n-Butyl Acrylate Polymerization Mediated by a PROXYL Nitroxide

Neil R. Cameron* and Alistair J. Reid

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

Received September 25, 2002; Revised Manuscript Received November 6, 2002

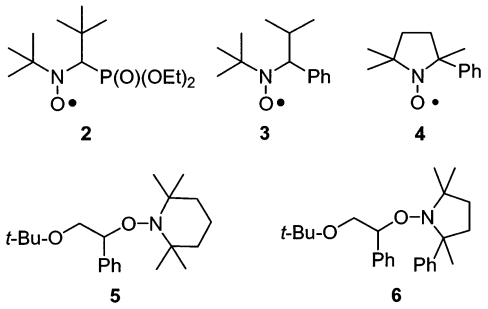
ABSTRACT: *n*-Butyl acrylate has been polymerized in the presence of an alkoxyamine initiator derived from the PROXYL nitroxide 2,2′,5-trimethyl-5′-phenylpyrrolidinyl-1-oxyl. It was found that polymerizations were rapid, reaching almost complete conversion within 2 h; in contrast, no conversion was observed when TEMPO was used as the mediator. The addition of a small amount of free nitroxide resulted in slower polymerizations although an induction period, the length of which varied with excess nitroxide concentration, was observed. Size exclusion chromatography indicated that polymerization control was poor; M_n initially increased rapidly and then much more slowly, and polydispersities were found to be broad and to increase with conversion. Quantitative ^{13}C NMR spectroscopy revealed the resulting poly(*n*-butyl acrylate) to be branched. Despite the poor control, the PBA was able to act as a macroinitiator for the polymerization of styrene, yielding a block copolymer with a growth in M_n and a reduction of polydispersity with conversion. It is suggested that the polymerization of *n*-butyl acrylate in the presence of the substituted PROXYL derivative is living but not controlled.

Introduction

Controlled radical polymerization (CRP) is a technique for the preparation of polymers of tailored architectures using experimentally simple techniques.[1] The CRP methods that have received the most attention are nitroxide-mediated radical polymerization (NMRP),[2,3] atom transfer radical polymerization (ATRP),[4] and reversible addition−fragmentation transfer (RAFT) polymerization,[5] the first two of which are characterized by a mechanism that involves equilibria between dormant and active polymerizing moieties. For NMRP, this involves nitroxide stable free radicals, such as TEMPO (**1**),[2] which combine rapidly but *reversibly* with alkyl radicals (Scheme 1). In addition to the reactions shown in Scheme 1, irreversible termination between carbon-centered radicals occurs, leading to dead material. However, this causes an excess of nitroxide relative to alkyl radicals to be produced, which consequently suppresses further irreversible termination. This is known as the persistent radical effect (PRE),[6] and its result is that the growth of the chains after an initial period occurs in a controlled fashion. In addition, it has been demonstrated that reinitiation and block copolymer formation are possible in NMRP as the vast majority of chains have terminal nitroxide residues once the polymerization is complete.

After seminal early work by Georges et al.,[3,7] it was realized that **1** was largely unsuitable for the bulk polymerization of monomers other than styrene or derivatives thereof, in particular acrylates and methacrylates being beyond its scope. This was reckoned[8] to be due to the low equilibrium constant between dormant and active species (in Scheme 1, $K \sim 10^{-11}$). The associated low radical concentration is supplemented by the autopolymerization of styrene at reaction temperature (typically 125 °C). Nonetheless, recent work[9] has shown that poly(styrene-*b*-*n*-butyl acrylate) copolymers can be prepared in miniemulsion with TEMPO at 135 °C. An initially prepared polystyrene seed latex is swollen with *n*-butyl acrylate and heated for 6 h at 135 °C, yielding a block copolymer latex of narrow polydispersity (1.18) in quantitative yield. It was speculated that TEMPO was partitioning between aqueous and organic phases, leading to a lower concentration at the locus of polymerization and thus permitting a reasonable rate of polymerization. Addition of ascorbic acid to the aqueous phase, to reduce excess TEMPO, enabled the miniemulsion homopolymerization of *n*-butyl acrylate although polydispersities were quite broad (1.6−1.9).[10] Despite the above reports, TEMPO is not an ideal mediator for acrylate polymerizations. Recent years have seen the development of novel nitroxides based on open-chain structures, DEPN (**2**) and TIPNO (**3**), Chart 1, which have been shown to be much more successful.[11,12] These can mediate effectively the polymerization of styrene as well as monomers such as acrylates and acrylamides. It has been shown that such nitroxides produce significantly higher values of K than TEMPO (10^{-8}−10^{-9}) and so can be used to mediate the polymerization of monomers that do not undergo autopolymerization.[13] Recent work by Fischer and co-workers[14] has further elucidated the reasons for the differences between TEMPO and DEPN. DEPN always leads to higher values of k_d together with lower k_c than TEMPO, due to increased steric bulk of the former. For a given combination of nitroxide and monomer, there exists a range of values of k_c, k_d, and k_p that permit a living and controlled polymerization. For TEMPO with styrene,

Chart 1. Structures of DEPN (2), TIPNO (3), and the Nitroxide and Alkoxyamines Employed in the Present Study



2 **3** **4** **5** **6**

* Corresponding author: e-mail n.r.cameron@durham.ac.uk.

10.1021/ma0256892 CCC: $22.00
Published on Web 12/07/2002

both livingness and control are predicted and are observed; however, for *n*-butyl acrylate k_p is much too large, leading to living but uncontrolled polymerizations (broad polydispersities). DEPN, on the other hand, fulfills all the conditions for living and controlled polymerizations with both styrene and *n*-butyl acrylate, although the latter monomer gives very rapid polymerizations and an excess of free nitroxide is required to provide control.

A common perception is that all cyclic nitroxides perform like TEMPO and that open-chain structures are the only species to behave any differently. However, examination of the literature shows this not to be the case; in particular, substituted pyrrolidinyloxyl (PROXYL) derivatives, the five-membered ring analogues of TEMPO, have been shown to give faster styrene polymerization than TEMPO. Veregin et al.[15] demonstrated that 3-carboxy-PROXYL did indeed mediate styrene polymerization significantly more rapidly than TEMPO, when used in conjunction with benzoyl peroxide (BPO) as the radical source. Furthermore, ESR experiments indicated that a model low molecular weight alkoxyamine derived from the PROXYL species had a C−O homolysis activation energy ∼20 kcal mol^{-1} lower than that for the corresponding TEMPO analogue. A chiral C-2 symmetric 2,5-diphenyl-subsituted PROXYL derivative has been used in CRP employing BPO in a bimolecular initiating strategy.[16] This mediator was also found to result in a significantly faster polymerization of styrene than TEMPO. The IBM group led by Hawker in collaboration with Braslau et al. also employed this mediator in the form of an alkoxyamine unimolecular initiator and similarly observed a faster rate of styrene polymerization compared to TEMPO.[12] Furthermore, it was shown that *n*-butyl acrylate could be polymerized in its presence, although broad polydispersities (∼2) were obtained. Yamada and co-workers[17] employed a number of PROXYL nitroxides to polymerize styrene, and it was found that ring-substituted species led to rate enhancements over TEMPO or PROXYL itself. However, the polymerizations employed bimolecular initiating systems, which are less reliable than alkoxyamines. Workers at Ciba[18] trapped cyanopropyl radicals with the nitrone 2,5,5′-pyrrolidin-*N*-oxide, generating a substituted PROXYL species. The rapid and controlled polymerization of styrene with this mediator was observed, but *n*-butyl acrylate resulted in broad polydispersities and poor control. Viklund et al.[19] used 3-carboxy-PROXYL as a mediator to prepare poly(styrene−DVB) porous monoliths with high surface areas and permeabilities and observed that polymerizations proceeded much more rapidly than with TEMPO.

From these studies, it is evident that PROXYL species behave differently from their six-membered ring analogues and indeed that there is scope for the polymerization of acrylates, which to our knowledge is not possible in bulk with TEMPO. The reasons for the differences between the two mediating systems are not clear, and evidently there is scope for further investigation. In our previous work,[20] we examined the influence of the structure of PROXYL nitroxides substituted in the 2-position on the polymerization of styrene and found that one variant bearing a phenyl group (**4**) could lead to a controlled polymerization that proceeded more than twice as fast as that involving **1**. In the work described here, we report our results on the use of PROXYL nitroxide **4** to mediate the polymerization of *n*-butyl acrylate. Polymerizations have been conducted using alkoxyamines (**5** and **6**), which generate the nitroxide mediators during polymerization, as the initiating species.

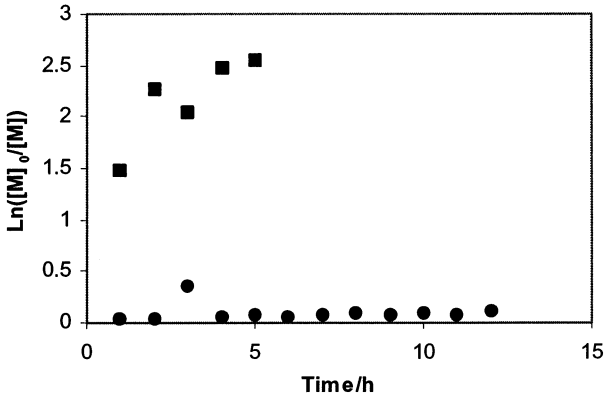


Figure 1. Polymerization of *n*-butyl acrylate in the presence of 0.125 mmol of **5** (●) and **6** (■).

Experimental Section

Materials and Instrumentation. *n*-Butyl acrylate and styrene were freed of inhibitor by passing through basic alumina and were distilled under N_2 immediately prior to use. TEMPO (**1**) was purified by vacuum sublimation. Size exclusion chromatography (SEC) at 30 °C with refractive index, viscosity, and light scattering detectors, using THF as a solvent at a flow rate of 1 mL min^{-1}, was employed to determine molecular weights and molecular weight distributions. NMR spectroscopy was performed using a Varian Inova 300 MHz spectrometer, employing $CDCl_3$ as a solvent. Spectra were referenced to the $CHCl_3$ impurity in the solvent, at 7.27 δ.

Synthesis of Nitroxides and Alkoxyamines. Nitroxide **4** and alkoxyamine initiators **5** and **6** were synthesized and purified according to known procedures;[20,21] characterization data in all cases were in agreement with literature values.[20,22]

***n*-Butyl Acrylate Polymerization.** A solution of *n*-butyl acrylate (5.0 g, 39 mmol) and alkoxyamine (**5** or **6**, 0.125 mmol) in a round-bottomed flask was degassed by three freeze−pump−thaw cycles. The flask was back-filled with N_2 following the last cycle. The solution was then divided between several previously purged GC vials with PTFE seals by syringe transfer. The vials were heated at 125 °C in an oil bath, withdrawn periodically, and immediately cooled in an ice bath. Conversion was determined by ^{1}H NMR spectroscopy; molecular weights and polydispersity were determined without further purification by SEC.

Styrene Polymerization Initiated by a Poly(*n*-butyl acrylate) Macroinitiator. Poly(*n*-butyl acrylate) was prepared from *n*-butyl acrylate (5.0 g, 39 mmol) and alkoxyamine **6** (48 mg, 0.125 mmol) as described above and was isolated by precipitation into methanol followed by decantation and drying in vacuo, giving 4.8 g (95%) of polymer. SEC analysis of the product gave M_n = 30 800, M_w = 68 100, and M_z = 112 000 g mol^{-1}. The resulting PBA macroinitiator (4.0 g, 0.1 mmol of nitroxide moiety) was added to styrene (5.0 g, 48 mmol), and polymerization was conducted as described above.

Results and Discussion

Our initial studies involved heating a solution of **5** in *n*-butyl acrylate at 125 °C for 12 h, after which time very little conversion had been achieved (Figure 1). In contrast, **6** under the same conditions led to essentially complete (96%) conversion to polymer after only 4 h. Therefore, it can be seen that the structure of the nitroxide component of the alkoxyamine has a profound influence on the latter's ability to bring about the polymerization of *n*-butyl acrylate. Some scatter in the

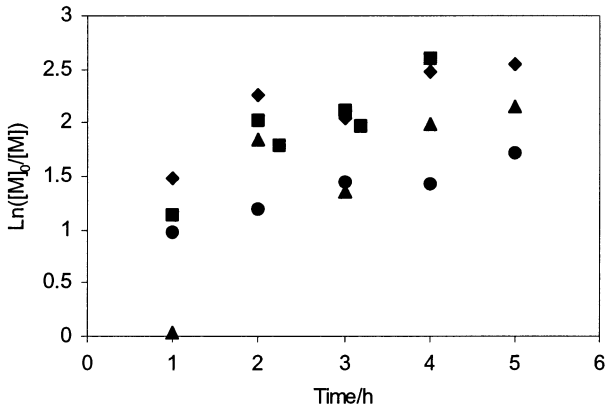


Figure 2. Polymerization of *n*-butyl acrylate in the presence of 0.125 mmol of **6** and a small quantity of **4** relative to **6**: 0 equiv (◆); 0.03 equiv (●); 0.05 equiv (■); 0.10 equiv (▲).

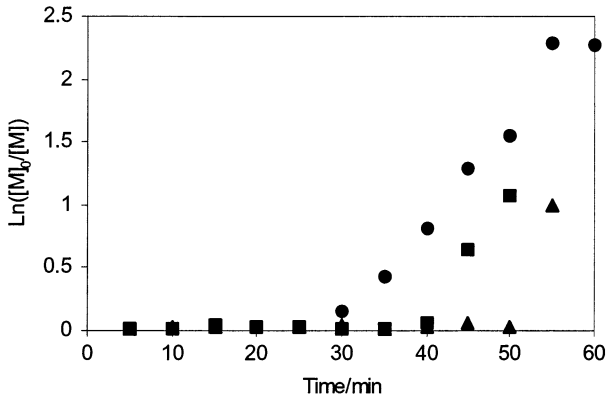
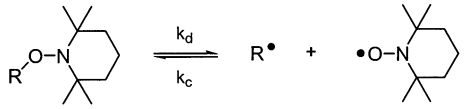


Figure 3. Initial period of the polymerization of *n*-butyl acrylate in the presence of 0.125 mmol of **6** and a small quantity of **4** relative to **6**: 0.03 equiv (●); 0.05 equiv (■); 0.10 equiv (▲).

data can be seen in Figure 1 (the third data point for alkoxyamine **5**; points 2 and 3 for alkoxyamine **6**). This is probably due to the experimental procedure, where the polymerization mixture is divided between a number of prepurged vials. This method was employed as it was found to be impossible to sample a solution by syringe at moderate conversions, due to very high viscosities. However, it is more prone to error as many more reaction vessels need to be prepared, increasing the possibility of oxygen ingress.

The polymerization of *n*-butyl acrylate in the presence of **6** was further investigated. As shown in Figure 2, high conversion to polymer was observed after 1 h of reaction (the first data point to be sampled). Related studies by Hawker et al.[12] and Lacroix-Desmazes et al.[23] describe the rapid and uncontrolled polymerization of *n*-butyl acrylate unless a small excess of nitroxide, typically 5 mol % relative to the alkoxyamine concentration, is added. This produces an excess of nitroxide relative to propagating radicals from the beginning of the polymerization, which leads to a more controlled reaction. Also shown in Figure 2 are the results of polymerizing *n*-butyl acrylate in the presence of **6** plus a small excess of nitroxide **4**. It can be seen that excess nitroxide concentrations of either 0.03 or 0.05 equiv lead to high but incomplete conversion after 1 h, followed by a steady increase in conversion over time. A higher amount of added nitroxide results in an induction period extending beyond the first hour of reaction. Figure 2 appears to indicate that polymerization with 0.05 equiv of excess nitroxide is more rapid than that with 0.03 equiv added. However, this is a misleading conclusion as conversion is already high (>63%) when the first data point is sampled. More meaningful information is obtained by comparing different excess nitroxide concentrations during the first hour of polymerization. Consequently, the experiments depicted in Figure 2 were repeated with samples being taken every 5 min over the first hour; the results are presented in Figure 3. As in Figure 2, an excess nitroxide concentration of 0.10 equiv leads to a long induction period of around 1 h, whereas lower added quantities of **4** result in shorter periods of low or zero polymerization (around 20 min for 0.03 equiv added). For an excess nitroxide concentration of 0.03 equiv, the polymerization proceeds at a constant rate with a linear increase in $\ln([M]_0/[M])$, indicating a constant number of polymerizing centers. The reason for the presence of the induction period is unknown. Zero polymerization implies that the equilibrium in Scheme 1 lies too far to the left. A finite period of no polymerization followed by rapid conversion, i.e., an induction period, suggests that the equilibrium constant is changing during the reaction. This could be brought about by nitroxide decomposition during polymerization, an explanation used by Lacroix-Desmazes et al.[23] to describe an upward deviation in the gradient of the plot of $\ln([M]_0/[M])$ vs time for the polymerization of *n*-butyl acrylate mediated by **2**. Alternatively, the ending of the induction period could occur by external radical generation. Since *n*-butyl acrylate is widely believed to be unsusceptible to autopolymerization, such radicals would have to be generated by impurities such as peroxides. Both processes would result in a reduction of excess nitroxide concentration, altering the position of the equilibrium in Scheme 1 until polymerization was permitted to occur. The direct dependence of the length of the induction period on the quantity of excess nitroxide added lends weight to these arguments. Attempts to identify peroxide impurities by headspace GC-MS were unsuccessful, suggesting that external radicals are not responsible. However, at the present time we are otherwise uncertain of the source of the induction period. There appears to be discrepancies in conversion between polymerizations conducted in the presence of the same quantity of added nitroxide. For instance, with 0.1 equiv of added **4** zero conversion is found after 1 h in Figure 2, whereas conversion is around 60% after 55 min in Figure 3. We ascribe these differences to errors in the timing of sampling, which are greatly exacerbated by the speed of polymerization. Other differences between Figures 2 and 3 are most likely due to inherent errors in NMR integration.

Scheme 1. Equilibrium between Dormant and Active Species in Nitroxide-Mediated Radical Polymerization (NMRP)



1

Molecular weight data for the samples obtained in the presence of **6** and an excess nitroxide concentration of 0.03 equiv are presented in Figure 4. What is immediately apparent is that the polymerization is poorly controlled. M_n increases very rapidly to around 50 000 at low conversion, much higher than that predicted on

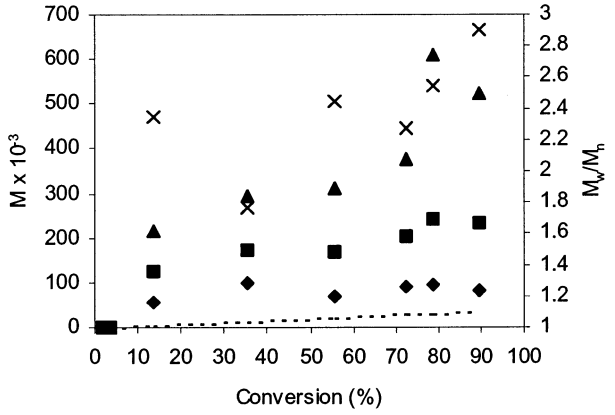


Figure 4. Molecular weight data, obtained by SEC, for the polymerization of *n*-butyl acrylate in the presence of 0.125 mmol of **6** and 0.03 equiv of **4** relative to **6**: M_n (◆); M_w (■); M_z (▲); M_w/M_n (×). Dotted line shows the theoretical evolution of M_n with conversion.

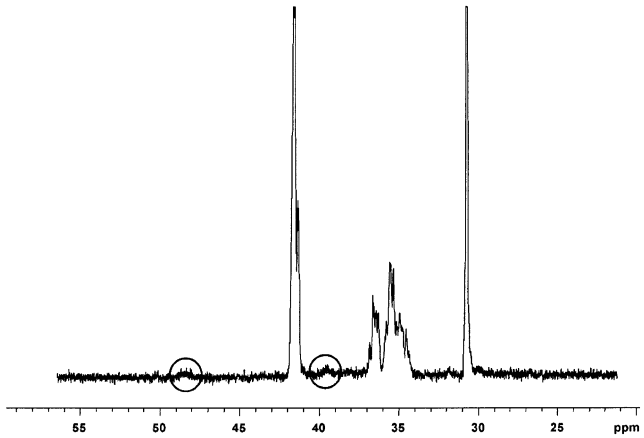


Figure 5. Quantitative ^{13}C NMR spectra of poly(*n*-butyl acrylate) prepared in the presence of **6** at 46% conversion

the basis of the ratio of alkoxyamine to monomer, and then does not rise much on increasing conversion. M_w and especially M_z increase to very high levels with increasing conversion, as does polydispersity. These data indicate that the control over the polymerization mediated by **4** is poor and are comparable to previous results obtained for the polymerization of *n*-butyl acrylate with PROXYL nitroxides. For example, Hawker and Barslau et al.[12] obtained PBA of $M_n = 32\,000$ (theoretical 25 400) and polydispersity = 2.05 with an alkoxyamine derived from 2,5-dimethyl-2,5-diphenylpyrrolidinyl-1-oxyl after 16 h at 123 °C. Zink and co-workers[18] similarly observed molecular weights much higher than predicted together with broad polydispersities for the polymerization of BA in the presence of an in-situ formed PROXYL nitroxide.

Branching in *n*-butyl acrylate polymerization is well-known[24] and has been observed during both its atom transfer radical polymerization[25] and nitroxide-mediated CRP in bulk and miniemulsion.[26] We performed quantitative ^{13}C NMR spectroscopy to investigate whether branching was occurring in our polymerizations. Figure 5 shows the spectrum of PBA after 46% conversion and the presence of small signals at around 39 and 48 ppm (circled) can clearly be seen. Following the work of Lovell et al.,[24] we assign these to the CH_2/CH and the quaternary C resonances of the monomer units adjacent to a branch point. Although the extent of branching was not quantified, the size of the peaks

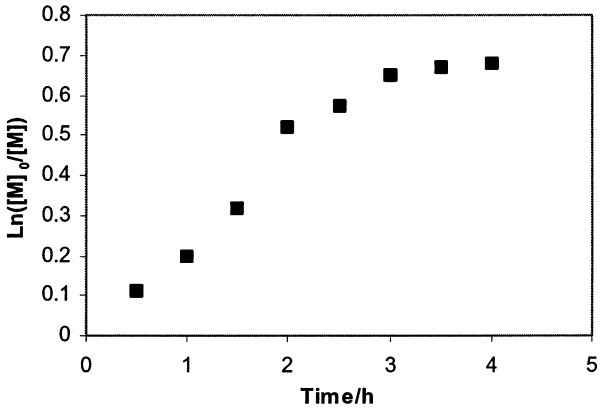


Figure 6. Polymerization of styrene initiated by a PBA macroinitiator.

in Figure 5 suggests that it is similar to that found by Farcet et al.,[26] and so we estimate it to be around 2% at complete conversion. Branching in *n*-butyl acrylate polymerization can occur by either an inter- or an intramolecular (backbiting) mechanism. Lovell and co-workers[24] found that the mechanism of transfer depended on the concentration of monomer in solution polymerizations, intramolecular processes occurring in dilute solution switching to an intermolecular mechanism at higher concentration. In contrast to this, Charleux et al.[26] concluded that backbiting dominates in nitroxide-mediated *n*-butyl acrylate bulk and miniemulsion polymerization. The differences may be due to the higher temperature used in the latter case (112 vs 70 °C). Although branching in PBA has been demonstrated, we conclude that the high polydispersities shown here are more likely to be due to poor control. The possible reasons for this are discussed below.

Despite the poor control over the polymerization of *n*-butyl acrylate by **4**, we decided to investigate the ability of the resulting poly(*n*-butyl acrylate) to act as a macroinitiator for subsequent polymerizations. Accordingly, PBA was prepared by polymerization of *n*-butyl acrylate by **6** at 125 °C for 12 h. The resulting polymer was isolated by precipitation, dried to constant mass in vacuo (95% yield; $M_n = 30\,800$, $M_w = 68\,100$, and $M_z = 112\,000$ g mol^{-1}) and subsequently added to a charge of styrene. The solution was divided between a number of sample vials, which were heated at 125 °C and withdrawn periodically. The polymerization of styrene with time is shown in Figure 6 and is seen to proceed linearly up to around 50% conversion. This indicates that the PBA macroinitiator is indeed capable of initiating the polymerization of styrene. However, the polymerization appears to stop at longer times, indicating that termination and loss of activity occur.

The molecular weight data of the resulting p(BA−S) copolymers were obtained again by SEC. Interestingly, M_n was seen to increase with conversion and the polydispersity to decrease (Figure 7). This indicates a controlled polymerization, suggesting that the PBA macroinitiator is capable of producing a block copolymer and that the polymerization of styrene proceeds in a controlled manner (although M_n lies slightly above the theoretical values based on the ratio of macroinitiator to monomer). SEC data obtained with a light scattering detector (Figure 8) indicate that the molar mass of the PBA macroinitiator increases on reinitiation with little or no evidence of bimodality in the block copolymer trace, indicating that the macroinitiator contained little

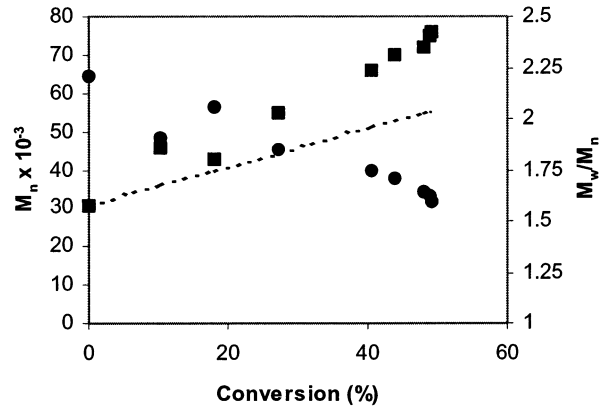


Figure 7. Molecular weight data, obtained by SEC, for the polymerization of styrene initiated by a PBA macroinitiator: M_n (■); M_w/M_n (●). Dotted line shows the theoretical evolution of M_n with conversion.

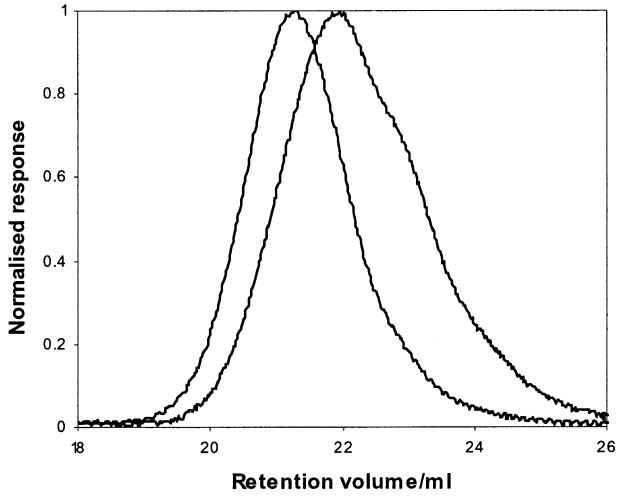


Figure 8. SEC traces for a poly(*n*-butyl acrylate-*b*-styrene) copolymer and the original poly(*n*-butyl acrylate) macroinitiator (right-hand trace).

or no dead PBA material. The narrowing of the polydispersity values of the copolymer is most probably due to better control over formation of the styrene block plus its assumed linearity, as styrene has little or no propensity for branching.

The ability of PBA to initiate and induce some control in the polymerization of styrene with little evidence of dead material indicates that the vast majority of PBA chains possess a nitroxide moiety. However, the polymerizations are characterized by poor control and broad polydispersities. Fischer[6,27] has pointed out that living character and polymerization control are separate phenomena and that it is indeed possible to have a living polymerization, producing little or no dead material, that gives a broad polydispersity product. Livingness is determined by K, which has a limiting value, dependent on k_p and k_t for the monomer in question, above which large fractions of dead material are produced at high conversion. On the other hand, control is determined by the product $k_d k_c$, which should be larger than a threshold value, again peculiar to each monomer, required to give a low polydispersity. Thus, for a given set of values of k_p and k_t and initial initiator concentration there is a range of values of k_d and k_c that gives rise to a polymerization that is both living *and* controlled. It is likely that the product $k_d k_c$ for **4** in *n*-butyl acrylate is relatively small, leading to poor control, while K ($=k_d/k_c$) is still sufficiently low to ensure that little dead material is produced. The differences in performance between **4** and TEMPO (**1**) could be due to differences in k_d and k_c; we found previously[20] that **4** gave a higher rate of styrene polymerization than **1**, which suggests a higher value of K. The results of an investigation of the homolysis of alkoxyamine **6** and related compounds will be reported elsewhere. Fischer et al.[14] recently predicted that the polymerization of *n*-butyl acrylate with TEMPO should also show living/uncontrolled characteristics. However, in our hands very little conversion of *n*-butyl acrylate occurred in the presence of TEMPO. It is known that TEMPO is prone to causing hydrogen abstraction,[28] and indeed we have found that the 1-phenethyl alkoxyamine derived from **1** gives rise to much more styrene and hydroxylamine than the corresponding alkoxyamine obtained from **4**.[29] This may in fact be the crucial difference between **4** and **1**.

Conclusions

An alkoxyamine derived from a PROXYL nitroxide is able to mediate the polymerization of *n*-butyl acrylate, but control is much poorer than that achieved with initiators produced from open-chain nitroxides. Branched poly(*n*-butyl acrylate) is produced, which is able to act as an efficient macroinitiator for the polymerization of styrene, indicating that most PBA chains possess a nitroxide moiety. It is suggested that the polymerization of *n*-butyl acrylate in the presence of **4** is living but not controlled. Differences observed between PROXYL nitroxides and TEMPO may be due to differences in equilibrium constant between dormant and active chains or to a greater tendency of TEMPO to bring about β-hydrogen abstraction at the active center.

Acknowledgment. The authors thank the EPSRC and Schlumberger for funding this work, Dr. G. Tustin of Schlumberger Cambridge Research for helpful discussions, and Mr. D. Carswell for performing the SEC analyses.

References and Notes

(1) *Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2000; Vol. 768.
(2) Solomon, D. H.; Rizzardo, E.; Caciolo, P. Eur. Pat. Appl. 135280, 1985.
(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987−2988.
(4) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721−1723.
(5) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.
(6) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581−3610.
(7) Georges, M. K.; Veregin, R. P. N.; Daimon, K. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Vol. 685, Chapter 20.
(8) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393−6398. Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746−2754. Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661−7670.
(9) Keoshkerian, B.; MacLeod, P. J.; Georges, M. K. *Macromolecules* **2001**, *34*, 3594−3599.
(10) Keoshkerian, B.; Szkurhan, A. R.; Georges, M. K. *Macromolecules* **2001**, *34*, 6531−6532.

(11) Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Vol. 685, Chapter 14.
(12) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.
(13) Lacroix-Desmazes, P.; Lutz, J. F.; Boutevin, B. *Macromol. Chem. Phys.* **2000**, *201*, 662−669. Lutz, J.-F.; Lacroix-Desmazes, P.; Boutevin, B. *Macromol. Rapid Commun.* **2001**, *22*, 189−193.
(14) Ananchenko, G. S.; Souaille, M.; Fischer, H.; Le Mercier, C.; Tordo, P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3264−3283.
(15) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391−4398.
(16) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323−3325.
(17) Yamada, B.; Miura, Y.; Nobukane, Y.; Aota, M. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Vol. 685, Chapter 12.
(18) Zink, M.-O.; Kramer, A.; Nesvadba, P. *Macromolecules* **2000**, *33*, 8106−8108.
(19) Viklund, C.; Nordstrom, A.; Irgum, K.; Svec, F.; Frechet, J. M. J. *Macromolecules* **2001**, *34*, 4361−4369.
(20) Cameron, N. R.; Reid, A. J.; Span, P.; Bon, S. A. F.; van Es, J. J. G. S.; German, A. L. *Macromol. Chem. Phys.* **2000**, *201*, 2510−2518.
(21) Hideg, K.; Hankovszky, H. O.; Halasz, H. A.; Sohar, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2905−2911. Hideg, K.; Lex, L. *J. Chem. Soc., Chem. Commun.* **1984**, 1263−1265. Keana, J. F. W.; Seyedrezai, S. E.; Gaughan, G. *J. Org. Chem.* **1983**, *48*, 2644−2647. Bon, S. A. F.; Chambard, G.; German, A. L. *Macromolecules* **1999**, *32*, 8269−8276.
(22) Couet, W. R.; Brasch, R. C.; Sosnovsky, G.; Lukszo, J.; Prakash, I.; Gnewuch, C. T.; Tozer, T. N. *Tetrahedron* **1985**, *41*, 1165−1172.
(23) Lacroix-Desmazes, P.; Lutz, J. F.; Chauvin, F.; Severac, R.; Boutevin, B. *Macromolecules* **2001**, *34*, 8866−8871.
(24) Ahmad, N. M.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822−2827.
(25) Roos, S. G.; Muller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 864−867.
(26) Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. *Macromolecules* **2002**, *35*, 4912−4918.
(27) Souaille, M.; Fischer, H. *Macromolecules* **2000**, *33*, 7378−7394.
(28) Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 3520−3525. Skene, W. G.; Scaiano, J. C.; Yap, P. A. *Macromolecules* **2000**, *33*, 3536−3542. Souaille, M.; Fischer, H. *Macromolecules* **2001**, *34*, 2830−2838.
(29) Bacon, C. A.; Cameron, N. R.; Reid, A. J. Unpublished results.

MA0256892