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Living Radical Polymerization: Use of an Excess of Nitroxide as a Rate Moderator

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ABSTRACT: The kinetics of the living radical polymerization of *n*-butyl acrylate (BuA) in the presence of an excess of *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (DEPN) as a rate moderator has been studied in the temperature range 115−125 °C. The equilibrium rate constant $K = k_d/k_c$ between dormant and active chains was determined experimentally from the slope of $\ln([\mathrm{BuA}]_0/[\mathrm{BuA}])$ vs time. It obeys the following Arrhenius relation: $K = 4.93 \times 10^5 \exp(-119.3\ \mathrm{kJ\ mol^{-1}}/RT)$, i.e., $K = 1.09 \times 10^{-10}$ mol L^{-1} at 125 °C. Some straightforward analytical kinetic equations that only depend on the excess of DEPN as the experimental parameter were established. These equations were successfully applied to simulate the DEPN-mediated polymerization of *n*-butyl acrylate initiated by either a styryl-DEPN alkoxyamine or an AIBN/DEPN bicomponent system. Last, the slow degradation of DEPN was considered in order to account for the upward deviation of the kinetics when a great excess of DEPN was used.

Introduction

Nitroxide-mediated polymerization (NMP) is an efficient and elegant method to tailor well-defined polymers by radical polymerization.[1] Nitroxide-mediated polymerization has long been limited to styrene and its derivatives and to statistical copolymers containing styrene.[2] However, after several attempts,[3−8] the use of new stable radicals such as *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (DEPN, **1**) or 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO, **2**) (Scheme 1) has widened the range of monomers that can be controlled in this manner (for instance: acrylates,[9−12] dienes such as butadiene and isoprene,[13] and even statistical copolymers with methacrylate[13]).

In particular, the living radical polymerization of acrylate monomers is now attainable. *n*-Butyl acrylate (BuA) is a widely used monomer in industry.

As illustrated in many theoretical works,[14−17] the determination of the equilibrium constant *K* between dormant and active chains is particularly useful to discuss the kinetics of the polymerization (eqs 1 and 2) further.

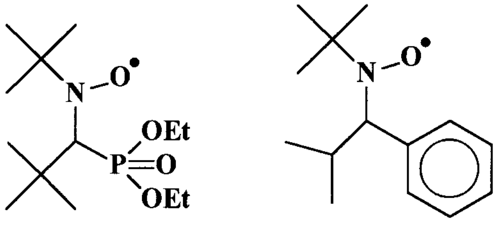
$$\mathrm{P{-}X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \mathrm{P}^\bullet + \mathrm{X}^\bullet \qquad (1)$$

$$K = k_d/k_c = [\mathrm{P}^\bullet][\mathrm{X}^\bullet]/[\mathrm{P{-}X}] \qquad (2)$$

Gnanou et al.[12] recently reported *K* for the system *n*-BuA/DEPN by determining [P$^\bullet$] from a kinetic analysis and [X$^\bullet$] from electron spin resonance analysis (ESR).

We previously reported a simpler method for determining *K* for the system styrene/DEPN.[18] Herein, we apply this method, where an excess of nitroxide is used to govern the rate of polymerization, to determine *K* for the system *n*-BuA/DEPN. Afterward, we will check the reliability of our value of *K* by comparing experimental data with theoretical simulation for a standard polymerization recipe. This paper focuses on the use of excess nitroxide as a rate moderator and proposes the appropriate analytical kinetic equations.

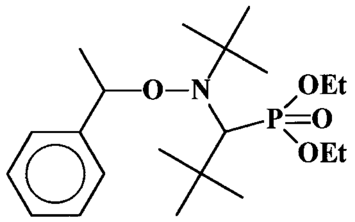
Scheme 1. Structure of the Nitroxides DEPN (1) and TIPNO (2)



1
DEPN

2
TIPNO

Scheme 2. Structure of the Alkoxyamine Styryl-DEPN (3)



3
Styryl-DEPN

Experimental Section

Materials. Styrene (Aldrich, 99%) and *n*-butyl acrylate (Aldrich, 99%) were distilled before use. AIBN (Aldrich, 98%) was recrystallized from ethanol. DEPN (73% pure) and the alkoxyamine styryl-DEPN (**3**) (Scheme 2) (purity 95.3%) were kindly supplied by Centre de Recherche Rhône-Alpes (ATOFINA) and used as received.

Synthesis of the Alkoxyamine Polystyrene-DEPN (PS-DEPN). A PS-DEPN alkoxyamine was prepared by a procedure reported elsewhere.[18] In a Schlenk reactor were incor-

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porated 43.0 mg of AIBN (0.262 mmol), 296 mg of DEPN (0.73 mmol), and 10.0 g of styrene (96 mmol). After three freeze–thaw–pump cycles, the polymerization was conducted under argon with magnetic stirring at 125 °C for 6 h 30 min. The polymer solution was diluted in tetrahydrofuran, precipitated in cold methanol, and dried under vacuum at 35 °C (10^{-1} mmHg). We recovered 7.43 g of polymer (yield = 74%). SEC analysis of the PS-DEPN alkoxyamine gave $M_n = 17\,100$ g/mol and $M_w/M_n = 1.17$.

Kinetics of Bulk Polymerization of *n*-Butyl Acrylate with an Alkoxyamine as Initiator in the Presence of Excess DEPN Nitroxyl Free Radicals. In a typical run, 0.500 g of PS-DEPN (29.2 μmol), 9.0 mg of DEPN (22.3 μmol), and 8.58 g of *n*-butyl acrylate (66.9 mmol) were introduced into a Schlenk reactor. After three freeze–thaw–pump cycles, the reactor was immersed in an oil bath at 125 °C. The polymerization was conducted under argon with magnetic stirring. Samples were withdrawn from the reactor with a glass syringe through a septum and under positive argon purge. Conversion was determined by ^{1}H NMR analysis on crude samples in $CDCl_3$. We used the integral I_1 of the resonance at 5.6 ppm (q, $J_{cis} = 10.3$ Hz, $J_{gem} = 1.8$ Hz, 1H, $-HC{=}C\langle\rangle$) relative to the residual monomer and the integral I_2 of the resonance at 3.8–4.2 ppm (t + broad peak, $J = 6.5$ Hz, 2H, $-O-CH_2-$) relative to monomer and polymer. The fractional conversion was given by $1-2 \times I_1/I_2$.

Caution: violent polymerization may occur in the absence of excess DEPN.

Kinetics of Polymerization with a Bicomponent System AIBN/DEPN. In a Schlenk reactor were incorporated 20.3 mg of AIBN (124 μmol), 100 mg of DEPN (248 μmol), and 5.04 g of *n*-butyl acrylate (39.3 mmol). After thoroughly purging with argon, the reactor was immersed in an oil bath at 123 °C. The polymerization was conducted as above.

Characterization. Molecular weights were determined on crude samples by size exclusion chromatography (SEC) calibrated with polystyrene standards. SEC was performed with a Spectra Physics Instruments SP8810 pump and a Shodex RIse-61 refractometer detector (eluent tetrahydrofuran, 1 mL/min, two 300 mm columns PL gel 5 μm mixed D from Polymer Laboratories, $T = 30$ °C). For poly(butyl acrylate) samples, the reported values are related to the universal calibration with the following Mark–Houwink coefficients: $k_{PS} = 11.4 \times 10^{-5}$ dL g^{-1} and $\alpha_{PS} = 0.716$, and $k_{PBuA} = 12.2 \times 10^{-5}$ dL g^{-1} and $\alpha_{PBuA} = 0.700$.[19] ^{1}H NMR analyses were conducted on a Bruker spectrometer at 200 MHz in $CDCl_3$ with tetramethylsilane as a reference.

Numerical Simulation. Numerical simulations of *n*-butyl acrylate polymerizations initiated by styryl-DEPN (**3**) were performed with the PREDICI software package, version 5.35.1, used in moments mode. We used essentially the same kinetic scheme as reported elsewhere,[20] with the following rate constants ($T = 120$ °C): styryl-DEPN, $k_d = 5.5 \times 10^{-3}$ s^{-1}, $k_c = 5.6 \times 10^6$ L mol^{-1} s^{-1};[11] coupling of two styryl radicals (we actually took the value for polystyryl radicals), $k_{t1} = 3.35 \times 10^8$ L mol^{-1} s^{-1};[21] first propagation step (estimated as the cross-propagation rate $k_{styrene/BuA}$), $k_{p1} = 2590$ L mol^{-1} s^{-1};[22] primary termination, $k_{t12} = 2.0 \times 10^8$ L mol^{-1} s^{-1};[23] PBuA-DEPN, $k_{dp} = 7.1 \times 10^{-3}$ s^{-1},[12] $k_{cp} = k_{dp}/K = 1.0 \times 10^8$ L mol^{-1} s^{-1} (with K calculated by eq 5, this work); termination, $k_t = 2.0 \times 10^8$ L mol^{-1} s^{-1};[23] propagation, $k_p = 87\,780$ L mol^{-1} s^{-1}.[19]

Results and Discussion

We[18] showed previously that the kinetics of the polymerization should obey the well-known relation (eq 3)[24] in the presence of excess nitroxide. Under conditions where the time dependence of [P–X] and [X•] can be neglected, one can obtain eq 4 (with $N = [X^\bullet]_0/[P-X]_0$).

$$-\mathrm{d}(\ln[M]) = k_p(K[P-X]/[X^\bullet])\,\mathrm{d}t \tag{3}$$

$$\ln([M]_0/[M]) = k_p(K[P-X]_0/[X^\bullet]_0)t = k_p(K/N)t \tag{4}$$

For convenience, in this study, we have used a PS-DEPN alkoxyamine as initiator which was synthesized and characterized as previously described.[18] This is because a PBuA-DEPN alkoxyamine is much more difficult to purify and to handle due to the low glass transition temperature (T_g) of the PBuA homopolymer ($T_g = -54$ °C).[25]

Table 1. Bulk *n*-Butyl Acrylate Polymerizations in the Presence of an Excess of Nitroxide

run	*T* (°C)	PS-DEPN[a] (g, mmol)	DEPN (mg, mmol)	*n*-butyl acrylate (g, mmol)	*K* (mol L^{-1})
1	125	0.500, 0.0292	9.1, 0.0226	4.25, 33.1	1.14×10^{-10}
2	125	0.500, 0.0292	9.0, 0.0223	8.58, 66.9	1.05×10^{-10}
3	115	0.501, 0.0293	10.6, 0.0263	8.51, 66.4	4.34×10^{-11}

[a] PS-DEPN: $M_n = 17\,100$ g mol^{-1} and $M_w/M_n = 1.17$.

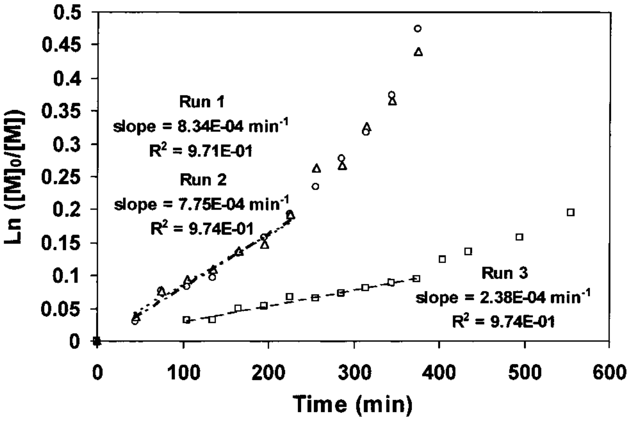

Figure 1. Kinetics of bulk polymerization of *n*-butyl acrylate at different temperatures and alkoxyamine concentrations but at a constant ratio $[DEPN]_0/[PS\text{-}DEPN]_0 \approx 0.8$. Run 1: $T = 125$ °C, $[PS\text{-}DEPN]_0 = 5.59 \times 10^{-3}$ mol L^{-1} (○). Run 2: $T = 125$ °C, $[PS\text{-}DEPN]_0 = 2.90 \times 10^{-3}$ mol L^{-1} (△). Run 3: $T = 115$ °C, $[PS\text{-}DEPN]_0 = 2.93 \times 10^{-3}$ mol L^{-1} (□). See Table 1 for the exact recipes. For each run, the linear regression at low conversion is plotted in dashed line (run 1, - — -; run 2, - - -; run 3, — —).

We first checked the reliability of eq 4 by performing two experiments (Table 1, entries 1 and 2). There is a factor of almost 2 difference for the initial concentration of the alkoxyamine between the two experiments (the amount of monomer is 2-fold in the second experiment), but the ratio $[X^\bullet]_0/[P-X]_0$ is kept constant at about 0.77. As depicted in Figure 1 (runs 1 and 2), we can observe that at low conversion all the kinetic points fall on the same line vs time, as expected from the theoretical relation eq 4. It means that under these conditions the equilibrium value can actually be directly calculated from the slope of the curve. From these two experiments, we calculated a mean value of $K = 1.09 \times 10^{-10}$ mol L^{-1} at 125 °C (our calculated values are related to the following Arrhenius relation for the propagating rate constant $k_p = 1.8 \times 10^7 \exp(-17.4$ kJ mol$^{-1}/RT)$).[19] This method is much more simple than the extensively used method based on both the kinetic and ESR analysis. Also, in contrast with another method recently published by us and based on the kinetic law related to the persistent radical effect,[20] no rate constants other than k_p is needed to calculate the value of K (especially the value of the termination rate constant k_t is not required).

As previously reported in the polymerization of styrene,[18] there is an upward deviation from linearity at higher conversion in Figure 1. This phenomenon is ascribed to side reactions; DEPN undergoes a slow

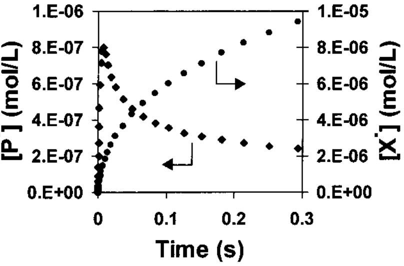

Figure 2. Numerical simulation (PREDICI software package, version 5.35.1, used in moments mode) showing the evolution of the concentration of the propagating radicals [P•] (◆) and the nitroxide [X•] (●) vs time in the bulk polymerization of butyl acrylate in the absence of added nitroxide. Conditions: $T = 120$ °C, $[\mathrm{BuA}]_0/[\mathrm{Sty\text{-}DEPN}]_0 = 156$, $k_d = 5.5 \times 10^{-3}\ \mathrm{s}^{-1}$, $k_c = 5.6 \times 10^6\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_{t1} = 3.35 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_{p1} = 2590\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_{t12} = 2.0 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_{dp} = 7.1 \times 10^{-3}\ \mathrm{s}^{-1}$, $k_{cp} = 1.0 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_t = 2.0 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $k_p = 87\ 780\ \mathrm{L\ mol^{-1}\ s^{-1}}$.

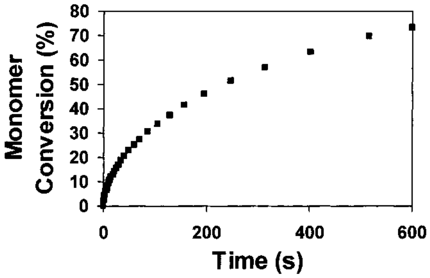

Figure 3. Numerical simulation (PREDICI software package, version 5.35.1, used in moments mode) showing the evolution of the monomer conversion (■) vs time in the bulk polymerization of butyl acrylate in the absence of added nitroxide. Conditions: same as in Figure 2.

thermal degradation to yield *tert*-butyl radicals.[26] Thus, the slow consumption of DEPN as well as the production of propagating primary radicals may be responsible for this positive drift in Figure 1. This behavior will be discussed further later in the paper.

To evaluate the temperature dependence of K, we have determined the equilibrium rate constant at a lower temperature ($T = 115$ °C) and found $K = 4.34 \times 10^{-11}\ \mathrm{mol\ L^{-1}}$ (Table 1, entry 3) (Figure 1, run 3). From the three runs, by using the relation $\Delta G = -RT \ln K = \Delta H - T\Delta S$, we can calculate by linear regression $\Delta H = 119.3\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = 109\ \mathrm{J\ K^{-1}\ mol^{-1}}$ (with a correlation $R^2 = 0.9534$). These values agree well with known values.[18,27,28] On a more practical way, K can be expressed by the following Arrhenius relation (eq 5).

$$K = 4.93 \times 10^5 \exp(-119.3\ \mathrm{kJ\ mol^{-1}}/RT) \qquad (5)$$

The value of K calculated at 120 °C ($K = 6.95 \times 10^{-11}\ \mathrm{mol\ L^{-1}}$) is close to the value determined by Gnanou et al. ($K = 1.2 \times 10^{-10}\ \mathrm{mol\ L^{-1}}$)[12].

We[11] and others[10] have already noticed that a slight excess of free DEPN nitroxide is necessary to moderate the rate of polymerization in the case of butyl acrylate. In the absence of free nitroxide, the polymerization is somewhat explosive. To explain this behavior, we have simulated the system by numerical simulation with PREDICI software. As depicted in Figure 2, the concentration of the propagating radicals goes through a maximum and then decreases due to self-termination, while the nitroxide accumulates (persistent radical effect).[29] In the same time (Figure 3), the monomer conversion increases very sharply and should theoretically reach values as high as 70% in a few minutes. This is due to the very high value of k_p for the *n*-butyl acrylate monomer.[19] However, in practice, such a fast exothermic polymerization reaction results in a rapid increase in the temperature of the medium (unless the heat of the polymerization is very efficiently removed), leading to nonreproducible and somewhat explosive reactions.

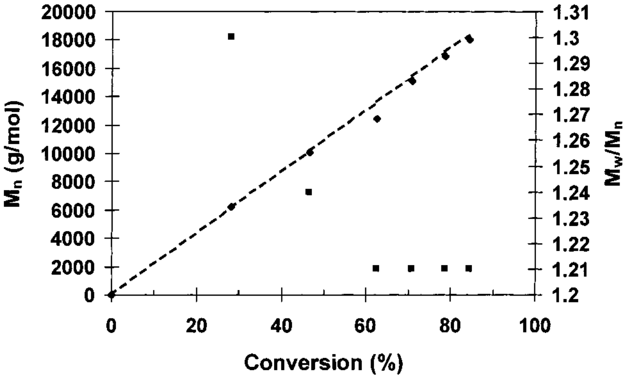

Figure 4. Mean number molecular weight M_n (◆, experimental points; – –, theoretical curve corresponding to $M_n = [n\text{-BuA}]_0 \times \text{conversion} \times 128.17/[\mathrm{Sty\text{-}DEPN}]_0$) and polydispersity index M_w/M_n (■) vs conversion for the bulk polymerization of *n*-butyl acrylate at 123 °C in the presence of DEPN as rate moderator: $[n\text{-BuA}]_0/[\mathrm{Sty{-}DEPN}]_0 = 170$, $[\mathrm{DEPN}]_0/[\mathrm{Sty\text{-}DEPN}]_0 = 0.054$.

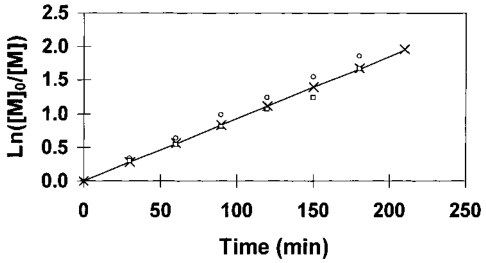

Figure 5. Kinetics of bulk polymerization of *n*-butyl acrylate at 123 °C in the presence of DEPN as rate moderator at a fixed initial ratio $[\mathrm{DEPN}]_0/[\mathrm{Sty\text{-}DEPN}]_0 = 0.054$: $[n\text{-BuA}]_0/[\mathrm{Sty\text{-}DEPN}]_0 = 170$ (○: experimental points); $[n\text{-BuA}]_0/[\mathrm{Sty\text{-}DEPN}]_0 = 838$ (□: experimental points); kinetic simulation based on eq 4 with $K = 9.2 \times 10^{-11}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ calculated from eq 5 and $k_p = 91\ 390\ \mathrm{L\ mol^{-1}\ s^{-1}}$ (—); kinetic simulation based on the equation of Fukuda eq 6 with $[\mathrm{Sty\text{-}DEPN}]_0 = 4.09 \times 10^{-2}\ \mathrm{mol\ L^{-1}}$, $[\mathrm{DEPN}]_0 = 2.2 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$, and $k_t = 2 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$ (×).

Hence, a slight excess of free nitroxide as low as 5 mol % based on the concentration of the alkoxyamine is preferably added to the system to provide an accurate and controlled polymerization. Using these conditions, Figure 4 shows that the experimental molecular weight varies as theoretically expected. Furthermore, the polydispersity index of the final polymer is very low ($M_w/M_n = 1.21$). Last, the kinetics is still fast (Figure 5), but not too much in order to easily regulate the temperature of the medium. Interestingly, the theoretical simulations using either eq 4 or the complete equation derived by Fukuda et al.[28] using a finite initial concentration of free nitroxide (eq 6) agree almost perfectly with the experimental data. (The derivative vs time of eq 6 at time zero is the same as that of eq 4.)

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = (k_p/2k_tK[\mathrm{P{-}X}]_0)\{(3k_tK^2[\mathrm{P{-}X}]_0{}^2t + [\mathrm{X^\bullet}]_0{}^3)^{2/3} - [\mathrm{X^\bullet}]_0{}^2\} \qquad (6)$$

This confirms the reliability of our value of K. It also indicates that eq 4 is valid from very low initial concentration of DEPN for the system n-BuA/DEPN, in contrast to the system styrene/DEPN where a rather high excess of DEPN is necessary to apply eq 4. This is intuitively related to the difference in the equilibrium constants: $K_{\mathrm{PS-DEPN}} = 6.1 \times 10^{-9}$ mol L^{-1} $\gg K_{\mathrm{PBuA/DEPN}} = 9.2 \times 10^{-11}$ mol L^{-1} at $T = 123$ °C.[18,20] This point will be discussed further in the last section of the paper. The kinetics of the bulk polymerization of n-butyl acrylate in the presence of a small amount of DEPN as rate moderator is almost independent of the initial concentration of the alkoxyamine, provided that the value of $[\mathrm{X}^\bullet]_0/[\mathrm{P{-}X}]_0$ be kept fixed. This peculiar behavior is illustrated in Figure 5 where the concentration of the alkoxyamine is varied from 0.0409 to 0.0083 mol L^{-1} without a major effect on the kinetics.

The method described herein can also be applied to atom transfer radical polymerization (ATRP) to determine the equilibrium value in such systems (eqs 7 and 8), providing that the corresponding kinetic law is used (eq 9) (with $N' = [\mathrm{Mt}^{n+1}]_0/([\mathrm{P{-}X}]_0[\mathrm{Mt}^n]_0)$).

$$\mathrm{P{-}X} + \mathrm{Mt}^n\mathrm{L} \underset{k_{\mathrm{dec}}}{\overset{k_{\mathrm{a}}}{\rightleftharpoons}} \mathrm{P}^\bullet + \mathrm{XMt}^{n+1}\mathrm{L} \tag{7}$$

$$K = k_{\mathrm{a}}/k_{\mathrm{dec}} = [\mathrm{P}^\bullet][\mathrm{XMt}^{n+1}\mathrm{L}]/([\mathrm{P} - \mathrm{X}][\mathrm{Mt}^n\mathrm{L}]) \tag{8}$$

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = k_{\mathrm{p}}(K[\mathrm{P{-}X}]_0[\mathrm{Mt}^n]_0/[\mathrm{Mt}^{n+1}]_0)t = k_{\mathrm{p}}(K/N')t \tag{9}$$

Since Mt^n species are usually rather sensitive to oxidation, the amount of Mt^{n+1} should be nonzero at the beginning of the polymerization. Thus, such systems are likely to obey eq 9 even if Mt^{n+1} species were not intentionally added initially in the system. Also, in the case of nitroxide-mediated polymerization, depending on the purity of the alkoxyamine (or the efficiency of the initiator in a bicomponent system), the amount of nitroxide could be nonzero at the beginning of the polymerization. Thus, such systems are likely to obey eq 4 even if nitroxide is not intentionally added initially in the system. This should linearize the plot $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs time.

Here, we took this phenomenon into account for the kinetic simulation of the polymerization of n-butyl acrylate in the presence of the bicomponent system AIBN/DEPN (stoichiometric ratio). We determined the efficiency of AIBN from molecular weight measurements ($f = M_{\mathrm{n,theoretical}}/M_{\mathrm{n,experimental}} \approx 0.82$) (Figure 6). For simplicity, we assumed that the initiation by AIBN at 123 °C is almost instantaneous (fast decomposition rate: $t_{1/2} = 44$ s at 123 °C).[30] Thus, by using the appropriate relation for a bicomponent system (eq 10) where $[\mathrm{I}_2]_0$ stands for the initial initiator concentration and $N'' = [\mathrm{X}^\bullet]_0/(2[\mathrm{I}_2]_0)$, we successfully predicted the kinetics of the polymerization (Figure 7).

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = k_{\mathrm{p}}K(2f[\mathrm{I}_2]_0)/([\mathrm{X}^\bullet]_0 - 2f[\mathrm{I}_2]_0)t = k_{\mathrm{p}}Kf/(N'' - f)t \tag{10}$$

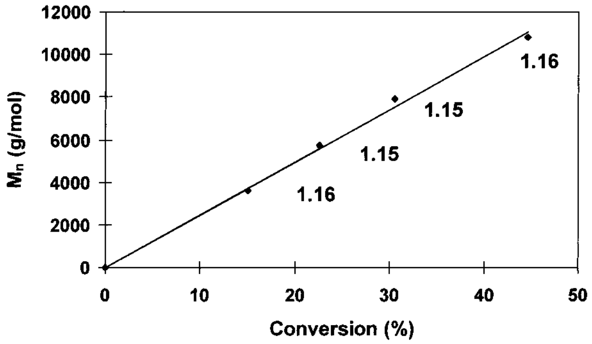

Figure 6. Mean number molecular weight M_{n} (♦: experimental points) and polydispersity index $M_{\mathrm{w}}/M_{\mathrm{n}}$ (labels) vs conversion for the bulk polymerization of n-butyl acrylate at 123 °C in the presence of a bicomponent system AIBN/DEPN: $[n\text{-BuA}]_0/[\mathrm{AIBN}]_0 = 317$, $[\mathrm{DEPN}]_0/[\mathrm{AIBN}]_0 = 2$. The theoretical curve corresponds to $M_{\mathrm{n}} = [n\text{-BuA}]_0 \times \text{conversion} \times 128.17/(2f[\mathrm{AIBN}]_0)$ with $f = 0.82$ (—).

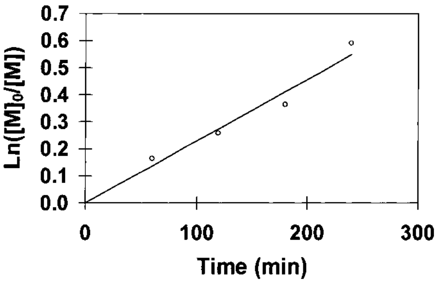

Figure 7. Kinetics of bulk polymerization of n-butyl acrylate at 123 °C in the presence of a bicomponent system AIBN/DEPN: $[n\text{-BuA}]_0/[\mathrm{AIBN}]_0 = 317$ (○: experimental points); kinetic simulation based on eq 10 with $K = 9.2 \times 10^{-11}$ L mol^{-1} s^{-1} calculated from eq 5 and $k_{\mathrm{p}} = 91\,390$ L mol^{-1} s^{-1} (—).

Finally, in an attempt to model the upward deviation observed in Figure 1, we took into account the slow degradation of DEPN (i.e., $[\mathrm{X}^\bullet]$ depends on time). From the ESR data of Le Mercier,[31] the concentration of DEPN followed a first-order decay (eq 11). Because the two pathways of DEPN consumption were all taken into account, i.e., the slow degradation (rate constant k_1) as well as the fast coupling with *tert*-butyl radicals (rate constant k_2, $k_2 \gg k_1$), the experimentally obtained k_{deg} ($k_{\mathrm{deg}} = 2.79 \times 10^{-5}$ s^{-1} at 123 °C in *tert*-butylbenzene under argon) is actually an apparent rate constant ($k_{\mathrm{deg}} \cong 2 \times k_1$). *tert*-Butylbenzene was chosen because it is less prone to hydrogen abstraction than for instance ethylbenzene (nitroxides are usually powerful hydrogen abstractors).[32] For our purpose, we considered two borderline cases by integration of eq 3. It must be kept in mind that this degradation scheme is very rough and that other byproducts could also alter the kinetics.

$$[\mathrm{X}^\bullet] = [\mathrm{X}^\bullet]_0 \exp(-k_{\mathrm{deg}}t) \tag{11}$$

In the first case, the primary propagating radicals (*tert*-butyl radicals) formed as byproducts were assumed to totally react with DEPN to form a rather stable *t*Bu-DEPN alkoxyamine (i.e., $[\mathrm{P{-}X}] = [\mathrm{P{-}X}]_0$), leading to eq 12.

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = (k_{\mathrm{p}}K/k_{\mathrm{deg}})([\mathrm{P{-}X}]_0/[\mathrm{X}^\bullet]_0)(\exp(k_{\mathrm{deg}}t) - 1) = (k_{\mathrm{p}}K/k_{\mathrm{deg}})(\exp(k_{\mathrm{deg}}t) - 1)/N \tag{12}$$

In the second case, the primary radicals are expected to propagate before being trapped by DEPN to form labile PBuA-DEPN alkoxyamines (i.e., $[\mathrm{P{-}X}]$ depends on time as indicated in eq 13), leading to eq 14.

$$[\mathrm{P{-}X}] = [\mathrm{P{-}X}]_0 + ([\mathrm{X}^\bullet]_0/2)(1 - \exp(-k_{\mathrm{deg}}t)) \qquad (13)$$

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = (k_\mathrm{p}K)\{(1/k_{\mathrm{deg}})(\exp(k_{\mathrm{deg}}t) - 1)([\mathrm{P{-}X}]_0/[\mathrm{X}^\bullet]_0 + {}^1/_2) - t/2\} = (k_\mathrm{p}K)\{(1/k_{\mathrm{deg}})(\exp(k_{\mathrm{deg}}t) - 1)(1/N + {}^1/_2) - t/2\} \qquad (14)$$

By applying these equations and despite the oversimplified degradation scheme used herein, the simulation now fairly well agrees with the experimental data (Figure 8). The upward deviation is enhanced by the rather large excess of nitroxide used in this experiment. Indeed, from a few simulations for various experimental conditions, the difference between eq 14 and eq 12 increases when the initial ratio $N = [\mathrm{X}^\bullet]_0/[\mathrm{P{-}X}]_0$ increases. Also, for a low initial ratio $[\mathrm{X}^\bullet]_0/[\mathrm{P{-}X}]_0$, the difference between the ideal behavior (eq 4) and the other models (eq 12 or 14) becomes significant only at high conversion (typically above about 70% conversion for an initial ratio $[\mathrm{X}^\bullet]_0/[\mathrm{P{-}X}]_0 = 0.05$). This is the reason why eq 4 fits well the experimental data in Figure 5 where only a slight excess of nitroxide is used as a rate moderator.

As mentioned in a previous paper, the strategy used herein is not universal since it is not applicable to styrene/TEMPO for instance.[18] To address the limitations of the use of excess nitroxide to moderate the polymerization rate, we can calculate the average lifetime of propagating radicals (τ) as well as the average number of monomer units (ν) added during each activation–deactivation cycle (characteristic time for activation $\theta = 1/k_\mathrm{d}$) (eqs 15 and 16). Finally, one can roughly estimate the time $t_{5\%}$ required to reach 5% conversion of the monomer (eq 17). Again, only the experimental value of N as well as the constants k_p and K are required to directly estimate $t_{5\%}$. Note that eq 17 also corresponds to the approximate integration of eq 4 (at low conversion).

$$\tau = 1/(k_\mathrm{c}[\mathrm{X}^\bullet]_0 + k_t[\mathrm{P}^\bullet]) \cong 1/(k_\mathrm{c}[\mathrm{X}^\bullet]_0) \qquad (15)$$

$$\nu = k_\mathrm{p}[\mathrm{M}]\tau \qquad (16)$$

$$t_{5\%} \cong 0.05(([\mathrm{M}]_0/[\mathrm{P{-}X}]_0)/\nu)(\theta + \tau) \cong 0.05\theta/(k_\mathrm{p}[\mathrm{P{-}X}]_0\tau) = 0.05N/(k_\mathrm{p}K) \qquad (17)$$

Using the conditions from Figure 5 ($[\mathrm{P{-}X}]_0 = 4.09 \times 10^{-2}$ mol L^{-1}, $[\mathrm{X}^\bullet]_0 = 2.2 \times 10^{-3}$ mol L^{-1}) in eqs 15–17 gives $\nu = 0.03$ and $t_{5\%} = 175$ h for styrene/TEMPO (with $k_\mathrm{d} = 5.2 \times 10^{-4}$ s^{-1}, $k_\mathrm{c} = 2.5 \times 10^8$ L mol^{-1} s^{-1})[11] and $\nu = 1.4$ and $t_{5\%} = 22$ min for styrene/DEPN (with $k_\mathrm{d} = 5.5 \times 10^{-3}$ s^{-1}, $k_\mathrm{c} = 5.6 \times 10^6$ L mol^{-1} s^{-1})[11] at $T = 120$ °C ($k_\mathrm{p} = 2050$ L mol^{-1} s^{-1}).[22] From a different set of equilibrium constants, one can also calculate $t_{5\%} = 15$ h for styrene/TEMPO (with $K = 2.1 \times 10^{-11}$ mol L^{-1} [33] and $k_\mathrm{p} = 2320$ L mol^{-1} s^{-1} [22] at $T = 125$ °C) and $t_{5\%} = 4$ min for styrene/DEPN (with $K = 6.1 \times 10^{-9}$ mol L^{-1} [20] and $k_\mathrm{p} = 2210$ L mol^{-1} s^{-1} [22] at $T = 123$ °C). Despite the discrepancies due to different values found in the literature for K (the former set refers to low molecular weight alkoxyamines styryl-X while the second set refers to macromolecular alkoxyamines polystyryl-X), it clearly shows that the polymerization of styrene is strongly inhibited by excess TEMPO while the polymerization still proceeds at a reasonable rate with excess DEPN. Almost no polymerization will occur before the excess TEMPO is consumed by external initiation such as thermal initiation. More generally, for systems with external initiation $R_i \neq 0$ and a high value of $N/(k_\mathrm{p}K)$, the time t_i (where $t_i = ([\mathrm{X}^\bullet]_0 - K[\mathrm{P{-}X}]_0(k_t/R_i)^{1/2})/R_i \cong [\mathrm{X}^\bullet]_0/R_i$) required to consume the excess nitroxide should be much larger than the time required to reach a finite conversion such as the time $t_{5\%}$. This condition is not fulfilled in the case of styrene/TEMPO since $t_i \cong 3$ h $\ll t_{5\%} \cong 15$ h (with $R_i = 2.5 \times 10^{-7}$ mol L^{-1} s^{-1} at 125 °C).[34] Thus, this simple calculation is a good indication as to whether the strategy presented herein (i.e., excess nitroxide) is well-suited to moderate the polymerization rate for a given monomer/nitroxide system.

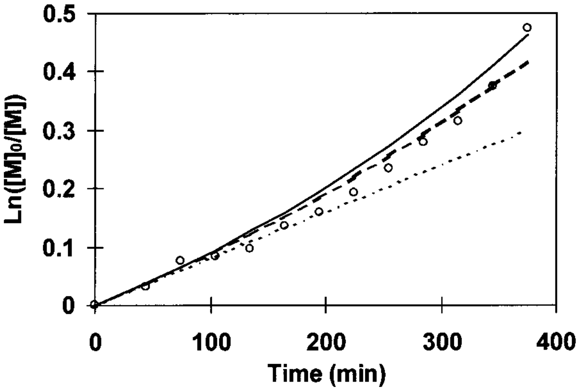

Figure 8. Kinetics of bulk polymerization of *n*-butyl acrylate at 125 °C in the presence of DEPN: $[\mathrm{DEPN}]_0/[\mathrm{PS\text{-}DEPN}]_0 = 0.77$; see Table 1 (run 1) for the exact recipe (○: experimental points); kinetic simulations based on eq 4 (- - -), eq 12 (— —), and eq 14 (—) with $K = 1.09 \times 10^{-10}$ L mol^{-1} s^{-1} calculated from eq 5; $k_\mathrm{p} = 93848$ L mol^{-1} s^{-1} and $k_{\mathrm{deg}} = 2.79 \times 10^{-5}$ s^{-1}.

Another point of interest is to predict the excess of nitroxide which is necessary to apply eq 4. During the preparation of this manuscript, Fischer et al.[35] proposed an elegant theoretical approach to this issue. They demonstrated that eq 4 should hold in the period of time $t_1 < t < t_2$ where $t_1 = 1/(k_\mathrm{c}[\mathrm{X}^\bullet]_0)$ is in the millisecond region and $t_2 = [\mathrm{X}^\bullet]_0^3/(3K^2[\mathrm{P{-}X}]_0^2k_\mathrm{t})$, corresponding to a 90% monomer conversion if $N > (3 \ln(10)Kk_\mathrm{t}/(k_\mathrm{p}[\mathrm{P{-}X}]_0))^{1/2}$. For poly(*n*-butyl acrylate), it indicates that N should be greater than 0.6% for a stationary state of $[\mathrm{P}^\bullet]$ in the conditions of Figure 5 (i.e., $T = 123$ °C, $[\mathrm{P{-}X}]_0 = 4.09 \times 10^{-2}$ mol L^{-1}). So, we are above the critical value of N ($N = 5.4\%$ in Figure 5), and we actually noted a linear dependence of $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs time. A similar calculation for polystyrene indicates that N should be greater than 40% for a stationary state of $[\mathrm{P}^\bullet]$ in the conditions of Figure 5 ($T = 123$ °C, $[\mathrm{P{-}X}]_0 = 4.09 \times 10^{-2}$ mol L^{-1}, with $K = 6.1 \times 10^{-9}$ mol L^{-1},[20] $k_\mathrm{p} = 2210$ L mol^{-1} s^{-1} [22] and $k_\mathrm{t} = 3.41 \times 10^8$ L mol^{-1} s^{-1} [21]). This also supports the high excess of DEPN ($N = 260\%$) used in our earlier work[18] on the styrene/DEPN system. However, in practice, with such a big excess of DEPN, the side reactions (degradation of DEPN, proton abstraction by DEPN) become very important and may explain the strong and early upward curvature of the kinetic plots that we observed for this system.[18] So, the theoretical work of Fischer et al.[35] confirms our experimental findings: much more DEPN is required for styrene in comparison with *n*-butyl acrylate in order to apply eq 4. Furthermore, their relation gives some useful limitations of the present method in the light of reaction parameters.

Conclusions

The method we previously reported for determining K for polystyrene, where an excess of nitroxide is used to govern the rate of the polymerization, has been applied to the system *n*-butyl acrylate/DEPN. We have determined $K = 4.93 \times 10^5 \exp(-119.3 \text{ kJ mol}^{-1}/RT)$. The reliability of the method is further supported by the successful kinetic simulation of a standard living polymerization. This method is very straightforward; moreover, it is also applicable to other related controlled polymerizations such as ATRP. Last, this work is particularly useful since in practice, some systems should incidentally obey the analytical kinetic equations presented herein, due to either a finite amount of persistent radical impurities in the initial system or to an initiator efficiency lower than unity in the case of a bicomponent system (initiator/nitroxide, reverse ATRP). The addition of a slight excess of DEPN efficiently moderates the rate of the bulk polymerization of *n*-butyl acrylate, which would otherwise be somewhat explosive.

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References and Notes

(1) (a) Bertin, D.; Destarac, M.; Boutevin, B. In *Polymer and Surfaces: A Versatile Combination*; Hommel, D., Ed.; Research Signpost: Trivandrum, India, 1998; pp 47−75. (b) Malmström, E. E.; Hawker, C. J. *Macromol. Chem. Phys.* **1998**, *199*, 923−935. (c) Matyjaszewski, K. In *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; p 2.

(2) Devenport, W.; Michalak, L.; Malmström, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. *Macromolecules* **1997**, *30*, 1929−1934

(3) (a) Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. *Macromolecules* **1996**, *29*, 8992−8993. (b) Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. *Macromolecules* **1998**, *31*, 7559−7561. (c) Georges, M. K.; Hamer, G. K.; Listigovers, N. A. *Macromolecules* **1998**, *31*, 9087−9089. (d) Goto, A.; Fukuda, T. *Macromolecules* **1999**, *32*, 618−623. (e) Ohno, K.; Izu, Y.; Yamamoto, S.; Miyamoto, T.; Fukuda, T. *Macromol. Chem. Phys.* **1999**, *200*, 1619−1625. (f) Pradel, J. L.; Boutevin, B.; Améduri, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3293−3302. (g) Burguière, C.; Dourges, M.-A.; Charleux, B.; Vairon, J.-P. *Macromolecules* **1999**, *32*, 3883−3890.

(4) Gaynor, S.; Greszta, D.; Shigemoto, T.; Mardare, D.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 585−586.

(5) Georges, M. K.; Listigovers, N. A.; Odell, P. G.; Hamer, G. K.; Quinlan, M. H.; Veregin, R. P. N. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 454−455.

(6) McLeod, P. J.; Georges, M. K.; Quinlan, M.; Moffat, K. A.; Listigovers, N. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 459−460.

(7) Odell, G.; Rabien, A.; Michalak, L. M.; Veregin, R. P. N.; Quinlan, M. H.; Moffat, K. A.; McLeod, P. J.; Listigovers, N. A.; Honeyman, C. H.; Georges, M. K.. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (2), 414−415.

(8) Keul, H.; Achten, D.; Höcker, H.. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 368−369.

(9) (a) Grimaldi, S.; Finet, J.-P.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Gnanou, Y.; Fontanille, M.; Nicol, P.; Pierson, J.-F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 651−652. (b) Benoit, D.; Grimaldi, S.; Finet, J.-P.; Tordo, P.; Fontanille, M.; Gnanou, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 729−730. (c) Benoit, D.; Grimaldi, S.; Finet, J.-P.; Tordo, P.; Fontanille, M.; Gnanou, Y. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998; p 225. (d) Puts, R.; Lai, J.; Nicholas, P.; Milam, J.; Tahilliani, S.; Masler, W.; Pourahmady, N. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 323−324. (e) Chong, Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. *Macromolecules* **1999**, *32*, 6895−6903.

(10) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.

(11) Le Mercier, C.; Lutz, J.-F.; Marque, S.; Le Moigne, F.; Tordo, P.; Lacroix-Desmazes, P.; Boutevin, B.; Couturier, J.-L.; Guerret, O.; Martschke, R.; Sobek, J.; Fischer, H. In *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; p 108.

(12) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc***.** **2000**, *122*, 5929−5939.

(13) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363−370

(14) Johnson, C. H. J.; Moad, G.; Solomon, D. H.; Spurling, T. H.; Vearing, D. J. *Aust. J. Chem.* **1990**, *43*, 1215−1230.

(15) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661−7670

(16) Fischer, H. *Macromolecules* **1997**, *30*, 5666−5672.

(17) He, J.; Zhang, H.; Chen, J.; Yang, Y. *Macromolecules* **1997**, *30*, 8010−8018.

(18) Lacroix-Desmazes, P.; Lutz, J.-F.; Boutevin, B. *Macromol. Chem. Phys.* **2000**, *201*, 662−669.

(19) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206−4215.

(20) Lutz, J.-F.; Lacroix-Desmazes, P.; Boutevin, B. *Macromol. Rapid Commun.* **2001**, *22*, 189−193.

(21) Buback, M.; Kuchta, F.-D. *Macromol. Chem. Phys.* **1997**, *198*, 1455−1480.

(22) (a) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.; D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267. (b) Kostanski, L. K.; Hamielec, A. E. *Polymer* **1992**, *33*, 3706.

(23) Beuermann, S.; Buback, M.; Schmaltz, C. *Ind. Eng. Chem. Res.* **1999**, *38*, 3338−3344.

(24) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746−2754.

(25) Andrews, R. J.; Grulke, E. A. In *Polymer Hanbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; Section 6, p 193.

(26) Guerret, O.; Couturier, J.-L.; Centre de Recherche Rhône Alpes, Elf Atochem, private communication.

(27) (a) Kothe, T.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1553−1559. (b) Goto, A.; Fukuda, T. *Macromol. Chem. Phys.* **2000**, *201*, 2138−2142.

(28) Fukuda, T.; Goto, A.; Ohno, K. *Macromol. Rapid Commun.* **2000**, *21*, 151−165.

(29) Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1885−1901

(30) Dixon, K. W. In *Polymer Hanbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; Section 2, p 1.

(31) Le Mercier, C. Thèse de Doctorat, Université Aix-Marseille I, 11 Décembre 2000.

(32) Lacroix-Desmazes, P.; Delair, T.; Pichot, C.; Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3845−3854.

(33) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393−6398.

(34) Hui, A. W.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1974**, *16*, 749.

(35) Souaille, M.; Fischer, H. *Macromolecules*, in press.

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