Kinetics and Mechanism of Controlled Free-Radical Polymerization of Styrene and *n*-Butyl Acrylate in the Presence of an Acyclic β-Phosphonylated Nitroxide[†]

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Abstract: This study investigates the kinetics of free radical polymerization of styrene and *n*-butyl acrylate carried out in the presence of *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN). With this stable radical as chain growth moderator, it is demonstrated that the polymerization of these two monomers exhibits a controlled character. The mechanism of polymerization is essentially the same as that described for other "living"/controlled radical polymerizations: the chains form a large pool of dormant species that can be reversibly activated, and only a minute fraction of them propagate at a given time. Using dilatometry and electron spin resonance (ESR), the evolution of the concentration of polymeric radicals and that of DEPN could be measured as a function of time. It appears that these DEPN-mediated polymerizations are driven toward a pseudo-stationary state that is reached after an initial period of a few minutes. During this pseudo-stationary phase, the concentration of polymeric radicals and that of DEPN remained essentially constant, which allowed us to determine the (K) equilibrium constant between dormant and active species and also the rate constants of reversible activation (k_d) and deactivation (k_{rec}) for each monomer. For purposes of comparison, a series of polymerizations were simulated using the PREDICI package: both experimental and simulated data were found to fall in rather good agreement.

Introduction

Important progress has been made over the last years to control free radical polymerizations and better understand the mechanisms involved. Three main methods with their specificity and limitations have been shown to allow a controlled propagation of free radicals: either nitroxide-mediated radical polymerization (NRP),[1] atom transfer radical polymerization (ATRP),[2] or reversible addition–fragmentation chain transfer (RAFT)[3] can indeed be used to prepare well-defined polymeric samples from miscellaneous monomers. However, these three methods are not alike: compared to ATRP and RAFT, NRP appears until now of limited applicability; only two families of monomers, namely styrenics and alkyl acrylates, have actually been shown to polymerize under "living"/controlled conditions in the presence of nitroxides. Despite this, NRP still attracts much interest because it is based on potentially simpler systems than ATRP or RAFT and does not call for any added metal complex or complicated syntheses. Since the initial report by Georges and co-workers[1b] on the use of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to control the polymerization of styrene, many other contributions have been made to improve and expand NRP through the use of miscellaneous nitroxides. For example, we showed in a previous report[4a–f] that *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN) is not only efficient at controlling the radical polymerizations of styrene and of alkyl acrylates, affording samples of polystyrene (PS) and poly(*n*-butyl acrylate) (PBuA) with polydis-

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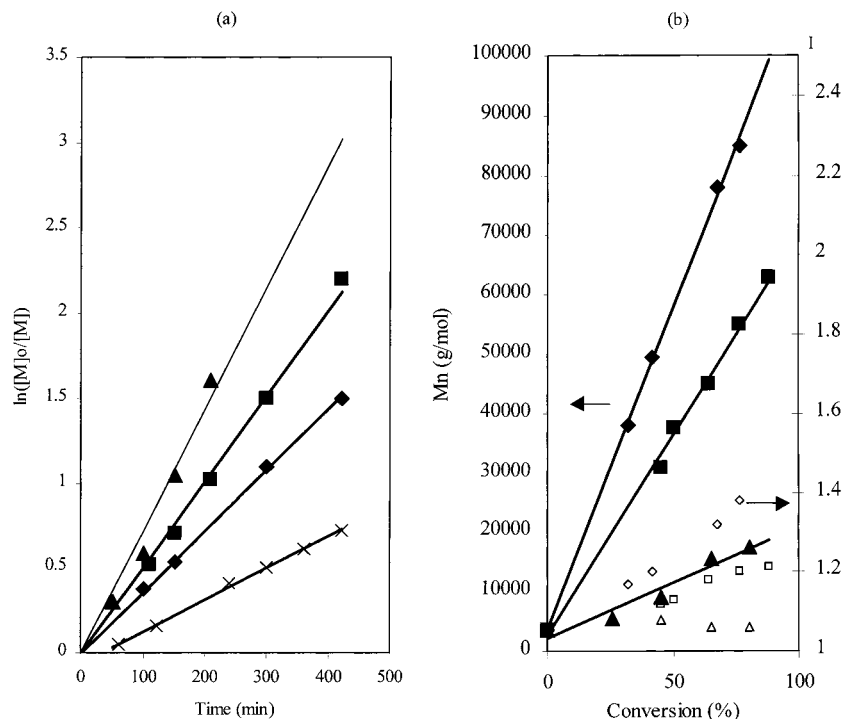
Figure 1. Variation of $\ln([M]_o/[M])$ versus time (a) and evolution of $\overline{M}_n$ as a function of the conversion (b) in DEPN-mediated polymerization of styrene, PS$_{\overline{35}}$DEPN being used as macroinitiator; ◆: $[PS_{\overline{35}}DEPN]_0 = 0.76 \times 10^{-2}$ M (120000 g/mol targeted); ■: $[PS_{\overline{35}}DEPN]_0 = 1.3 \times 10^{-2}$ M (70000 g/mol targeted); ▲: $[PS_{\overline{35}}DEPN]_0$ 4.3×10^{-2} M (20000 g/mol targeted); ×: Thermal polymerization. Variation of polydispersity index (*I*) as a function of conversion: the corresponding empty symbols have been used □: $[PS_{\overline{35}}DEPN]_0 = 1.3 \times 10^{-2}$ M (70000 g/mol targeted) for instance.

persities lower than 1.1, but it also allows faster propagation than any other nitroxides.

Thanks to the seminal investigations of Matyjaszewski,[5] Georges,[6] Fukuda,[7] and Fischer[8a-c] and others,[9] we now have a clear picture of the mechanism that is involved in polymerization mediated by TEMPO. In this study, we explore the kinetics of polymerization of styrene and *n*-butyl acrylate with DEPN as chain growth moderator. Mechanistically, this system should not be different from other controlled radical polymerizations that imply the reversible activation−deactivation of growing chains.

Using the methodology described by Fukuda,[7c,d] we have determined the rate constant of activation (k_d) of dormant PS-DEPN and PBuA-DEPN oligomeric adducts that were purposely prepared in separate experiments. In situ ESR measurements have been concomitantly conducted in order to monitor the level of free DEPN formed as a function of time. From the knowledge of the concentration of DEPN, the equilibrium constant ($K = k_d/k_{rec}$) could be calculated; the rate constant of reversible deactivation (k_{rec}) was then easily deduced.

To check whether the rate constants measured and the mechanism proposed correspond to reality, we have used the PREDICI program and simulated the DEPN-mediated polymerization of styrene. The main purpose of these simulations was to compare experimental data (conversion, [DEPN], etc.) with simulated ones and demonstrate that the rate constants measured are indeed consistent.

Results and Discussion

Kinetics of DEPN-Mediated Polymerization of Styrene. Before undertaking the determination of the rate constants of

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activation (k_d) and reversible deactivation (k_{rec}), we felt it was essential to first check whether the polymerization of styrene exhibits a controlled character under the experimental conditions that were designed for the kinetic study. Three experiments were therefore carried out with three different concentrations of PS-DEPN used as macroinitiator in bulk styrene. These polymerizations were conducted at 120 °C, and the conversions were followed by gravimetry and cross-checked by dilatometry. Aliquots were removed from the reaction medium and characterized by SEC in order to monitor the evolution of $\overline{M_n}$ as a function of conversion.

It can be seen from Figure 1 that the free radical polymerization of styrene exhibits a truly controlled character when initiated by PS-DEPN: the two criteria that are generally taken as indicators of the livingness of a chain process are indeed concomitantly fulfilled; all points in the conversion curve as well as those of the $\overline{M_n}$ curve are found to form straight lines passing through the origin.

For the kinetic study that was subsequently undertaken, a dilatometer and an ESR tube were filled with a same solution of styrene containing a known concentration of PS$_{\overline{35}}$DEPN (2.0×10^{-2} M). After three cycles of degassing, the two reactors were respectively placed in an oil bath and an ESR spectrometer thermostated to 120 °C. Both the conversion of styrene and the concentration of free DEPN formed by the persistent radical effect were recorded as a function of time. From the $\ln[M]_0/[M]$ versus time plot, it is easy to calculate the actual concentration of [PS•] and establish its evolution with time: the data points in the conversion plot can either be taken equal to $k_p[PS•]_t$ following the classical formalism or be identified with $(3/2)k_p[PS•]_{tF}$ using the expression established by Fischer[8d] who demonstrated that the concentration of transient radicals obeys an unusual law:

$$[P•] = \left(\frac{K[I]_0}{3k_t}\right)^{1/3} \cdot t^{-1/3}$$

if their irreversible self-termination is not neglected or omitted from such a mechanism. As to the value of k_p for styrene at 120 °C, it could be found in the literature ($k_p = 2000$ L·mol^{-1}·s^{-1} ,[10h]). Figure 2a shows how [PS•] varies—that differs from [PS•]$_F$ only by a factor 3/2—as a function of time; two phases can be distinguished: the first step is characterized by a surge of polymeric radicals with a steep increase of [PS•] that lasts about 10 min. In this initial phase, the dissociation of alkoxyamines predominates and the rise in [PS•] is accompanied by substantial irreversible termination because the rate of the latter process is faster than the rate of reversible deactivation by DEPN, its concentration in the medium being still too low. As polymerization proceeds (Figure 2b) in this initial phase, DEPN accumulates and reaches a level that becomes more favorable to an efficient trapping of polymeric radicals: the
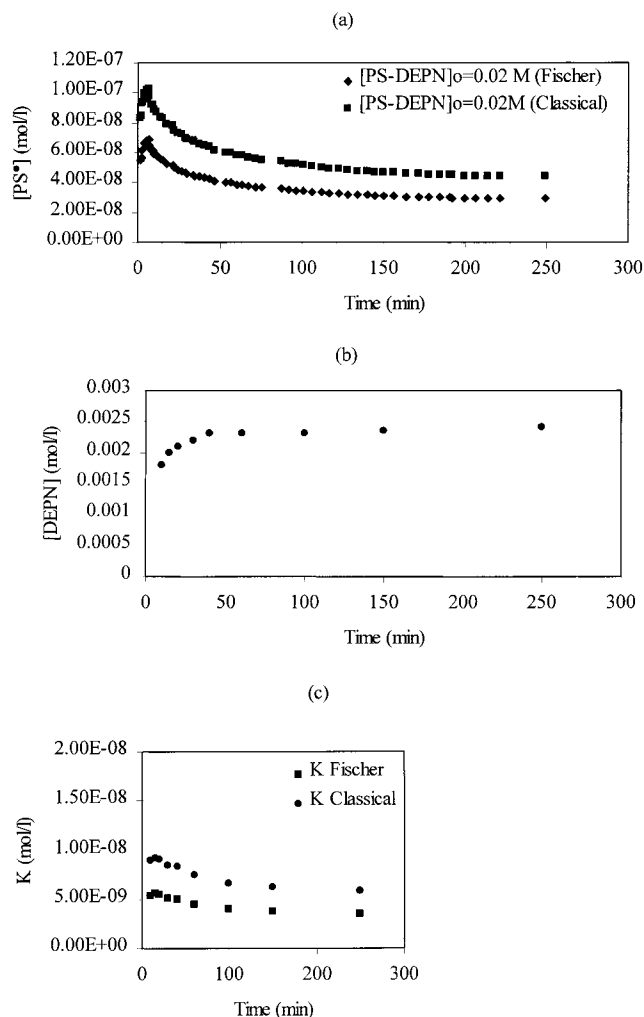
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(a)

(b)

(c)

Figure 2. Variation of [PS•] (a) and [DEPN] (b) as a function of time in DEPN-mediated polymerization of styrene with [PS$_{\overline{35}}$DEPN] as a macroinitiator; [PS$_{\overline{35}}$DEPN]$_0$ = 2.0×10^{-2} M. Evolution of K with time (c).

equilibrium between active and dormant chains is then compelled to shift toward the latter species. This eventually results in the decrease of [PS•] which occurs after it passes through a maximum.

In the second phase, the decrease of [PS•] that is observed is not monotonic. After experiencing a sharp diminution, [PS•] then decreases only marginally. Indeed, one can still notice a decay of [PS•] in the final phase, but this loss of polymeric radicals is hardly perceptible so that [PS•] can be considered constant [PS•] $\approx 3.0 \times 10^{-8}$ mol/L. This overall variation of [PS•] as a function of time is very similar to the profiles simulated by Fukuda et al.[7c] in their investigation of the TEMPO-mediated polymerization of styrene and by Fischer et al.[8b,c] in their study of the homolysis of TEMPO-based alkoxyamines. The only differences that can be discerned between the profiles of [PS•] as determined by us and those calculated by these two authors concerns the final phase: both Fukuda and Fischer's simulations show a continuous decrease of polymeric radicals whereas this study unveiled such a tiny dwindling of the concentration of polymeric radicals that it can be assumed quasi-constant. This discrepancy certainly arises from the fact that the Fischer and Fukuda models assume the rate constant of irreversible termination (k_t) to be independent of the chain size and the probability for bimolecular termination to be only dependent on [PS•]. In reality, it is well established[10]

that the rate constant of termination is chain size and viscosity dependent and tends to decrease as the chains grow which is reflected in our experiments by an almost stabilization of the concentration of polymeric radicals.

On the other hand, the in situ ESR characterization of the reaction medium shows that the concentration of DEPN steeply increases during the first 10 min and then experiences only a very modest rise throughout polymerization, approaching its pseudostationary value from below: this is slightly different from the results simulated by Fischer who predicted that the concentration of nitroxide should continue to grow for the same reason as that previously invoked. The profiles of [PS$^{\bullet}$] and [DEPN] reveal how the system self-regulates and generates its excess of DEPN that is necessary for a controlled propagation to occur: the level of DEPN formed gives an indication of the extent of termination ($\approx$10% of chains irreversibly deactivated) the system undergoes in the initial phase of polymerization. As the chains get longer, the probability for irreversible termination obviously decreases, and the system has produced enough free DEPN to reversibly deactivate polymeric radicals into dormant alkoxyamines.

Since the evolution of [PS$^{\bullet}$] and [DEPN] as a function of time is known from dilatometry and ESR experiments, all the data needed to calculate the equilibrium constant (K) are available. The expression of the rate of disappearance of polymeric can be written as:

$$-\frac{d[PS^{\bullet}]}{dt} = k_d[PS_{\overline{35}}DEPN]_t - k_{rec}[PS^{\bullet}]_t[DEPN]_t + k_t[PS^{\bullet}]_t^2 \tag{1}$$

As previously shown, [PS$^{\bullet}$] can reasonably be assumed constant, provided both [PS$^{\bullet}$] and [DEPN] values are taken long after the initial phase of polymerization.

In that event, -d[PS$^{\bullet}$]/dt can be considered as being equal to 0 and therefore the $k_t[PS^{\bullet}]_t^2$ term can be neglected. The previous eq 1 can then be rewritten and the equilibrium constant K expressed as:

$$K = \frac{k_d}{k_{rec}} = \frac{[PS^{\bullet}]_t \cdot [DEPN]_t}{[PS_{\overline{35}}DEPN]_t} \tag{2}$$

For $t = 250$ min, K can easily be deduced at this precise time from [PS$^{\bullet}$]$_{250min}$ and [DEPN]$_{250min}$ after remembering that [PS-DEPN]$_{250min}$ represents only 90% of its initial value ([PS-DEPN]$_0 = 2.0 \times 10^{-2}$ M). To obtain the mean value of K, the K versus time plot was established (Figure 2c) using the above equation. It can be seen that K stays constant during the second phase of the polymerization and is equal to:

$$K = 6.0 \times 10^{-9} \, mol \cdot L^{-1} \quad at \quad 120 \, °C$$

These values of K are at least 2 orders of magnitude higher than the one determined for the TEMPO-mediated polymerization of styrene,[7c,d] indicating that DEPN-controlled systems can secure a higher concentration of active radicals and yet exhibit a controlled character.

K_F can also be determined using the Fischer expression which is more general than eq 2; since the kinetic analysis of the persistent radical effect proposed by the same author does take into account irreversible termination at any instant, 2bis is valid throughout polymerization (unlike eq 2). Provided $K_F <$
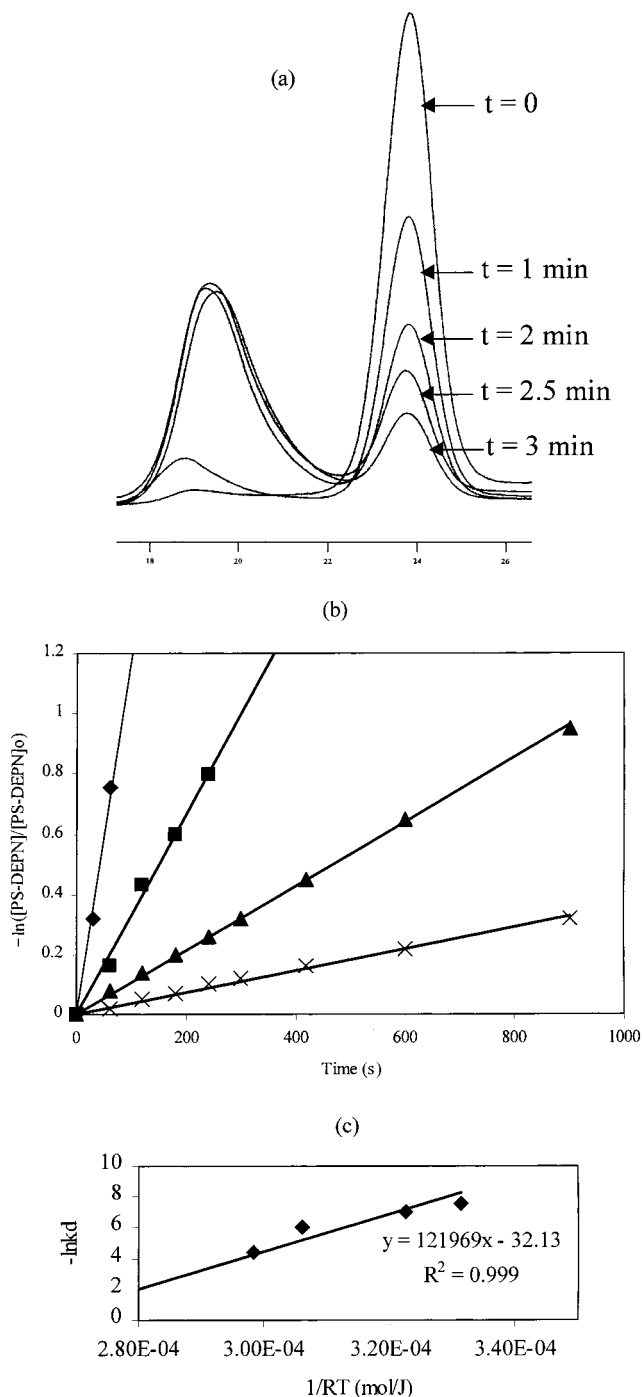

Figure 3. Disappearance of PS$_{\overline{35}}$DEPN at 120 °C as followed by SEC (a); determination of the rate constant of dissociation (k_d) of PS$_{\overline{35}}$DEPN at four different temperatures (b): $\blacklozenge$ = 130 °C; $\blacksquare$ = 120 °C; $\blacktriangle$ = 100 °C; $\times$ = 90 °C, and the corresponding Arrhenius plot (c).

[PS-DEPN]k_{rec}/4k_t, K_F can be written as:

$$K_F = \frac{k_d}{k_{rec}} = \frac{[PS^{\bullet}]_{t,F} \cdot [DEPN]_t}{[PS_{\overline{35}}DEPN]_0} \tag{2bis}$$

For $t = 250$ min, (2bis) gives $K_F = 3.5 \times 10^{-9} mol \cdot L^{-1}$ at 120 °C. This value of K_F is not only close to the one (K) obtained using the classical approach, but it is also in rather good agreement with the K value determined for molecular DEPN-based alkoxyamine in absence of any monomer.
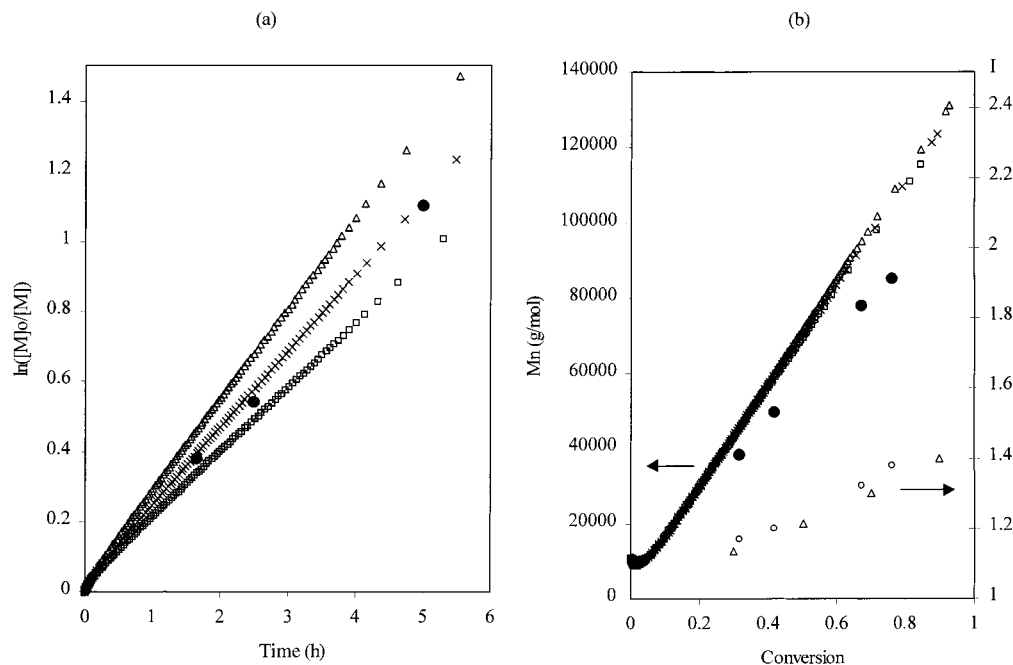
(a)   (b)

Figure 4. Simulated variations of $\ln([M]_0/[M])$ versus time (a) and evolution of $\overline{M_n}$ as a function of the conversion (b) in DEPN-mediated polymerization of styrene at 120 °C with $[PS\text{-}DEPN]_0 = 0.76 \cdot 10^{-2}$ mol/L as macroinitiator: ●: experimental points, △: using $k_{rec} = 5.7 \cdot 10^5$ L·mol^{-1}, □: using $k_{rec,F} = 9.7 \cdot 10^5$ L·mol^{-1}, ×: using $k_{rec,m} = 7.7 \times 10^5$ L·mol^{-1} ($\log(7.7 \times 10^5) = [\log(5.7 \times 10^5) + \log(9.7 \times 10^5)]/2$. Variation of polydispersity index (I) as a function of conversion (empty corresponding symbols).
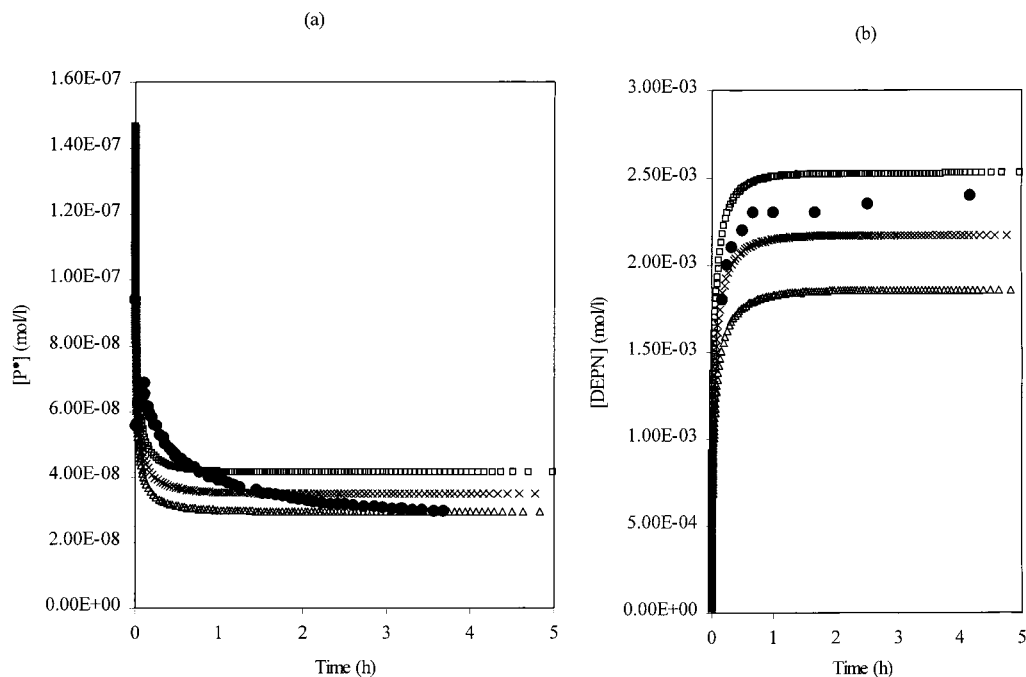
(a)   (b)

Figure 5. Simulated variations of $[P^{\bullet}]$ (a) and $[DEPN]$ (b) in DEPN-mediated polymerization of styrene at 120 °C with $[PS\text{-}DEPN]_0 = 2.0 \times 10^{-2}$ mol/L as a macroinitiator. ●: experimental points, △: using $k_{rec} = 5.7 \cdot 10^5$ L·mol^{-1}, □: using $k_{rec,F} = 9.7 \times 10^5$ L·mol^{-1}, ×: using $k_{rec,m} = 7.7 \times 10^5$ L·mol^{-1} ($\log(k_{rec,m}) = [\log(5.7 \times 10^5) + \log(9.7 \times 10^5)]/2$).

Following the determination of K, we attempted to evaluate k_d, using the methodology first described by Fukuda et al,[7c,d] who used SEC to monitor the disappearance of PS-TEMPO precursor. Styrene was mixed with a precise concentration of $PS_{\overline{35}}DEPN$, and the mixture obtained was divided in equal amounts in a series of five tubes; the latter were then degassed and heated to 120 °C for a prescribed time that was in any case chosen very short: each sample removed at time t was then analyzed by SEC. The initial concentration of $PS_{\overline{35}}DEPN$ was

purposely chosen rather low $[PS\text{-}DEPN]_0 \approx 10^{-4}$ mol/L so as to favor at the most propagation over other possible events and let the chains grow long enough before being blocked by DEPN. Under these experimental conditions and assuming that once activated the macroinitiator can only grow, the rate of disappearance of $PS_{\overline{35}}DEPN$ can be written as:

$$\frac{d[PS_{\overline{35}}DEPN]}{dt} = -k_d[PS_{\overline{35}}DEPN]_t \tag{3}$$
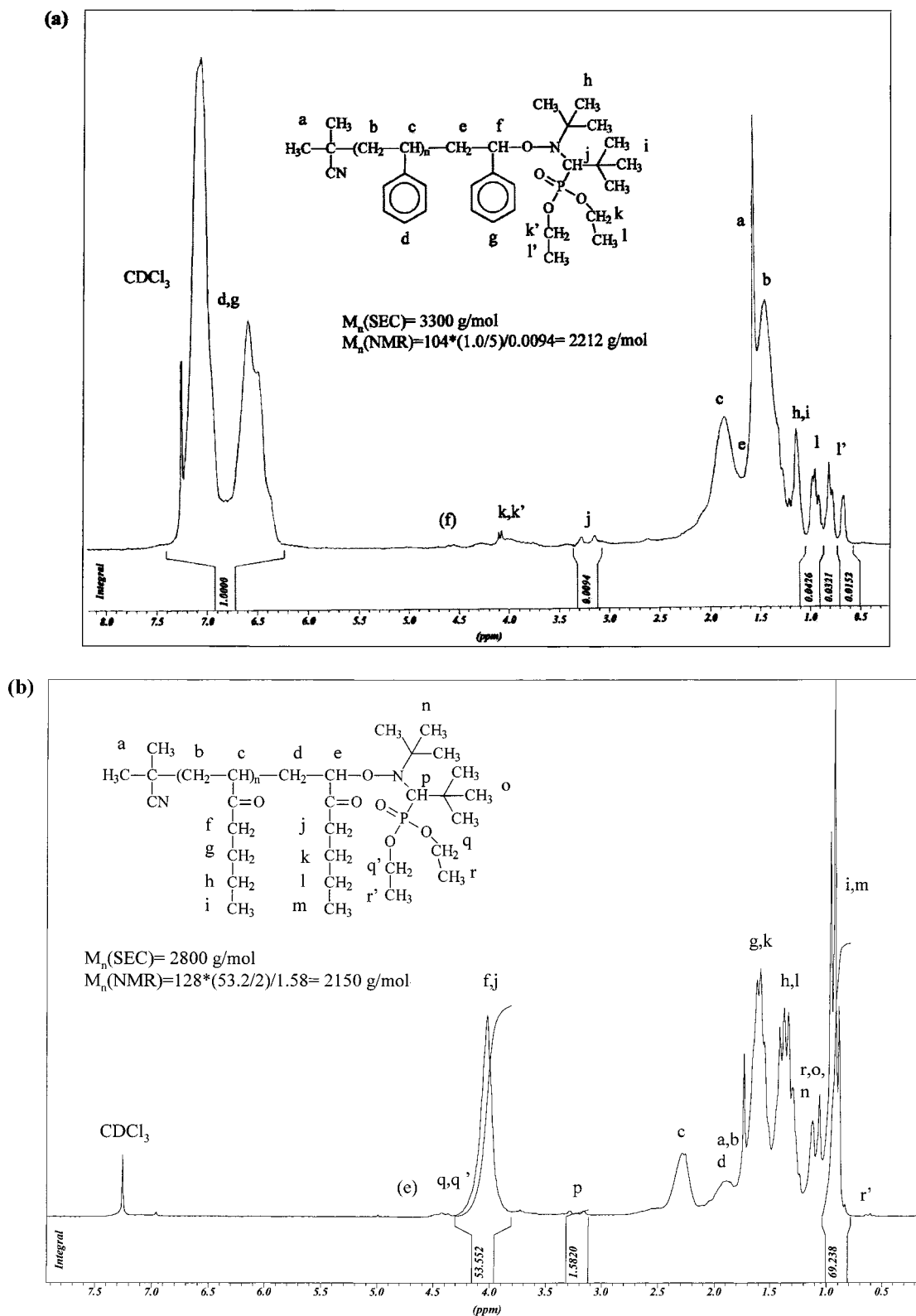
Figure 6. ^1H NMR spectra of $PS_{\overline{35}}DEPN$ adduct (a) and of $PBuA_{\overline{28}}DEPN$ macroinitiator (b).

Upon integration one obtains:

$$\ln\left(\frac{[PS_{\overline{35}}DEPN]_0}{[PS_{\overline{35}}DEPN]_t}\right) = k_d t \qquad (4)$$

Provided rigorously identical amounts of materials are injected in the SEC columns for each of the aliquots, one can identify the area (S) corresponding to the macroinitiator in the SEC traces

with its actual concentration and write (Figure 3a):

$$\ln\left(\frac{S_0}{S_t}\right) = \ln\left(\frac{[PS_{\overline{35}}DEPN]_0}{[PS_{\overline{35}}DEPN]_t}\right) = k_d t \qquad (5)$$

Figure 3b shows the variation of $\ln([PS_{35}\text{-}DEPN]_0/[PS_{35}\text{-}DEPN]_t)$ as a function of time. It can be stressed that all points fall into a same straight line, the absence of any deviation

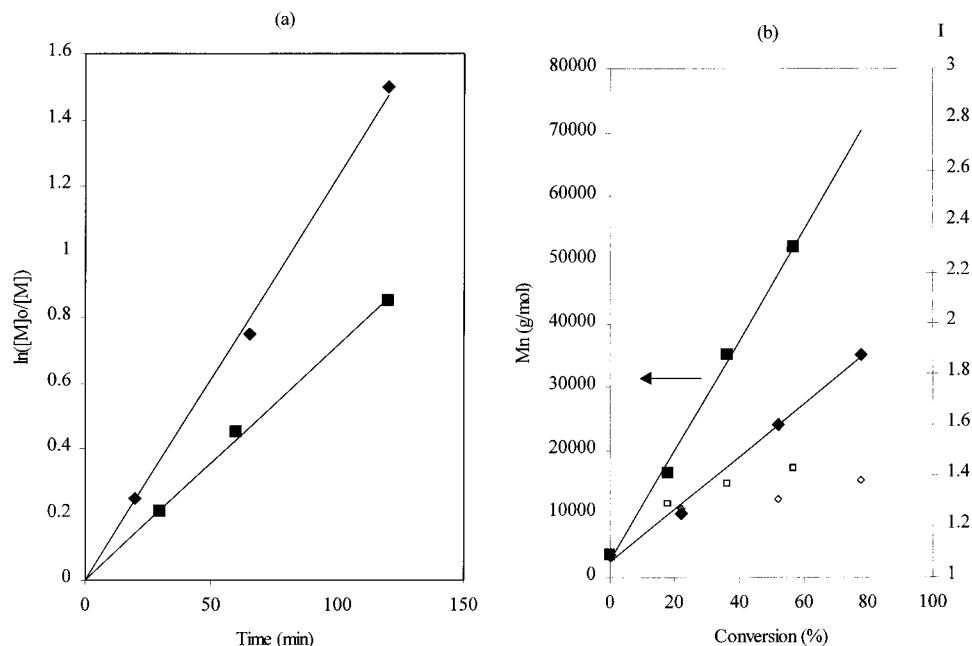**Figure 7.** Variation of $\ln([M]_o/[M])$ versus time (a) and evolution of $\overline{M}_n$ as a function of conversion (b) in DEPN-mediated polymerization of *n*-butyl acrylate at 120 °C, PBuA$_{35}$DEPN being used as macroinitiator; ◆: $[PBuA_{35}DEPN]_0 = 2 \times 10^{-2}$ M; ■: $[PBuA_{35}DEPN]_0 = 1 \times 10^{-2}$ M. Variation of polydispersity index (*I*) as a function of conversion: the corresponding empty symbols have been used □: $[PS_{35}DEPN]_0 = 1 \times 10^{-2}$ M (70000 g/mol targeted) for instance.

indicating that the assumptions made were all sound. k_d could then be easily obtained by taking the slope of this straight line. At 120 °C k_d was found to be equal to 3.4×10^{-3} s^{-1}, a value which is three times higher than the rate constant of dissociation determined by Fukuda et al.[7f] for TEMPO-based alkoxyamines. On the other hand, Tordo and co-workers[4h] obtained for molecular alkoxyamines based on DEPN a value of k_d that turned to be two times higher than ours by resorting to another methodology.

The knowledge of *K* as well as K_F and k_d prompted us to deduce the rate constant of reversible deactivation (k_{rec}) of polystyryl radicals by DEPN:

$$k_{rec} = 5.7 \times 10^5 \, \text{L·mol}^{-1}\text{·s}^{-1}$$

$$k_{rec,F} = 9.7 \times 10^5 \, \text{L·mol}^{-1}\text{·s}^{-1} \quad (\text{using} \quad K_F)$$

Whatever the approach followed to determine [PS•] and *K*, the value of k_{rec} obtained appears to be particularly low for a rate constant of recombination between two radicals; this merely reflects the difficulty encountered by DEPN in trapping moderately reactive polystyryl radicals owing to its hindering phosphonate substituent. This feature results in a faster polymerization of styrene than that observed for TEMPO-based systems, but one has to acknowledge that about 10% of chains are lost in irreversible termination in the initial period of the process, before it reaches a pseudostationary state.

Taking advantage of the methodology followed for the determination of k_d at 120 °C, similar experiments were carried out at 130, 100, and 90 °C in order to evaluate k_d at these temperatures.

From these measurements of k_d, an Arrhenius plot was drawn (Figure 3c). The k_d versus temperature for PS-DEPN reads as:

$$k_d(\text{s}^{-1}) = 10^{14} \times \exp\left(\frac{-121 \text{ kJ/mol}}{RT}\right)$$

In comparison, the activation energy (E) found for the dissociation of the C—O bond in PS-TEMPO was in the same range indicating that the C—O bond energy in the latter system is comparable to the one measured in DEPN-based alkoxyamines. Therefore, if k_d is larger for PS-DEPN than for PS-TEMPO, this must be essentially due to its larger frequency prefactor that reflects the dependence of the entropy of reaction on the extent of steric hindrance, obviously larger for PS-DEPN than for PS-TEMPO.

Computer Simulations Using PREDICI. The data ([PS•], [DEPN]) used for the determination of *K* were taken within the phase of the polymerization where pseudostationary conditions apply: the kinetic eq 1 could thus be simplified and *K* easily deduced. However, one can wonder whether the assumption made ([PS•] = constant) is really justified; after all, irreversible bimolecular termination reactions still occur as pointed out by Fischer, and unlike TEMPO-based systems, DEPN-controlled polymerizations never experience a truly stationary state as shown in their [PS•] and [DEPN] profiles. Indeed, in TEMPO-mediated polymerizations the loss of radicals by termination is compensated by the thermal production of radicals, which is obviously not the case in our polymerization system. One of the most elegant ways to check which of the series of [PS•], *K*, and k_{rec} values—those obtained under the assumption that bimolecular termination is insignificant in the pseudostationary phase and those derived using the Fischer approach—are trustworthy is to resort to computer simulations.

In this simulation, which is aimed at modeling experimental conditions, the polymerization begins with the reversible dissociation of the macroinitiator PS$_{35}$-DEPN (See Appendix 1 for the detail of the reactions computed and Table 1 for the rate constants). The oligomeric styryl radicals can then propagate by addition of monomer units, recombine with DEPN, and return to a dormant alkoxyamine form or undergo irreversible self-termination. The contribution due to self-polymerization of styrene was also taken into account, using the data provided by Hamielec et al.[9k] Since DEPN was recently shown to undergo

thermal degradation into totally inert products, this reaction was addressed as well, its rate constant being taken from the work of Tordo et al.[4h] Except for the rate constant of self-termination (k_t), all other rate constants were taken independent of the chain length, considering that they reflect reactions between macromolecular chains and molecular entities (monomer, stable radicals). In contrast k_t was deemed as varying with the chain size,[10] and termination was assumed to occur by recombination only. To evaluate the chain length dependence of k_{tc} in the case of styrene, we referred to the work of Gilbert[10k] who established the following variation of k_t:

$$k_t(\mathrm{DP}) = k_t(0) \times \mathrm{DP}^{-(0.664+2.02\mathrm{DP}/\mathrm{DP}_{\mathrm{aimed}})}$$

where $k_t(0)$ is the rate constant of self-termination of α-methylbenzyl radicals and was taken equal to 5×10^9 L·mol^{-1}·s^{-1}.

On the other hand, the effect of viscosity on these rate constants (k_t) was taken into consideration: according to Yamada[10f] and co-workers who measured the effect of viscosity on k_t at 100 °C for styrene, the rate constant of self-termination for polymers of 10^5 g·mol^{-1} molar mass dramatically decreases only above 40% conversion. As enough experimental data were obtained below 40% conversion, comparison can well be made between simulated values and experimentally measured ones until reaching that value of conversion. As to the other rate constants (k_d, k_{rec}, k_p), they were either drawn from the literature—k_p being taken from a recent publication by Gilbert[10h]—or from our own measurements (k_d) and estimations (k_{rec}). Since the rate constant of recombination of DEPN with growing radicals was deduced following two different approaches, the opportunity for comparing which of the two affords the best fit with experimental data was taken.

In Figure 4a,b and Figure 5b are, respectively, simulated the variations of ln([M]$_o$/[M]) as a function of time, the dependence of $\overline{M}_n$ on conversion and the evolution of [DEPN] with time for one particular concentration of PS-DEPN macroinitiator. Are also represented in the same figures the experimental data appearing as solid points.

From the ln([M]$_o$/[M]) versus time curve, it can be seen that the two sets of simulated data straddled very closely experimentally measured points: depending upon the approach used to estimated [PS•] and then k_{rec}, the simulated conversion values were slightly lower (for the Fischer approach) or higher (for the classical treatment) than the actual ones. Taking k_{rec} as the mean value of those used in the first instance resulted in a perfect fit with the experimental conversion points. As to the evolution of [PS•] with time, a rather good agreement between the two sets of experimental and simulated results is observed with identical trends for both calculated and experimental profiles. In particular, one can notice that [PS•]$_{simulated}$ goes through a maximum (Figure 5a) before dwindling toward its pseudo-stationary value as it was observed in the experiments. In contrast, [DEPN]$_{simulated}$ is found to steeply increase during the initial phase and progressively head toward its pseudostationary value, bearing out our experimental observations. As to the evolution of $\overline{M}_n$ with conversion, it closely follows that determined from kinetic study. The same conclusions could be inferred from the computation of data using another initial concentration of [PS$_{35}$-DEPN] macroinitiator.

Kinetics of DEPN-Mediated Polymerization of *n*-Butyl Acrylate. It has been shown by several teams that commercially available nitroxides such as TEMPO or di-*tert*-butyl nitroxide exhibit only a moderate aptitude to control the polymerization
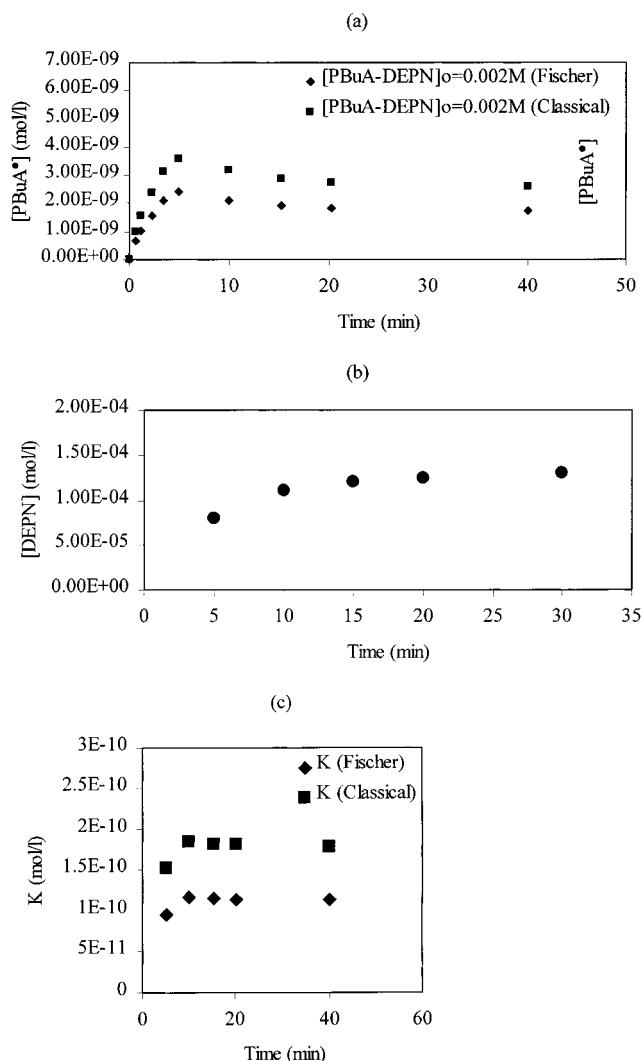

(a)

(b)

(c)

Figure 8. Variation of [PBuA•] (a) and [DEPN] (b) as a function of time in DEPN-mediated polymerization of *n*-butyl acrylate with [PBuA$_{\overline{35}}$DEPN] as a macroinitiator; [PBuA$_{\overline{35}}$DEPN]$_0$ = 2.0 × 10^{-3} M. Evolution of K with time (c).

of alkyl acrylates. Solomon and co-workers[1a] obtained oligoacrylates with such nitroxides whereas Listigovers et al.[6g,h] had to heat above 140 °C to isolate polymers of higher molar masses. In a recent addition Goto and Fukuda[7f] elegantly analyzed the mechanism occurring in such polymerization, revealing the formation of ω-unsaturated chains by β-hydrogen abstraction along with hydroxylamine.

On the other hand, we showed[4c,d] that DEPN behaves totally differently when used to control the propagation of acrylic radicals: samples with remarkably low PDI's and expected molar masses were indeed obtained.

Before investigating in detail the actual mechanism of polymerization of alkyl acrylates in the presence of DEPN, it is crucial to check its "living"/controlled character. Similarly to the study conducted on the polymerization of styrene, a macroinitiator (PBuA$_{\overline{35}}$DEPN) of oligomeric size and end-fitted with a DEPN-based alkoxyamine function was prepared. This macroinitiator was thoroughly characterized by ^{1}H NMR and no terminal unsaturation resulting from a β-hydrogen abstraction could be detected (Figure 6).

Two experiments were then carried out with this PBuA$_{\overline{35}}$DEPN as initiator of polymerization of *n*-butyl acrylate at 120 °C. The methodology to follow the conversion and
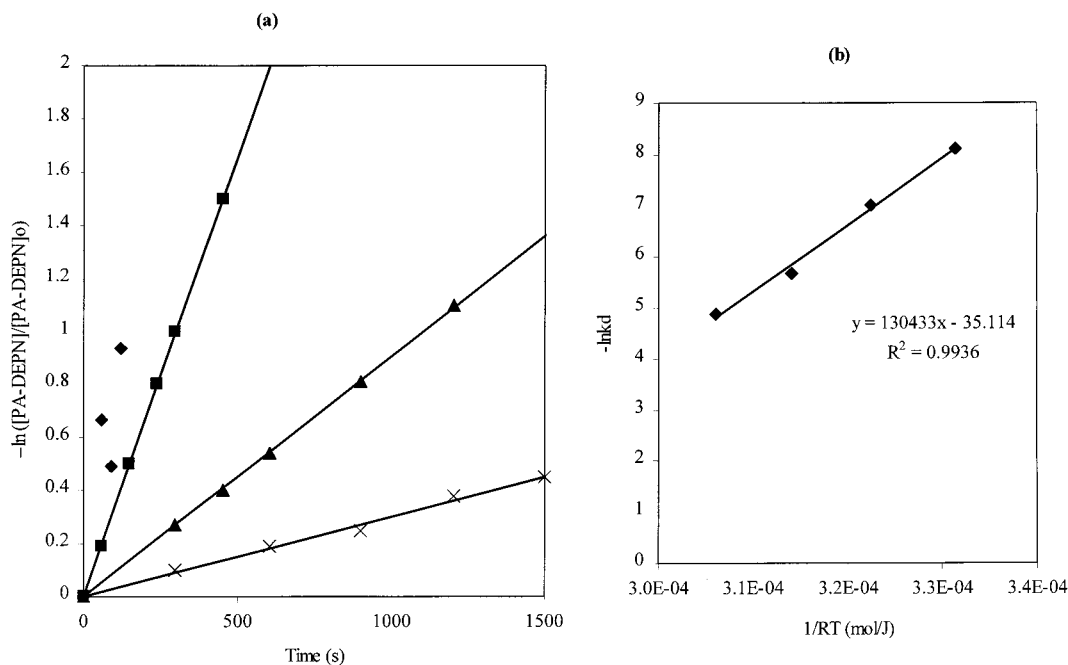
Figure 9. Determination of the rate constant of dissociation (k_d) of PBuA$_{\overline{35}}$DEPN at four different temperatures (a): $\blacklozenge$ = 120 °C; $\blacksquare$ = 110 °C; $\blacktriangle$ = 100 °C; $\times$ = 90 °C, and the corresponding Arrhenius plot (b).

monitor the evolution of $\overline{M}_n$ was the same as that previously described for styrene. As shown in Figure 7a,b, all points appearing in the conversion plot as well as those pertaining to the $\overline{M}_n$ curve are found to align in straight lines passing through the origin. Moreover, one can notice that the rate of polymerization depends on the concentration of macroinitiator, a higher concentration in PBuA$_{\overline{35}}$DEPN resulting in a faster consumption of monomer.

These features bear out our previous observations as to the genuinely controlled character of the DEPN-mediated polymerization of alkyl acrylates: no side reaction of the type described by Fukuda in TEMPO-mediated polymerization of *n*-butyl acrylate is indeed observed in our case.

Using an initial concentration of PBuA$_{\overline{35}}$DEPN equal to 2×10^{-3} M, a second series of experiments were then carried out to monitor the concentration of free DEPN and that of polyacrylic radicals by means of ESR and dilatometry, respectively. The concentration of growing radicals [PBuA$^\bullet$] was actually deduced from the conversion data, using the relation $\ln[M]_0/[M] = k_p[\text{PBuA}^\bullet]_t$ with $k_p = 84000$ L·mol^{-1}·s^{-1},[10i] (or $3/2k_p[\text{PBuA}^\bullet]_t$ using the Fischer treatment). Similarly to the case of styrene, one can distinguish two main phases from the [PBuA$^\bullet$] versus time curve (Figure 8a). Dissociation "predominates" in the initial phase; when enough free DEPN is accumulated in the medium because of irreversible termination, [PBuA$^\bullet$] decreases and eventually stabilizes to its pseudostationary value (2.6×10^{-9} M from the classical approach and 1.8×10^{-9} M using the Fischer approach).

On the other hand, [DEPN] steeply increases in the initial phase (Figure 8b) and rises only very moderately throughout the second phase. In contrast to the case of styrene, the pseudostationary concentration of DEPN is about 10 times lower than that of initial PBuA$_{\overline{35}}$DEPN, indicating that only 7% of chains were irreversibly deactivated before the system reached its pseudostationary regime: the maximum in the concentration of polymeric radicals therefore appeared sooner for polyacrylic radicals. Using the same assumption as in the case of styrene ([PBuA$^\bullet$] = constant in the pseudostationary phase) and taking

the pseudostationary regime values of [PBuA$^\bullet$] and [DEPN], K could be easily calculated (Figure 9c) at 120 °C:

$$K_{\text{PBuA}} = 1.7 \times 10^{-10} \text{ M}$$

Following the Fischer reasoning, one obtains:

$$K_{\text{PBuA,F}} = 1.2 \times 10^{-10} \text{ M}$$

These values, which are much lower than that found for polystyryl radicals, indicate that DEPN is particularly well suited to polyacrylic radicals. Despite this lower constant of equilibrium that merely reflects a lower stationary concentration of polyacrylic radicals, the DEPN-controlled polymerization of *n*-butyl acrylate proceeds faster than that of styrene because their respective rate constants of propagation differ one from the other by a factor higher than 40.

For the determination of k_d, an identical experimental procedure to that previously described for styrene was used: for reasons already discussed, aliquots were removed from the oil bath at early stages of polymerization and analyzed by SEC. The rate constant of dissociation (k_d) was determined from the rate of disappearance of the macroinitiator (PBuA$_{\overline{35}}$DEPN); at 120 °C, k_d which corresponds to the slope of $\ln[\text{PBuA}_{\overline{35}}\text{DEPN}]_0/[\text{PBuA}_{\overline{35}}\text{DEPN}]_t$, versus time curve is equal to $k_d = 7.1 \times 10^{-3}$ s^{-1} (Figure 9a).

Knowing K and k_d at 120 °C, it was easy to deduce the value of k_{rec} which amounts to:

$$k_{\text{rec}} = 4.2 \times 10^7 \text{ L·mol}^{-1}\text{·s}^{-1}$$

$$k_{\text{rec,F}} = 5.9 \times 10^7 \text{ L·mol}^{-1}\text{·s}^{-1}$$

depending upon the approaches (that of Fischer or the classical one).

The rate of dissociation was also measured at several other temperatures from 90 to 120 °C and the corresponding energy of activation was calculated (Figure 9b). The variation of k_d as a function of temperature is shown in the form of an Arrhenius

Scheme 1. Mechanism Proposed for the DEPN-Controlled Polymerizations of Both Styrene (A = phenyl group) and *n*-butyl Acrylate (A = COOBu group)

A= -C₆H₅, -CO₂Bu
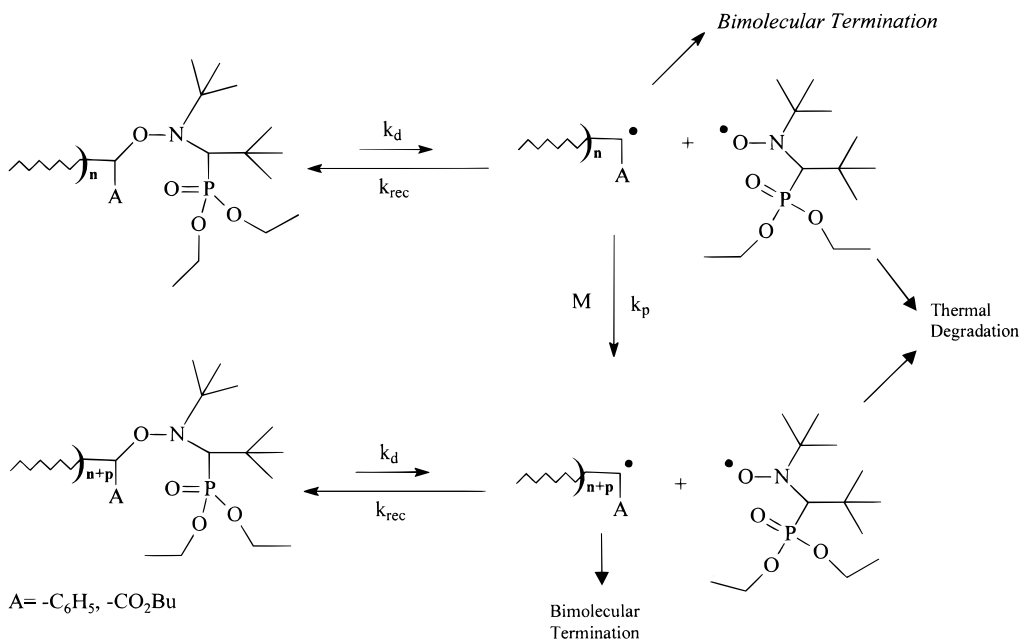
plot which reads:

$$k_d(s^{-1}) = 1.7 \times 10^{15} \exp\left(\frac{-130 \text{ kJ/mol}}{RT}\right)$$

As the dependence of the rate constant of irreversible termination on the chain size is not known in the literature for this class of monomers, the simulation of the DEPN-controlled polymerization of *n*-butyl acrylate was not attempted.

Data Useful for Macromolecular Engineering. To understand how the self-regulation mechanism in DEPN-controlled polymerizations operates, macroinitiators fitted with the corresponding alkoxyamines were used. For the persistent radical effect[8] to occur and the polymeric chains to grow under controlled conditions, the system has to pay a penalty in terms of irreversible bimolecular termination: approximately 10% of PS chains and only 7% of PBuA chains are indeed irreversibly lost in self-termination, and corresponding amounts of free DEPN are generated. The following mechanism can now be proposed for the two kinds of polymerization (Scheme 1).

As all data are available, one can easily calculate for the conditions previously discussed the average time of activity of growing chains between two periods of inactivity—when they are in the dormant form—and also the average number of monomer units added. The average lifetime of radicals (τ) can be written as:

$$\tau = \frac{[P^\bullet]}{k_{rec}[P^\bullet][DEPN]} = \frac{1}{k_{rec}[DEPN]} \quad (7)$$

whereas the number of monomer units ($\bar{v}$) added per cycle of activity is:

$$\bar{v} = k_p[M]\tau \quad (8)$$

For styrene one obtains:

$$\tau_{S/DEPN} = 7.6 \times 10^{-4} \text{ s}$$

and in the case of *n*-butyl acrylate

$$\tau_{BuA/DEPN} = 1.8 \times 10^{-4} \text{ s}$$

These values should be compared with the one found for the TEMPO-controlled polymerization of styrene: $\tau_{S/TEMPO} = 1.42 \times 10^{-4}$ s (using Fukuda's data). Likewise, the values found for $\bar{v}$ are much higher for DEPN-based polymerizations than for TEMPO-mediated processes:

$$\bar{v}_{S/DEPN} \approx 13 \quad \text{and} \quad \bar{v}_{BuA/DEPN} \approx 104$$

whereas Fukuda's data give $\bar{v}_{S/TEMPO} \approx 3$. If the aforementioned conditions were to be used in macromolecular engineering, samples with broad distributions and a large extent of terminated chains would be obtained. To successfully apply DEPN-mediated polymerizations in macromolecular engineering, it is essential to finely tune the concentration of free DEPN and add a slight excess of free DEPN from the onset of polymerization. In this way, one can provide the growing radicals with enough stable radicals to react and thus avoid the self-regulation process that results in the irreversible termination of 7–10% of chains. As shown in the two previous relations, τ and also $\bar{v}$, can be brought down by adding a slight excess of DEPN: under such conditions better controlled as well as narrowly distributed samples can be prepared. This aspect has already been discussed in a previous paper.[4f,g]

Conclusion

A few minutes after its onset, the DEPN-mediated polymerizations of styrene and *n*-butyl acrylate reach a pseudostationary regime that is characterized by a steady concentration of polymeric radicals and DEPN. Because the probability for irreversible termination likely decreases with the size of growing chains and with conversion, the loss of polymeric radicals is only marginal during the second phase of the polymerization; here lies the beauty of "living"/controlled radical polymerization. Under these conditions the kinetics of polymerization could then be treated within the framework of stationary-state systems, and the constant of equilibrium (K) between dormant and active species could be measured. Small differences were indeed found with data generated using the Fischer approach that do take in

account the self-termination of radicals throughout polymerization. Using ESR and SEC to, respectively, determine the concentration of free DEPN and the rate constant of dissociation of dormant alkoxyamines (k_d), k_{rec} could be obtained. A series of simulations was also carried out by means of the PREDICI program: the simulated results were found to be consistent with the scenario proposed from the experimentally measured values of these rate constants. DEPN was shown to behave quite differently whether it is used to control the polymerization of styrene or that of *n*-butyl acrylate. Despite a rather fast rate of propagation, only 7% of poly(*n*-butyl acrylate) chains were irreversibly lost in bimolecular termination in the conditions used for the kinetic study; in contrast, the extent of dead chains rose to 10% in the case of styrene in similar experimental conditions.

The key to success when applying DEPN-mediated polymerizations in macromolecular engineering is to add a slight excess of DEPN independently to the initiating system: polymerization is slowed but well-controlled samples of either PS or PBuA can be prepared in this way.

Experimental Section

Materials. DEPN was obtained according to an already described methodology.[4b]

Synthesis of Macroinitiator PS-DEPN and PBuA-DEPN. Polystyrene fitted with an end-standing DEPN-based alkoxyamine function was obtained by reacting under inert atmosphere DEPN (0.67 mmol), styrene (12 mL), and AIBN (0.268 mmol) in a dry Schlenk tube. The mixture of these components was first thoroughly degassed before being heated at 120 °C for 30 min. The solution was then cooled at room temperature. Residual monomer was removed by devolatilization at room temperature. Excess of DEPN was removed from the polymer by several precipitations at low temperature.

Poly(*n*-butyl acrylate) fitted with a terminal alkoxyamine function based on DEPN was obtained by reacting under inert atmosphere DEPN (1.357 mmol), *n*-butyl acrylate (15 mL), and AIBN (0.268 mmol) in a dry Schlenk tube. As previously mentioned, the mixture of reactants was first thoroughly degassed before being heated at 120 °C for 6 h. The solution was then cooled at room temperature. Residual monomer was removed by devolatilization at room temperature. The mixture was then purified by semipreparative HPLC until excess of DEPN was completely removed. Purity of these macroinitiators was checked by ^{1}H NMR and by ESR at room temperature. Unlike the case of TEMPO-mediated polymerizations,[7f] no terminal unsaturations could be seen in the NMR spectra indicating that essentially all polystyrene as well as poly(*n*-butyl acrylate) chains were end fitted with an alkoxyamine function (Figure 6). The purified polymers were stored at low temperature under inert atmosphere before being used.

Polymerizations. Polymerizations were performed in airproof glass tubes. The monomer and the required amount of macroinitiator were introduced under an inert atmosphere. The solution was then thoroughly degassed before being heated to the chosen temperature. The reactions were discontinued by cooling the reaction medium to low temperatures after variable times of polymerization. Polymers were analyzed without any precipitation.
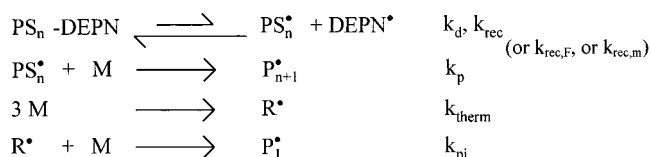
Characterizations. All molar masses were determined using size exclusion chromatography (SEC). The latter characterization was performed using a JASCO HPLC pump type 880-PU, a RI-3 refractive index detector, and a JASCO 875 UV/vis detector with THF as eluent. A calibration curve established with PS standards was used for the determination of the molar masses of PS samples. The molar masses of poly(*n*-butyl acrylate) samples were obtained from a SEC instrument equipped with a light scattering detector (Wyatt). ESR measurements were performed using a Bruker ESR 200 tt spectrometer to measure the amount of DEPN generated by the persistent radical effect.[8a] The solution of monomer and the corresponding macroinitiator were degassed in an ESR cell. Calibration curves were performed at room temperature.
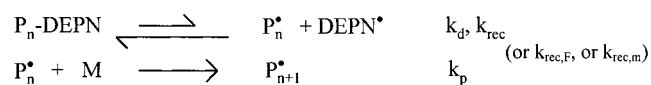
Appendix 1

Reactions and rate constants considered for the simulation of the DEPN-mediated free radical polymerization of styrene.

Initiation :

$$PS_n\text{-}DEPN \rightleftharpoons PS_n^\bullet + DEPN^\bullet \qquad k_d, k_{rec}$$
$$\text{(or } k_{rec,F}, \text{ or } k_{rec,m})$$
$$PS_n^\bullet + M \longrightarrow P_{n+1}^\bullet \qquad k_p$$
$$3\,M \longrightarrow R^\bullet \qquad k_{therm}$$
$$R^\bullet + M \longrightarrow P_1^\bullet \qquad k_{pi}$$

Propagation :

$$P_n\text{-}DEPN \rightleftharpoons P_n^\bullet + DEPN^\bullet \qquad k_d, k_{rec}$$
$$\text{(or } k_{rec,F}, \text{ or } k_{rec,m})$$
$$P_n^\bullet + M \longrightarrow P_{n+1}^\bullet \qquad k_p$$

Irreversible Termination :

$$PS_n^\bullet + PS_n^\bullet \longrightarrow D_{2n} \qquad k_{t0}$$
$$PS_n^\bullet + R^\bullet \longrightarrow D_n \qquad k_{t0}$$
$$R^\bullet + R^\bullet \longrightarrow D_n \qquad k_{t0}$$
$$PS_n^\bullet + P_m^\bullet \longrightarrow D_{n+m} \qquad k_{tP}$$
$$R^\bullet + P_m^\bullet \longrightarrow D_m \qquad k_{tP}$$
$$P_n^\bullet + P_m^\bullet \longrightarrow D_{n+m} \qquad k_t$$
$$P_n^\bullet + P_m^\bullet \longrightarrow D_n + D_m \qquad k_{td}$$
$$DEPN^\bullet + DEPN^\bullet \longrightarrow Inert \qquad k_{deg}$$

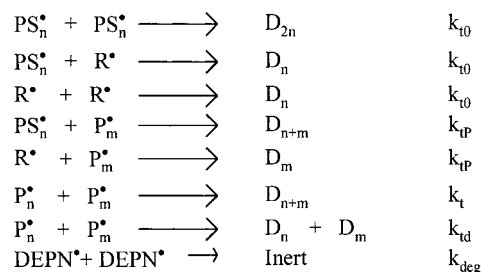**Table 1.** Rate Constants and Their Value

rate constant	numerical value	references
k_d	3.5×10^{-3} s^{-1}	this work
k_{rec}	5.7×10^5 L·mol^{-1}·s^{-1}	this work
$k_{rec,F}$	9.7×10^5 L·mol^{-1}·s^{-1}	this work
$k_{rec,m}$*	7.5×10^5 L·mol^{-1}·s^{-1}	this work
k_{therm}	1.2×10^{-10} L^2·mol^{-2}·s^{-1}	9k
k_{deg}	5.8×10^{-5} L·mol^{-1}·s^{-1}	4h
k_p	2.0×10^3 L·mol^{-1}·s^{-1}	10h
k_{pi}	2.0×10^4 L·mol^{-1}·s^{-1}	10j
k_{t0}	5×10^9 L·mol^{-1}·s^{-1}	10j
k_{tp}	2×10^9 L·mol^{-1}·s^{-1}	10j
$k_{t(0)}$	5×10^9 L·mol^{-1}·s^{-1}	10j
k_{td}	0	10j

* Logarithmic average of $k_{rec,F}$ and k_{rec}.