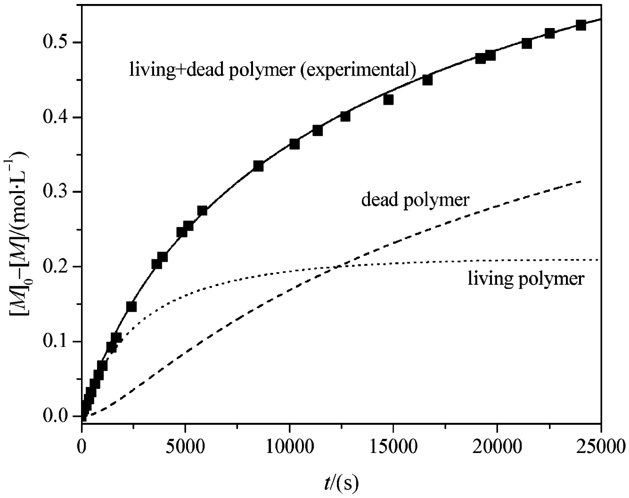

Figure 10. Experimental monomer concentration as a function of time and calculated contributions, according to eqs 8 and 9, of living (dotted line) and dead polymer (dashed line) concentrations for the 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate postpolymerization process after an illumination period in which the conversion was 18%.

those obtained from the simulated curves according to eq 5. As an example, for TRIS postpolymerization at the lowest initial conversion in the photopolymerization (in Figure 8 plotted as dotted line), the $\mathrm{DP}_{n,\mathrm{dark}}$ is 13 530, whereas the $\mathrm{DP}_{n,\mathrm{initial}}$ is 1564, and according to eq 11, the $[R]_0$ values obtained are 1.43×10^{-5} and 7.94×10^{-6} $\mathrm{mol\cdot L^{-1}}$ in the case of termination by coupling or by disproportionation, respectively. These values are much higher than those obtained from the simulation fitting of the experimental data according to eq 5 (listed in Table 2) by considering that k_p is independent of the chain length. Moreover, the $[R]_0$ values calculated according to eq 11 are even higher than those estimated during the photopolymerization period.

This uncertainty on the $[R]_0$ values led us to try an experimental determination under the same reaction conditions. For this purpose, EPR technique was used. This technique enables a quantitative determination of radical concentration. Under the same reaction conditions (illumination source, time intervals, temperature, and initiator concentration), it was experimentally impossible to detect radicals during the postpolymerization experiments presented in this work. The EPR detection limit is about 5×10^{-7} $\mathrm{mol\cdot L^{-1}}$, therefore, the $[R]_0$ values calculated by simulation fitting with eq 5 are more reliable than those obtained from eq 11. Similar results are obtained for all the experiments carried out in this work. This gives some validity to the use of constant k_p values determined from PLP experiments for describing the growth of these high-chain-length macromolecules. This result is not completely in disagreement with chain-length-dependent k_p theories, as it seems likely that the decrease of k_p with chain length will take place only up to a given molecular weight. The PLP-SEC k_p values reported in this work have been calculated from MWDs in which the first inflection point was located at a molecular weight higher than 90 000 Da, as it is shown in Figure 1. From such high-chain-length macromolecules on, a negligible influence of chain length on k_p may be presumed.

On the other hand, assuming that $[R]_0$ values given in Table 2 are reliable, the $\mathrm{DP}_{n,\mathrm{dark}}$ derived from eq 11 for the same TRIS postpolymerization are 1.57×10^6 and 0.87×10^6 in the case of termination by coupling or by disproportionation, respectively. These values are much higher than those determined experimentally by SEC. This disagreement is explained by the existence of transfer reactions during the polymerization because, as it is well-known, these events must not be considered negligible in FRP.

If transfer reactions are considered, then the rate of formation of dead polymer chains generated by transfer reactions, $[R]_{\mathrm{dead}}$, is given by

$$\frac{\mathrm{d}[R]_{\mathrm{dead}}}{\mathrm{d}t} = k_{\mathrm{tr_M}}[R][M] + k_{\mathrm{tr_P}}[R]([M]_0 - [M]) + k_{\mathrm{tr_I}}[R][I] \quad (12)$$

where $k_{\mathrm{tr_M}}$, $k_{\mathrm{tr_P}}$, and $k_{\mathrm{tr_I}}$ are the transfer rate constants to monomer, polymer, and photoinitiator, respectively.

The integration of this equation reads

$$[R]_{\mathrm{dead}} = \frac{(k_{\mathrm{tr_M}} - k_{\mathrm{tr_P}})[M]_0}{k_p}[1 - (1 + \langle k_t\rangle[R]_0 t)^{-[k_p/\langle k_t\rangle]}] + \frac{(k_{\mathrm{tr_P}}[M]_0 + k_{\mathrm{tr_I}}[I])}{\langle k_t\rangle}\ln(1 + \langle k_t\rangle[R]_0 t) \quad (13)$$

and the number-average molecular weight is then given by eq 14.

$$\mathrm{DP}_{n,\mathrm{dark}} = \frac{([M]_0 - [M])}{\left(\frac{2-\alpha}{2}\right)[R]_0 + \frac{\alpha}{2}[R] + [R]_{\mathrm{dead}}} + \mathrm{DP}_{n,\mathrm{initial}} \quad (14)$$

Thus, knowing the fraction of the dead chains terminated by coupling or disproportionation, the concentration of polymer chains terminated by transfer reactions

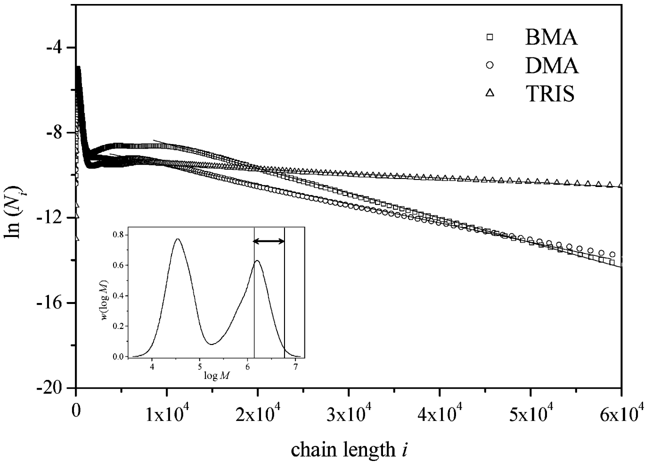

Figure 11. Semilogarithmic plot of the chain-length number fraction as a function of chain length for the two-step polymerization reactions of butyl methacrylate (BMA), dodecyl methacrylate (DMA), and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS). DMPA concentration was 7×10^{-3} mol·L^{-1} for all the experiments. Plotted in the insert is the SEC trace corresponding to the polymer yielded during the butyl methacrylate polymerization, showing the range of molecular weight for which the C_M is calculated.

can be determined. Assuming that the α value is close to one, the transfer contribution to the total polymer chains, described by the two-term eq 13, may be calculated.

It must be taken into account that, in bulk polymerization at low conversions, transfer to monomer is assumed to be more important than transfer to polymer or initiator. If this were true, $[R]_{\text{dead}}$ would refer to the transfer constant to monomer, C_M, defined by the relationship between k_{tr_M} and k_p, through eq 13 in its simplified form:

$$[R]_{\text{dead}} = C_M([M]_0 - [M]) \qquad (15)$$

Consequently, for coupling termination, the $\text{DP}_{n,\text{dark}}$ is given by eq 16.

$$\frac{1}{(\text{DP}_{n,\text{dark}} - \text{DP}_{n,\text{initial}})} = \frac{([R]_0 + [R])}{2([M]_0 - [M])} + C_M \qquad (16)$$

The values of C_M determined by this procedure are shown in the seventh column of Table 3. These values scale to those found for other vinyl monomers.[3]

A method to determine the transfer constant to monomer on the basis of the chain-length distribution (CLD) analysis was proposed by Gilbert et al.[26-29] This method can be applied if the transfer to the monomer is favored over other mechanisms, such as bimolecular termination of the macroradicals, and high molecular weights are obtained. The postpolymerization experiments are probably one of the most suitable examples for which these requirements are fulfilled. This allows an accurate determination of C_M values by using the CLD method.

According to the CLD method, in case of transfer to the monomer being the favored chain termination mechanism, the number fraction distribution of the polymer chains is given by eq 17.[30]

$$N_i = C_M \exp(-iC_M) \qquad (17)$$

A semilogarithmic plot of N_i as a function of chain length i for BMA, DMA, and TRIS polymerizations in the dark is plotted in Figure 11.

The C_M values are determined from the slopes of the straight lines for the high-molecular-weight range. An example of this determination process is shown in Figure 11. The range of molecular weight in which the C_M is calculated for the BMA postpolymerization is marked on the SEC trace shown in the insert. The values thus obtained and listed in Table 3 are lower than those calculated according to eq 16, also listed in Table 3. The reason for this disagreement may be the poor discrimination of the SEC set up at such high molecular weights ($>10^7$ Da) as can be detected in the MWDs, especially for the case of pTRIS. In any case, C_M follows the same trend no matter the method applied: TRIS is the monomer that exhibits the lowest C_M value, whereas the largest value corresponds to BMA (comparing experiments carried out with the same photoinitiator concentration).

It is also remarkable that, for DMA and TRIS polymerizations, the higher the conversion during photopolymerization time, the higher the C_M values. This can be due to the coexistence of transfer reactions to monomer and to the polymer.

On the other hand, as it is well-known, the hypothetical largest number-average molecular weight that can be obtained in a FRP reaction is controlled by the transfer constant to the monomer. Considering the BMA, DMA, and TRIS C_M values determined using the CLD method for the experiments with the lowest initiator concentration, the largest M_n values predicted are 1.2, 2.9, and 15.1×10^6 Da, respectively. As a consequence, the rate of transfer to monomer at this temperature is the major limitation for reaching molecular weights higher than those experimentally obtained during the postpolymerization. Nevertheless, this synthetic method allows for the preparation of relatively large amounts of extremely high-molecular-weight polymers.

Conclusions

The postpolymerization of three methacrylic monomers, butyl, dodecyl, and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate, after previous photoinduced polymerization, were studied. For all the monomers, the conversion (monitorized by FT-IR) reached in the absence of a source of initiator radicals was very important, especially for DMA and TRIS, which exhibit lower k_t values. The half-lifetimes of the surviving macroradicals ranged from 300 to 14 000 s. By applying ideal kinetics and independently obtaining k_p, the $\langle k_t \rangle$ values associated with these postpolymerization processes were determined. However, the bimolecular termination between macroradicals was not the preferred stop-chain event during polymerization in the dark. The transfer to the monomer controlled the final molecular weight during postpolymerization. Although the highest hypothetical molecular weights were not experimentally achieved, this method can be very useful for the preparation of high-molecular-weight polymers. In addition, the existence of these persistent radicals during FRP reactions, even at very low monomer conversion and for conventional methacrylic monomers, can explain some observed phenomena previously ascribed to experimental errors (such as the spontaneous polymerization, the occurrence of high-molecular-weight peaks in photopolymerization, etc).

This work constitutes the first stage of a more extensive research, leading to the quantitative evaluation of the influence of chain length on termination rate coefficients for different polymerization reactions. With the experiments carried out in this investigation, only an average termination rate coefficient is accessible. Well-designed series of postpolymerization experiments would be required to undertake a thorough study on the influence of chain length on k_t.

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