New Experimental Procedure To Determine the Recombination Rate Constants between Nitroxides and Macroradicals

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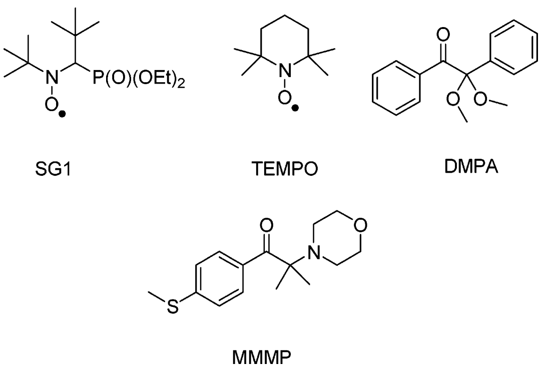
ABSTRACT: A new experimental procedure for the determination of the recombination rate constant, k_c, between a propagating macroradical and a nitroxide is proposed. It is based on a single pulse−pulsed lamp polymerization where the main chain growth breaking event between two consecutive pulses is the recombination of the macroradicals with the nitroxide. The recovered polymer is analyzed by size exclusion chromatography, and the parameters of the molar mass distribution are used to determine k_c, in a similar way as that traditionally applied in the determination of the chain transfer rate constants, i.e., the Mayo method using the number- or weight-average degrees of polymerization and the full chain length distribution method. We named the technique RNR−PLP−SEC for radical nitroxide recombination−pulsed lamp polymerization−size exclusion chromatography. The particular polystyryl macroradical−SG1 nitroxide system was tested to validate it. To apply a consistency check, the experimental parameters have been varied according to the recommendations made by the IUPAC for the measurements of the propagation rate constants via PLP. The recombination rate constant k_c was measured over a temperature range where no cleavage of the formed alkoxyamine might occur. At 40 °C $k_c = 2.6 \times 10^5$ L mol^{-1} s^{-1}, and the value increased from 1.1×10^5 L mol^{-1} s^{-1} at 15 °C to 4.0×10^5 L mol^{-1} s^{-1} at 82 °C. The extrapolation at 120 °C led to 5.3×10^5 L mol^{-1} s^{-1}, in good agreement with the values already reported in the literature.

Introduction

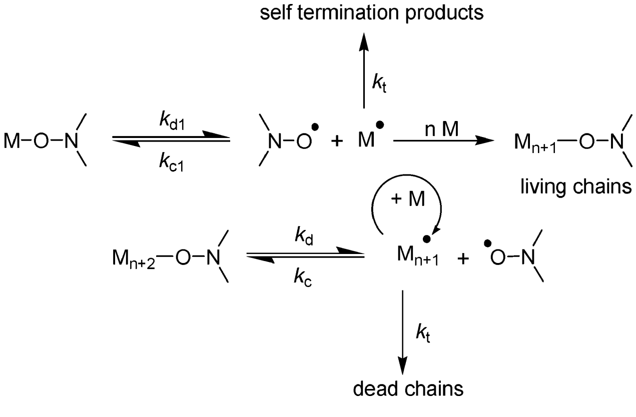
The synthesis of tailored polymers is an important aspect of polymer science since there is a growing demand for functionalized, well-defined materials to use as building blocks in many applications.[1] Controlled radical polymerization (CRP) has become a very interesting route to prepare these well-defined (co)polymers with predictable molar mass and narrow molar mass distribution.[2] Three major methods have emerged: atom transfer radical polymerization (ATRP),[3,4] reversible addition−fragmentation chain transfer (RAFT),[5,6] and nitroxide-mediated radical polymerization (NMP),[7] which is the oldest technique and therefore has been exhaustively studied.

Rizzardo[7] and Georges[8] have first introduced the use of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) to control the polymerization of styrene. To overcome the TEMPO limitations, other types of nitroxides were designed, and in particular alicyclic nitroxides like SG1[9,10] or TIPNO,[11,12] in which one of the α-carbons bears a hydrogen atom, in contrast to TEMPO, which exhibits two quaternary α-carbons (Scheme 1). Among the main three CRP methods, NMP is potentially the simplest one, since in most cases it only requires the addition of an appropriate alkoxyamine to the polymerization system.[13]

Scheme 1



Scheme 2. Mechanism of the NMP



NMP is grounded on the persistent radical effect (PRE),[14] and its principle is described in Scheme 2. The buildup of nitroxide which is the result of self-termination at the beginning of the polymerization promotes the cross-recombination reaction instead of irreversible terminations. A majority of dormant living chains can

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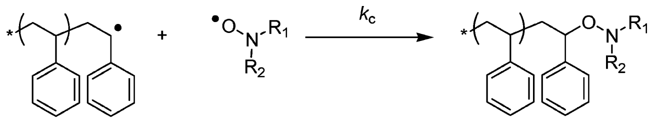
so keep growing until the monomer is depleted, resulting in a polymer with large living character and narrow molar mass distribution.

A complete kinetic analysis has been carried out by both Fukuda[15,16] and Fischer,[17,18] and the kinetic conditions required for a successful process have been established. They pointed out the importance of the dissociation and recombination rate constants on the livingness and the control. From this analysis, Fischer developed a predictive phase diagram,[19,20] which connects the values of the k_d, k_c couple with livingness and control, if no side reactions occur.

Numerous works[21−27] have been done about the values of the dissociation rate constant k_d. This kinetic parameter can be easily measured by ESR spectroscopy[28] by monitoring the appearance of the nitroxide radical in the presence of a carbon-centered radical scavenger. Other methods based on size exclusion chromatography[29] have been developed. Bertin et al.[30] reported an easy way using heteroatom NMR spectroscopy to determine the k_d value of alkoxyamines bearing a phosphorus, such as SG1-based alkoxyamines. From the large data available for model alkoxyamines, structure−reactivity relationships have been established, and whatever the structure of the nitroxide[31] or of the released alkyl group,[32] the dissociation rate constant k_{d1} (Scheme 2) can now be easily predicted. Dissociation rate constants for macroalkoxyamines k_d have been measured and compared to the values for model alkoxyamines. For the polystyrene−SG1 (PS−SG1), the values are similar,[33] but a chain length dependence has been shown for the poly(*n*-butyl acrylate)−SG1 (PBA−SG1).[34] PBA−SG1 macroalkoxyamines indeed exhibit a k_d that is 3−5 times higher than that of the model alkoxyamine.

Unlike the dissociation rate constant, fewer works[35−37] have been devoted to the recombination rate constant, k_c. Fischer[38] used laser flash photolysis (LFP) to determine k_c between various nitroxides and model alkyl radicals. For instance, the recombination rate constant between the styryl radical and SG1 is equal to 3.7×10^6 L mol^{-1} s^{-1} at 50 °C. He also demonstrated that the temperature dependence of this value shows a non-Arrhenius behavior and is merely controlled by a large negative entropy term. Recently, Bagryanskaya et al.[39] reported the k_c between TEMPO and model radicals using chemical-induced dynamic nuclear polarization−switch external magnetic field (CIDNP−SEMF) NMR technique. A good agreement between the various methods is observed. Nevertheless, the direct measurements of the recombination rate constant are only performed with model alkyl radicals, but never with macroradicals, which are of great interest for NMP experiments and simulations. In addition, the influence of the polymer chain on the recombination rate constant has never been investigated and is of major importance to establish the phase diagram. The values of k_c between a macroradical and a nitroxide have only been indirectly determined, either by simulation[40] or by determining the equilibrium constant $K = k_d/k_c$ knowing k_d. K can be derived from the slope of the $\ln([M]_0/[M])$ vs time plot,[41] from ESR[9,42] analyses, or by on-line monitoring of the reaction medium[43] (ACOMP technique). The values of k_c obtained by those various methods cannot be considered as very accurate because of the imprecision imparted by the determination of K and by the chain length dependence for k_d.

Scheme 3



In this work, an experimental procedure for the direct determination of the recombination rate constant between a macroradical and a nitroxide is proposed (Scheme 3). It consists of a pulsed laser polymerization (PLP) derivative method coupled with size exclusion chromatography and might be called radical nitroxide recombination−pulsed lamp polymerization−size exclusion chromatography (RNR−PLP−SEC). The PLP−SEC has become the method recommended by the IUPAC for the determination of the propagation rate constants[44] because of its high accuracy and reproducibility. Benchmark k_p have been published by the IUPAC for styrene,[44] methyl[45] and other alkyl methacrylates,[46,47] and *n*-butyl acrylate.[48] With the same apparatus, the determinations of chain transfer constants[49] and termination rate coefficients[50] along with the chain length dependency[51] are also in progress. We first present a description of this technique, its validation, and its experimental limitations. The determination of the recombination rate constant between polystyryl (PS) macroradical and the SG1 nitroxide has been performed, and the value of k_c is compared with data already reported in the literature (estimated values for the macroradical and experimental values for model radicals).

Experimental Section

Materials. Dimethoxyphenylacetophenone (DMPA), 2-methyl-4′-(methylthio)-2-morpholinopropiophenone (MMMP), and styrene were purchased from Aldrich. *N-tert*-Butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl nitroxide SG1 (85%) was supplied by ARKEMA (Scheme 1). Styrene was distilled under reduced pressure before use (see below). Photoinitiators (PI) and nitroxide were used as received.

Analytical Techniques. Size exclusion chromatography (SEC) was performed at 40 °C with two columns (PSS SDV linear M, 8 mm × 300 mm; 5 μm) at a flow rate of 1 mL min^{-1} with tetrahydrofuran (THF) as eluent. A differential refractive index detector (LDC Analytical refractoMonitor IV) was used, and molar masses were derived from a calibration curve based on polystyrene standards (from 266 to 1 090 000 g mol^{-1}) from Polymer Standards Service. This technique allowed to determine M_n (the number-average molar mass), M_w (the weight-average molar mass), PDI = M_w/M_n (the polydispersity index), and the molar mass distribution.

Pulsed Lamp Apparatus. The pulsed UV lamp has been constructed by ARKEMA and is based on a flash Perkin-Elmer FX-504 lamp and a Lite Pac FYD 506 trigger module. The assembly consists of a cavity in which a quartz cell can be introduced. The temperature is controlled by Peltier Effect. The UV beam is directed and collimated onto the quartz cell. A laser apparatus has also been used and is already described elsewhere.[52]

Typical Pulsed Lamp Polymerization Procedure. A solution of dimethoxyphenylacetophenone (DMPA) (10^{-1}−10^{-4} mol L^{-1}) and SG1 (10^{-2}−10^{-5} mol L^{-1}) in freshly distilled styrene was introduced in a quartz cell. After the temperature stabilization, the experiment was conducted under a continuously N_2 bubbling. The mixture was then evaporated, and the resulting polymer was analyzed by SEC.

Experimental Limitations. In these experiments, the purity of the monomer must be carefully checked, and only a freshly distilled one must be used. The tiny fraction of dead thermally induced polystyrene already present in the starting monomer can cause erroneous SEC measurements. This limitation is especially crucial when the chain length is low

($<$2000 g mol^{-1}), i.e., when high concentrations of nitroxide are used or when the value of k_c is high. After evaporating the residual monomer, a little quantity (i.e., 2 or 3 mg) of polymer obtained by the PLP is collected and analyzed by SEC. In this case, the quantity of thermally induced polymer not detectable by NMR or by SEC analysis of the monomer can hide the PLP distribution. The analysis is therefore distorted.

Results and Discussion

Description of the RNR–PLP–SEC. This method is based on the principle of the single pulse–pulsed laser polymerization, SP–PLP,[53] i.e., a very fast photoinitiation followed by a free evolution of the macroradicals in the medium until their complete disappearance. A photoinitiator (typically an acetophenone derivative) and a nitroxide are mixed with a monomer in a quartz cell. During the lamp pulse, a large amount of primary radicals are generated. These radicals initiate the polymerization and the operating conditions are chosen in order to force the recombination reaction between nitroxide and macroradicals instead of the alkyl radical self-termination reaction. The SP–PLP technique actually meets this requirement, in comparison with a continuous photoinitiation under steady-state conditions (which would, anyhow, be difficult to carry out from the technical viewpoint, owing to the need of very short irradiation times). With the pulsed lamp apparatus, the average initial concentration of primary radicals $[R^\bullet]_0$ can be estimated as 5.0×10^{-8} mol L^{-1}.[54] This small radical concentration is favorable to the recombination with the nitroxide vs the self-termination, even immediately after the lamp pulse ($k_c[NO^\bullet]_0/k_t[R^\bullet]_0 > 10$). Furthermore, in these conditions, the active chains are equal in length, and the presence of molecular radicals is avoided; this results in a slower diffusion process, leading to a lower value of k_t and therefore disadvantages the self-termination.[55] For instance, the SP–PLP conditions proved in the past to be efficient to favor transfer reactions over termination, allowing thus an accurate determination of the chain transfer constant to monomer.[56] In consequence, such a method should also favor termination of the propagating radicals by the nitroxide over self-termination. When all carbon-centered radicals are consumed, pulses are repeated to obtain sufficient polymer to be analyzed by SEC. The number of pulses is chosen such as to yield a low monomer conversion (typically $<$1% conversion) to assimilate monomer and nitroxide concentrations to the initial ones. The chain length of the obtained polymer is then directly related to the recombination rate, and the determination of the average molar mass by SEC should enable us to calculate the recombination rate constant k_c.

Three methods are described in the literature for the determination of the chain transfer rate constant, k_{tr}, in polymerizations where chain transfer reaction is the main chain growth breaking event. The standard procedure has always been the Mayo method,[57] even though the IUPAC underlined that there are many difficulties with this method and recommended to develop new methods for the determination of the transfer constants.[58] It is based on the determination of either the number-average molar mass or the weight-average molar mass.[59] Gilbert[60] has introduced the chain length distribution (CLD) method as a more accurate alternative way, when SEC fails in providing correct average molar masses owing to experimental noises or poor baseline determination or when only a part of the molar mass distribution represents the chains that have been predominantly stopped by the studied event. In this case, the plot representing the slope of the logarithmic number distribution, $d(\ln(x_i))/di$, vs the ratio of the transfer agent to monomer concentration allows one to calculate the chain transfer constant, $C_{tr} = k_{tr}/k_p$.

The same three methods might be applied to determine k_c, considering that the influence of a termination agent (here, the nitroxide) on the chain growth breaking is the same as that of a transfer agent, although the mechanism involved is fundamentally different. The first method considers the instantaneous degree of polymerization, calculated by the ratio of the rate of propagation (R_p) over the rates of the major chain growth breaking events (R_c and R_t, for the recombination with the nitroxide and the self-termination, respectively) (eq 1).

$$\mathrm{DP_n} = \frac{R_p}{R_c + R_t} = \frac{k_p[M]_0}{k_c[NO^\bullet]_0 + k_t[P^\bullet]} \quad \text{or} \quad \frac{1}{\mathrm{DP_n}} = \frac{k_c[NO^\bullet]_0 + k_t[P^\bullet]}{k_p[M]_0} \qquad (1)$$

where $[NO^\bullet]_0$ and $[M]_0$ are respectively the initial nitroxide and monomer concentration, and $[P^\bullet]$ is the concentration of propagating macroradicals. This equation is similar to the Mayo expression. When the alkyl radical self-termination is negligible, eq 1 simplifies into eq 2, and the plot of $\mathrm{DP_n}$ vs $1/[NO^\bullet]_0$ can be used to determine the recombination rate constant k_c.

$$\mathrm{DP_n} = \frac{k_p[M]_0}{k_c[NO^\bullet]_0} \qquad (2)$$

Usually, the measurement of the weight-average degree of polymerization $\mathrm{DP_w}$ by SEC is more reproducible than that of $\mathrm{DP_n}$.[61] Consequently, considering the theoretical polydispersity index of 2 for a Flory–Schulz distribution, $\mathrm{DP_n}$ is more precisely measured by $\mathrm{DP_w}/2$,[62] allowing to determine k_c from eq 3.

$$\frac{\mathrm{DP_w}}{2} = \frac{k_p[M]_0}{k_c[NO^\bullet]_0} \qquad (3)$$

The third method to determine k_c takes into account the chain length distribution according to Gilbert's method.[60] To calculate the chain length number distribution function $x_i = f(i)$, it is convenient to choose a statistical approach based on kinetic parameters.[63] In this case the logarithmic number distribution is given by

$$\ln(x_i) = \ln\left(\frac{1-\alpha}{\alpha}\right) - i(\alpha - 1) \qquad (4)$$

$$\alpha = \frac{R_p}{R_p + R_c + R_t} = \frac{k_p[M]}{k_p[M] + k_c[NO^\bullet] + k_t[P^\bullet]} \qquad (5)$$

In those equations, α is the probability for the macroradical to propagate instead of terminate. Assuming that recombination is the main chain growth breaking event, the recombination rate constant can then be derived from eq 6, by plotting the inverse of the slope of the logarithmic number distribution vs the inverse concentration of nitroxide.

$$\frac{\mathrm{d}(\ln(x_i))}{\mathrm{d}i} = -\frac{k_\mathrm{c}[\mathrm{NO}^\bullet]_0}{k_\mathrm{c}[\mathrm{NO}^\bullet]_0 + k_\mathrm{p}[\mathrm{M}]_0} \qquad (6)$$

Hutchinson[49] has validated the use of the CLD method coupled with PLP to determine the transfer constant for different mercaptans, provided that transfer is the dominant event even under non stationary conditions. It was assumed in this work that k_c and k_p are chain length independent when the degree of polymerization is higher than 5−10 (as recently stated by van Herk for the k_p).[64]

The three methods usually combine the variation of the concentration of the chain breaking agent and a graphical method, as stated above. Equations 2, 3, and 6 can also be used directly to calculate k_c on the basis of a single experiment, where the initial concentrations in monomer and nitroxide are not varied. It should, however, be kept in mind that the graphical methods lead to a more accurate value.

As mentioned before, the operating conditions have to be carefully determined. In particular, four main criteria must be fulfilled. First, to avoid termination by the primary radicals generated at the lamp pulse, the PLP experiment must be performed in a single pulse mode, so that all transient radicals are consumed during the time interval between consecutive pulses. Therefore, the first condition connects the frequency with the lifetime of the propagating radicals. By assuming a first-order decay of the macroradical concentration, due to the predominant recombination reaction with SG1 and a disappearance of at least 98% between two pulses[65] (time interval t_d, corresponding to the reverse of the frequency), eq 7 is obtained:

$$\frac{4}{k_\mathrm{c}[\mathrm{NO}^\bullet]_0} \le t_\mathrm{d} \qquad (7)$$

Considering eqs 2, 3, and 6, the accuracy of the k_c values depends mainly on the quality of the molar mass analysis. A technical limitation is reached for too high nitroxide concentrations conducting to oligomers ($M_\mathrm{n} < 1000$ g mol^{-1}), which cannot be precisely characterized by classical SEC analysis. A lower limit DP_MIN is set up, and the second condition is given by eq 8.

$$\frac{k_\mathrm{p}[\mathrm{M}]_0}{k_\mathrm{c}[\mathrm{NO}^\bullet]_0} \ge \mathrm{DP}_\mathrm{min} \qquad (8)$$

This new technique is essentially based on the hypothesis that recombination between a macroradical and the nitroxide is the predominant termination reaction and that self-terminations between alkyl radicals are prevented. Consequently, the experiments should be conducted with a small initial concentration of primary radicals, $[\mathrm{R}^\bullet]_0$, to reduce $[\mathrm{P}^\bullet]$ and hence the $k_\mathrm{t}[\mathrm{P}^\bullet]/k_\mathrm{c}[\mathrm{NO}^\bullet]_0$ ratio. In parallel, the nitroxide concentration has to be high enough, as indicated by eq 9.

$$k_\mathrm{c}[\mathrm{NO}^\bullet]_0 \gg k_\mathrm{t}[\mathrm{P}^\bullet]_0 \Rightarrow \frac{k_\mathrm{c}[\mathrm{NO}^\bullet]_0}{k_\mathrm{t}[\mathrm{P}^\bullet]_0} \ge 10 \qquad (9)$$

Because of the principle of the NMP, measurements cannot be performed at classical polymerization temperature (i.e., 120 °C). The reversibility of the recombination between macroradicals and nitroxides implies to work at a temperature where the cleavage of the macroalkoxyamine is negligible. Fischer has studied[66] the theoretical and experimental decay of alkoxyamines when the persistent radical effect occurs. The half-life time of the initiating alkoxyamine[66] (eq 10) depends on k_d1, k_c1, and k_t (Scheme 2).

$$t_{1/2} = \frac{[\mathrm{I}]_0 {k_\mathrm{c1}}^2}{24 {k_\mathrm{d1}}^2 k_\mathrm{t}} \qquad (10)$$

As Fischer noticed, the decay of the alkoxyamine is strongly delayed by the persistent radical effect, and another criterion has been chosen to describe the stability of the alkoxyamine. The cleavage temperature T_c has been used by Le Mercier et al.[67] to estimate the temperature, beyond which the dissociation of the alkoxyamine becomes nonnegligible. Below the cleavage temperature, the homolysis of the macroalkoxyamine should not occur during the experiment (eq 11).

$$T \le T_\mathrm{c} \qquad (11)$$

Fischer has shown that the temperature dependence of the recombination rate constant for model radicals is weak and should be governed by entropic considerations.[38] With this assumption, by combining the four inequalities (eqs 7−9 and 11) and the respective Arrhenius laws for k_p[44] and k_t,[68] a predictive phase diagram can be built to identify the nitroxide concentration and reaction temperature domain where the measurement can be carried out (eqs 12−15).

$$\frac{1}{T} \ge \frac{1}{T_\mathrm{c}} \qquad (12)$$

$$\log([\mathrm{NO}^\bullet]_0) \ge \log\left(\frac{4}{k_\mathrm{c} t_\mathrm{d}}\right) \qquad (13)$$

$$\frac{1}{T} \le \frac{R\ln(10)}{E_\mathrm{ap}}\left[-\log\left(\frac{k_\mathrm{c}\mathrm{DP}_\mathrm{min}}{A_\mathrm{p}[\mathrm{M}]_0}\right) - \log([\mathrm{NO}^\bullet]_0)\right] \qquad (14)$$

$$\frac{1}{T} \ge \frac{R\ln(10)}{E_\mathrm{at}}\left[\log\left(\frac{10A_\mathrm{t}[\mathrm{P}^\bullet]}{k_\mathrm{c}}\right) - \log([\mathrm{NO}^\bullet]_0)\right] \qquad (15)$$

This predictive phase diagram is only indicative because it requires the values of k_p, k_t, and especially an estimation of k_c. The predictive phase diagram for the PS−SG1 system is displayed in Figure 1 (the gray area represents the optimum operating conditions) and shows that the range of concentration and temperature is sufficiently broad to measure the recombination rate constant.

RNR−PLP−SEC Validation. The most important consistency check was to ensure that recombination was the main termination mode. All tests were conducted with the PS−SG1 system. From the predictive phase diagram shown in Figure 1, we have chosen to work at 40 °C, with an initiator concentration of 10^{-2} mol L^{-1}. The nitroxide concentration ranged from 10^{-2} to 5.0×10^{-5} mol L^{-1}. We then followed the evolution of the average degree of polymerization as a function of the nitroxide initial concentration, $[\mathrm{SG1}]_0$ (Mayo method).

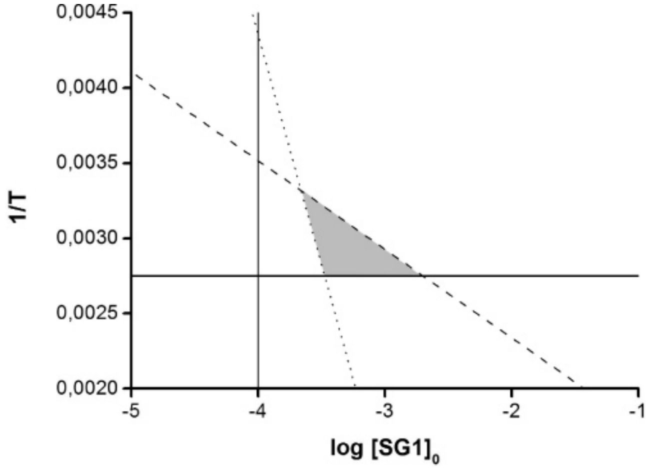


Figure 1. Predictive phase diagram for the PS−SG1 system. $k_p = 4.27 \times 10^7 e^{-32500/RT}$ mol^{-1} L s^{-1}; $k_t = 1.06 \times 10^9 e^{-6500/RT}$ mol^{-1} L s^{-1}; $[P^{\bullet}]_0 = 10^{-7}$ mol L^{-1} ; $DP_{min} = 10$; $[M]_0 = 8.74$ mol L^{-1} ; frequency = 10 Hz; $T_c = 90$ °C; preestimated $k_c = 4 \times 10^5$ L mol^{-1} s^{-1}. (—) Single-pulse condition: eq 13; (—) temperature condition: eq 12; (· · ·) recombination with SG1 as the main chain growth breaking event: eq 15; (- - -) SEC limitation: eq 14.

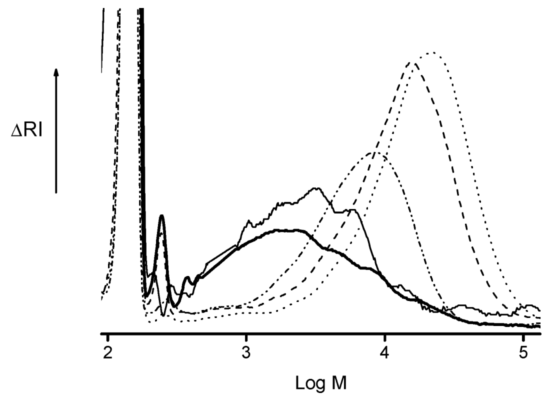


Figure 2. SEC traces (RI detector) of polystyrenes obtained by RNR−PLP−SEC at 40 °C with various SG1 concentrations. $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz; $[SG1]_0 = 7.7 \times 10^{-5}$ (· · ·); 5.04×10^{-5} (- - -); 1.1×10^{-4} (-· · -); 2.1×10^{-4} (—); 5.04×10^{-4} mol L^{-1} (**—**).

Even though the polymer characterization was more difficult at high $[SG1]_0$ (Figure 2), a linear evolution of DP_n or DP_w vs $1/[SG1]_0$ was obtained with the intercept close to 0 (Figures 3 and 4), confirming the validity of this measurement method. In the same manner, the plot of the inverse of the slope of the logarithmic number distribution (see Figure 5 for the slope) against $1/[SG1]_0$ validated the CLD method (Figure 6). The slope of the $\ln(x_i)$ vs i plot was calculated in the region of the maximum of the SEC peak, as discussed and recommended by Russell[62] and Moad.[69]

This new method to determine the recombination rate constant between macroradicals and nitroxides is based on PLP experiments. Consequently, it must fulfill the same reliability criteria, implying that it is necessary to check whether identical k_c values are obtained upon variation of specific experimental parameters. These are typically the frequency between two consecutive pulses and the nature and concentration of the photoinitiator. For some experiments, the frequency (Table 1), the concentration, and nature of the photoinitiator (Table 2) and the duration of experiment (Table 3) have been varied.

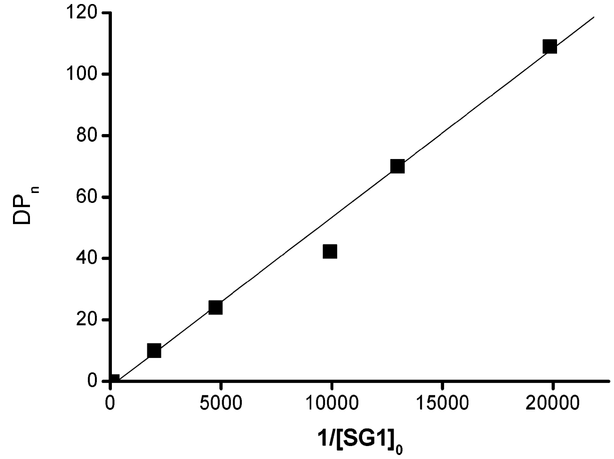


Figure 3. DP_n vs $1/[SG1]_0$ from the RNR−PLP−SEC experiments carried out at 40 °C for the PS−SG1 system; $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz.

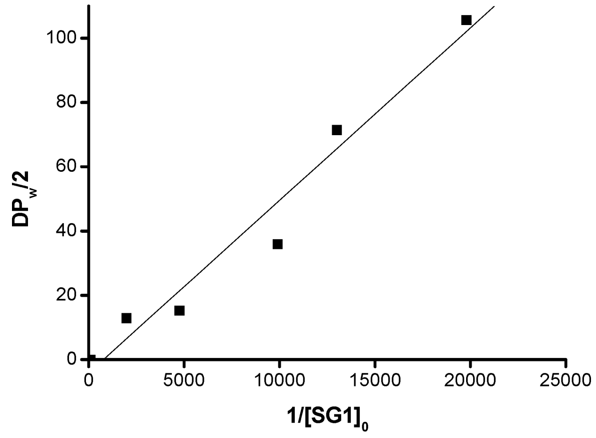


Figure 4. $DP_w/2$ vs $1/[SG1]_0$ from the RNR−PLP−SEC experiments carried out at 40 °C for the PS−SG1 system; $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz.

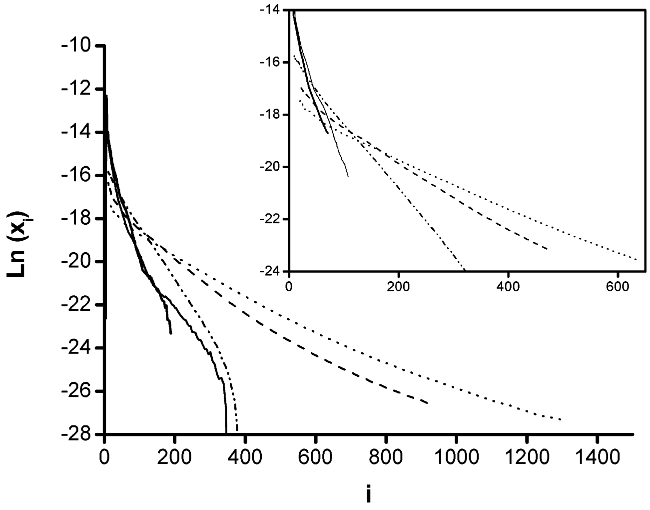


Figure 5. Logarithmic chain length number distribution of polystyrenes obtained by RNR−PLP−SEC at 40 °C with various SG1 concentrations. $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz; $[SG1]_0 = 7.7 \times 10^{-5}$ (· · ·); 5.04×10^{-5} (- - -); 1.1×10^{-4} (-· ·-); 2.1×10^{-4} (**—**); 5.04×10^{-4} mol L^{-1} (—).

As long as t_d fulfilled eq 7, no significant variation of k_c was observed by decreasing the frequency ($DP_n = 23 \pm 2$ for a frequency ranging from 3 to 10 Hz, for

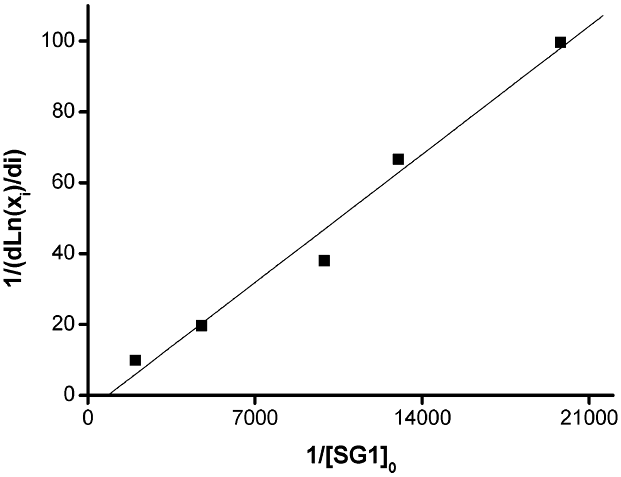


Figure 6. Inverse of the slope of the logarithmic chain length number distribution vs $1/[\mathrm{SG1}]_0$ for polystyrenes obtained by RNR−PLP−SEC at 40 °C, for the PS−SG1 system. $[\mathrm{DMPA}]_0 = 10^{-2}$ mol L^{-1}; $[\mathrm{M}]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz.

example) whatever the calculation method used. In the same manner, the photoinitiator concentration (10^{-1}–10^{-3} mol L^{-1}; see Table 2) did not influence the recombination rate constant value whatever the $[\mathrm{PI}]_0/[\mathrm{SG1}]_0$ ratio. In SP−PLP experiments, the choice of the photoinitiator is crucial for the validity of the measurement.[70] The photodecomposition of DMPA at low or moderate temperature produces two radicals with different reactivity toward monomer. On the time scale of the experiment, the acetal fragment does not initiate the polymerization and just acts as a terminator. This secondary reaction must be taken into account using a simulating software for the determination of k_t, but in our case, the acetal fragment can compete with the nitroxide to recombine with the macroradicals. Buback[71] recently presented a suitable photoinitiator (2-methyl-4′-(methylthio)-2-morpholinopropiophenone, MMMP), which produces two primary radicals, both adding rapidly to the monomer. Replacing DMPA by MMMP in our experiments (Table 2, entry 11) did not cause any significant change in the molar mass distribution and therefore in the k_c value. The type of apparatus has been moreover examined. A measurement using a Nd:YAG laser (355 nm) instead of the pulsed lamp (broad UV spectrum) has been carried out (Table 2, entry 10). Provided that a very low pulse energy (<5 mJ pulse^{-1}) is used to generate the initial $[\mathrm{R}^\bullet]_0$ at a sufficiently low level to favor the recombination with nitroxides with regard to the alkyl radical self-termination, no significant changes are obtained in the k_c value.

The effect of the experiment duration, t_R, has been examined, too. Pulsed lamp polymerizations at 40 °C, with a SG1 concentration of 7.7×10^{-5} mol L^{-1} and a DMPA concentration of 1.33×10^{-2} mol L^{-1}, have been carried out for 1−30 min. The k_c values determined in each experiment are summarized in Table 3, and the chromatogram for entries 4 and 6 are presented in Figure 7. These results show that there was a good repeatability for experiments having a reaction time below 5 min. For longer experiments a bimodal distribution appeared, most probably resulting from the irreversible alkyl radical self-termination operating after disappearance of the nitroxide. In this case, the shape of the molar mass distribution shown in Figure 7 resembles that of a PLP experiment where radical termination at the pulse is the dominant chain growth breaking event. As a result, the chain length number distribution did not exhibit the expected exponential evolution, and the polydispersity index was much larger than 2 (the theoretical polydispersity index of the Flory−Schulz distribution). Consequently, no reliable k_c could be derived. The CLD method is thus the best one to critically assess the results. Care must then be taken in using the Mayo technique alone, without a careful examination of the whole molar mass distribution, since it might lead to erroneous k_c values.

Discussion of the k_c Value for the PS−SG1 system. The accuracy of the measurements is certainly not better than 30%, as estimated by comparing the k_c value determined at 40 °C with the same SG1 concentration and various initiator concentrations. The major sources of error are the SEC analysis and the correct evaluation of the nitroxide concentration, which depends in particular on a reliable purity value.

The SG1 provided by ARKEMA had an estimated purity of 85% using a HPLC procedure.[72] ESR experiments using a solution of TEMPO as standard have been used to determine it more precisely: a value of 85 ± 2% was actually estimated.

The assessment of the recombination rate constant involves the measurement of different properties of the molar mass distribution. Bruessau et al.[61] have studied the repeatability and the reproducibility of SEC results, performing round robin tests with polystyrene samples. They recommended to work with M_w (9% of standard deviation for the reproducibility) rather than with M_n (16% of standard deviation for the reproducibility) to increase the precision of the measurement. The highest precision is obtained either with M_w or with the range of the molar mass distribution, which corresponds to 10−90% of the integral distribution curve (11% of standard deviation for the reproducibility).

In our case, when M_n was below 5000 g mol^{-1}, the three methods seemed to be efficient, giving repeatable and close results (see Tables 1 and 2). It can be noticed that the k_c values obtained from the Mayo procedure with both DP_n and $\mathrm{DP}_w/2$ were lower than those obtained from the CLD method (Table 2). Typically, the results were in the order $k_c(\mathrm{DP}_w/2) < k_c(\mathrm{DP}_n) < k_c(\mathrm{CLD})$. For low molar mass polymers the CLD method yielded more repeatable k_c (Table 1) as described by Russell[62] for the determination of chain transfer constants. The CLD method may thus lead to the most accurate k_c, and all the values discussed in the following have been obtained by this method.

From the slopes in Figures 3, 4, and 6, the recombination rate constant between PS macroradicals and SG1 can be determined (Table 4). The average value at 40 °C is equal to 2.6×10^5 L mol^{-1} s^{-1}. To assess the temperature effect, polymerizations were performed from 15 to 82 °C in the following conditions: $[\mathrm{SG1}]_0 = 8.3 \times 10^{-5}$ mol L^{-1} and $[\mathrm{DMPA}]_0 = 1.0 \times 10^{-2}$ mol L^{-1}. The plot of the k_c value against the temperature is presented in Figure 8. The experiments were conducted at a single SG1 concentration. The k_c value increased from 1.1×10^5 to 4.0×10^5 L mol^{-1} s^{-1} when the temperature was raised from 15 to 82 °C. Linear extrapolation with CLD method to 120 °C of the second part of the sigmoid displayed in Figure 8 leads to approximately 5.3×10^5 L mol^{-1} s^{-1}. This value is close to those estimated by Benoit et al.[9] ($k_c = 5.7 \times 10^5$ L mol^{-1} s^{-1} at 120 °C) and by Lutz et al.[41] ($k_c = 5.6 \times 10^5$ L mol^{-1} s^{-1} at 120 °C) and close to the value supposed

Table 1. Influence of the Frequencyon RNR−PLP−SEC Experiments Carried out at 40 °C for the PS−SG1 System[a]

entry	freq (Hz)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	d ln(x_i)/di	k_c[b] (L mol^{-1} s^{-1})	k_c[c] (L mol^{-1} s^{-1})	k_c[d] (L mol^{-1} s^{-1})	k_c[e] (L mol^{-1} s^{-1})
1	10	3100	8500	2.7	4.8×10^{-2}	2.6×10^5	1.7×10^5	3.3×10^5	2.6×10^5
2	7	2900	5400	1.9	5.2×10^{-2}	2.8×10^5	2.8×10^5	3.6×10^5	3.0×10^5
3	5	2500	4000	1.6	5.1×10^{-2}	3.3×10^5	3.8×10^5	3.6×10^5	3.6×10^5
4	3	2880	5500	1.9	5.1×10^{-2}	2.8×10^5	2.7×10^5	3.6×10^5	3.0×10^5

[a] $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; $[SG1]_0 = 7.86 \times 10^{-5}$ mol L^{-1}. [b] Calculated with eq 2. [c] Calculated with eq 3. [d] Calculated with eq 6. [e] Average recombination rate constant k_c determined by combining the three methods.

Table 2. Influence of the Photoinitiator/[SG1]$_0$ Couple for the Conditions 40 °C, $[M]_0 = 8.74$ mol L^{-1}, and Frequency = 10 Hz

entry	photo-initiator	$[PI]_0$ (mol L^{-1})	$[SG1]_0$ (mol L^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	d ln(x_i)/di	k_c[a] (L mol^{-1} s^{-1})	k_c[b] (L mol^{-1} s^{-1})	k_c[c] (L mol^{-1} s^{-1})	k_c[d] (L mol^{-1} s^{-1})
1	DMPA	1.01×10^{-1}	7.86×10^{-5}	7300	15 800	2.2	1.47×10^{-2}	2.7×10^5	2.4×10^5	2.7×10^5	2.6×10^5
2	DMPA	1.01×10^{-1}	7.86×10^{-5}	7850	17 300	2.2	1.52×10^{-2}	2.5×10^5	2.2×10^5	2.8×10^5	2.5×10^5
3	DMPA	5.53×10^{-2}	7.86×10^{-5}	7050	12 500	1.8	1.68×10^{-2}	2.8×10^5	3.1×10^5	3.0×10^5	3.0×10^5
4	DMPA	5.53×10^{-2}	7.86×10^{-5}	7220	13 000	1.8	1.68×10^{-2}	2.7×10^5	2.9×10^5	3.0×10^5	2.9×10^5
5	DMPA	1.3×10^{-2}	7.7×10^{-5}	7650	17 800	2.3	1.50×10^{-2}	2.6×10^5	2.2×10^5	2.8×10^5	2.6×10^5
6	DMPA	5.0×10^{-3}	7.86×10^{-5}	7700	15 000	1.9	1.45×10^{-2}	2.6×10^5	2.6×10^5	2.6×10^5	2.6×10^5
7	DMPA	5.0×10^{-3}	7.86×10^{-5}	7400	15 300	2.1	1.57×10^{-2}	2.7×10^5	2.5×10^5	2.9×10^5	2.7×10^5
8	DMPA	1.1×10^{-3}	7.86×10^{-5}	7200	15 000	2.1	1.60×10^{-2}	2.7×10^5	2.6×10^5	2.9×10^5	2.7×10^5
9	DMPA	1.1×10^{-3}	7.86×10^{-5}	7650	15 700	2.1	1.53×10^{-2}	2.6×10^5	2.5×10^5	2.8×10^5	2.6×10^5
10	DMPA[e]	1.0×10^{-2}	4.34×10^{-5}	11 900	22 400	1.9	8.7×10^{-3}	2.9×10^5	3.0×10^5	2.8×10^5	2.9×10^5
11	MMMP	1.01×10^{-2}	7.86×10^{-5}	7250	14 600	2.0	1.48×10^{-2}	2.7×10^5	2.6×10^5	2.7×10^5	2.7×10^5

[a] Calculated with eq 2. [b] Calculated with eq 3. [c] Calculated with eq 6. [d] Average recombination rate constant k_c determined by combining the three methods. [e] Using the laser apparatus (see Experimental Section).

Table 3. Influence of the Duration of the Experiment for the Conditions 40 °C, Frequency = 10 Hz, $[DMPA]_0 = 10^{-2}$ mol L^{-1}, and $[M]_0 = 8.74$ mol L^{-1}

entry	time (min)	[SG1] (mol L^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	d ln(x_i)/di	k_c[a] (L mol^{-1} s^{-1})	k_c[b] (L mol^{-1} s^{-1})	k_c[c] (L mol^{-1} s^{-1})	k_c[d] (L mol^{-1} s^{-1})
1	1	7.7×10^{-5}	7640	17 900	2.3	1.45×10^{-2}	2.6×10^5	2.2×10^5	2.7×10^5	2.5×10^5
2	2	7.7×10^{-5}	7600	14 000	1.8	1.51×10^{-2}	2.6×10^5	2.8×10^5	2.8×10^5	2.7×10^5
3	3	7.7×10^{-5}	7770	18 600	2.4	1.47×10^{-2}	2.6×10^5	2.1×10^5	2.7×10^5	2.5×10^5
4	5	7.7×10^{-5}	7650	17 800	2.3	1.50×10^{-2}	2.6×10^5	2.2×10^5	2.8×10^5	2.5×10^5
5	10	7.7×10^{-5}	11800	20 500	1.7	1.24×10^{-2}	1.7×10^5	1.9×10^5	2.3×10^5	1.9×10^5
6	30	5×10^{-4}	20500	150 000	7.3	*e*	1.5×10^4	3.9×10^3		9.2×10^3
7	3	0	15100	236 800	15.7	*e*				

[a] Calculated with eq 2. [b] Calculated with eq 3. [c] Calculated with eq 6. [d] Average recombination rate constant k_c determined by combining the three methods. [e] The molar mass distribution does not exhibit an exponential evolution.

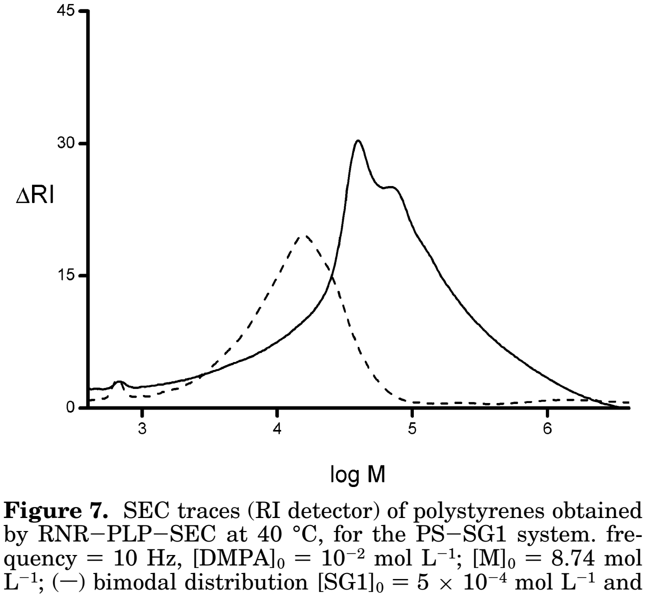


Figure 7. SEC traces (RI detector) of polystyrenes obtained by RNR−PLP−SEC at 40 °C, for the PS−SG1 system. frequency = 10 Hz, $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; (—) bimodal distribution $[SG1]_0 = 5 \times 10^{-4}$ mol L^{-1} and $t_R = 30$ min; (- - -) monomodal distribution $[SG1]_0 = 7.7 \times 10^{-5}$ mol L^{-1} and $t_R = 5$ min.

Table 4. Determination of the k_c Value for the Conditions 40 °C, Frequency = 10 Hz, $[DMPA]_0 = 10^{-2}$ mol L^{-1}, and $[M]_0 = 8.74$ mol L^{-1}

method	Figure	slope	r^2	k_c (L mol^{-1} s^{-1})
Mayo with DP_n	3	5.45×10^{-3}	0.9984	2.6×10^5
Mayo with $DP_w/2$	4	5.36×10^{-3}	0.9628	2.6×10^5
chain length distribution	6	5.16×10^{-3}	0.9793	2.7×10^5

by Fischer[20] in simulations ($k_c = 7.2 \times 10^5$ L mol^{-1} s^{-1} at 120 °C).

As already reported by Fischer[38] for model radicals, the temperature dependency of the rate constant cannot be described by the Arrhenius equation. Indeed, the sigmoid evolution of k_c vs the temperature shown in Figure 8 was also observed for the recombination of phenylethyl radical with SG1.[38] Fischer pointed out two potential explanations for this phenomenon:[38] (i) the presence of a short-lived intermediate to form the coupling product; (ii) a barrierless single-step reaction with a low exothermicity where the free energy of activation is dominated by a large negative entropy term. The second explanation was however presented by Fischer[38] as the most plausible one.

k_c Value for the PS−TEMPO System. The recombination rate constant k_c between PS macroradicals and TEMPO has been estimated to 6.7×10^7 L mol^{-1} s^{-1} by Fukuda[73,74] using $K = 2.1 \times 10^{-11}$ mol L^{-1} and $k_d = 1.6 \times 10^{-3}$ s^{-1}. In contrast to SG1, this value for TEMPO is very close to that measured for model radicals[38] (2.2×10^8 L mol^{-1} s^{-1}). The predictive phase diagram for the PS−TEMPO system is displayed in Figure 9 and

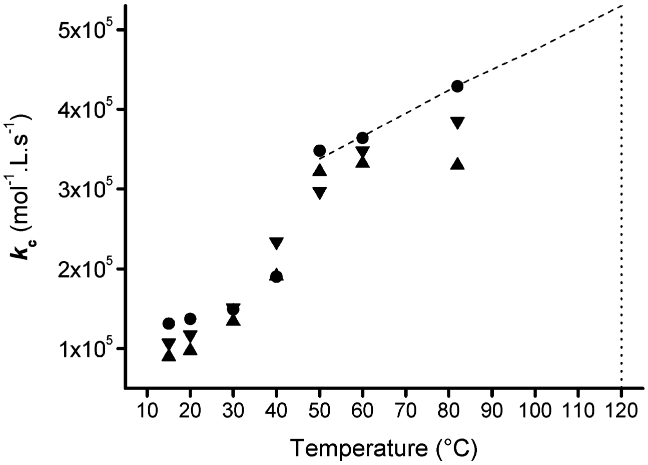


Figure 8. Temperature dependence of the recombination rate constant, k_c, between PS macroradicals and SG1. $[SG1]_0 = 8.3 \times 10^{-5}$ mol L^{-1}; $[DMPA]_0 = 10^{-2}$ mol L^{-1}; $[M]_0 = 8.74$ mol L^{-1}; frequency = 10 Hz. (▲) Mayo method with $DP_w/2$; (▼) Mayo method with DP_n; (●) chain length distribution method.

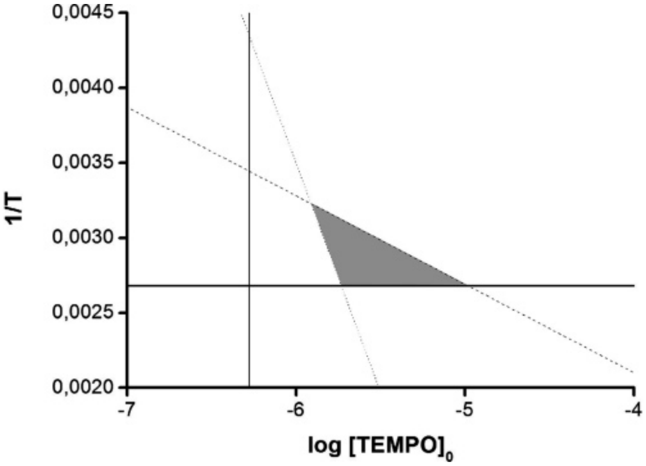


Figure 9. Predictive phase diagram for the PS−TEMPO system. $k_p = 4.27 \times 10^7 e^{-32500/RT}$ mol^{-1} L s^{-1}; $k_t = 1.06 \times 10^9 e^{-6500/RT}$ mol^{-1} L s^{-1}; $[P^\bullet]_0 = 10^{-7}$ mol L^{-1}; $DP_{MIN} = 10$; $[M]_0 = 8.74$ mol L^{-1} ; frequency = 10 Hz; $T_c = 100$ °C; preestimated $k_c = 10^8$ L mol^{-1} s^{-1}. (—) Single-pulse condition: eq 13; (**—**) Temperature condition: eq 12; (· · ·) Recombination with TEMPO as the main chain growth breaking event: eq 15; (- - -) SEC limitation: eq 14.

shows a more restricted domain than for PS−SG1 (area for PS−TEMPO system is equal to 8.14×10^{-6} mol L^{-1} K^{-1} compared with 1.71×10^{-3} mol L^{-1} K^{-1} for PS−SG1), owing to the much larger k_c. The nitroxide concentration should be lower than 5.0×10^{-7} mol L^{-1} to achieve M_n higher than 3000 g mol^{-1}. This is too low to maintain a constant concentration throughout the polymerization, unless conversion is kept very small (but then the limitation resides in the too low amount of recovered polymer for the SEC analysis).

In the range of TEMPO concentration between 10^{-3} and 10^{-6} mol L^{-1} at 40 °C, 10 Hz, and with a DMPA concentration of 1.0×10^{-2} mol L^{-1}, no polymer was detected. At $[TEMPO]_0 = 10^{-7}$ mol L^{-1}, a measurement could be performed and gave an average k_c value of 1.75×10^8 L mol^{-1} s^{-1} ($k_c(M_w/2) = 1.4 \times 10^8$; $k_c(M_n) = 1.8 \times 10^8$; $k_c(\mathrm{CLD}) = 2.1 \times 10^8$ L mol^{-1} s^{-1}). The recombination rate constant obtained by this way is in good agreement with the values given in the literature. Even if this method is not really well-suited for the PS−TEMPO system, the approximate value obtained was coherent with the other works on the determination of k_c.

Conclusions

Direct experimental measurements of the recombination rate constant between macroradicals and nitroxides have been performed by radical nitroxide recombination−pulsed lamp polymerization−size exclusion chromatography (RNR−PLP−SEC). This new method combines a single pulse PLP approach with the analysis of the SEC molar mass distribution. The molar masses are used to determine k_c, in a similar way as that traditionally applied in the determination of the chain transfer rate constants, i.e., the Mayo method using the number- and weight-average degrees of polymerization and the full chain length distribution method. The procedure has been validated by some consistency checks (influence of frequency, nature, and concentration in photoinitiator, duration of the experiment). We have shown that both procedures gave reliable results, but the CLD method allows to be more accurate when low molar mass polymers are obtained.

The recombination rate constant between PS macroradicals and SG1 has been measured: $k_c = 2.6 \times 10^5$ L mol^{-1} s^{-1} at 40 °C. The value increased from 1.1×10^5 L mol^{-1} s^{-1} at 15 °C to 4.0×10^5 L mol^{-1} s^{-1} at 82 °C. The extrapolation at 120 °C led to approximately 5.3×10^5 L mol^{-1} s^{-1}, in good agreement with the values already reported in the literature. The application of this technique to other systems depends on the predictive phase diagram, and in some cases like the PS−TEMPO system, this technique is not the most suitable because of a too small temperature−concentration domain available. Works are however in progress to expand the range of monomers and nitroxides.

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