# Verdazyl-Mediated Living-Radical Polymerization of Styrene and *n*-Butyl Acrylate

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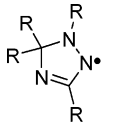
ABSTRACT: The radical polymerization of styrene and *n*-butyl acrylate is demonstrated to proceed under controlled conditions between 125 and 130 °C in the presence of either a 1,5-dimethyl-3-phenyl-6-oxoverdazyl radical or a 1,5-dimethyl-3-ethyl-6-oxoverdazyl radical producing polymers with polydispersity indices in the 1.2−1.3 range. While polymerizations initiated with benzoyl peroxide or 1,1-azobis(cyanocyclohexane) in the presence of verdazyl radical were unsuccessful, polymerizations initiated with a styrene/verdazyl unimolecular initiator proceeded in a living fashion, although quite slowly. An increase in polymerization rate was obtained with a 1,5-dimethyl-6-oxoverdazyl radical, producing higher yields of well-defined polymers. The livingness of the resulting styrene and *n*-butyl acrylate homopolymers is illustrated with chain extension reactions to make well-defined diblock copolymers. These results open a new front in the development of living-radical polymerization processes, and the ability to manipulate the verdazyl structure offers the opportunity to further control and modify this process.

## Introduction

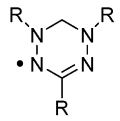
The controlled polymerizations of vinyl monomers by living-radical polymerization processes continue to fascinate scientists working in the polymer field. Three systems garner the most attention: the stable free-radical polymerization (SFRP)[1] system, atom transfer radical polymerization,[2] and reversible-addition fragmentation chain transfer.[3] These methods mimic ionic polymerizations in their ability to produce narrow polydispersity polymers but have distinct advantages inherent to free-radical polymerizations, including synthetic ease, versatility, and compatibility with monomers containing a wide variety of functional groups.

A number of persistent radicals have been employed as mediating species in the SFRP process with varying degrees of success, including (arylazo)oxyl,[4] galvinoxyl,[5] borinate,[6] highly substituted alkyl,[7] and nitroxide.[1,8] The nitroxides are by far the most successful and extensively studied of these, and work continues with emphasis on the development of new nitroxides allowing lower reaction temperatures and the ability to control the polymerization of (meth)acrylates.[9] Two other types of persistent radicals previously investigated as SFRP mediators are the closely related triazolinyls and verdazyls, the latter being the focus of the work presented in this paper. Klapper and Müllen demonstrated that the triazolinyl radical **1** (1,3,5,5-tetraphenyl-$\Delta^3$-1,2,4-triazolin-2-yl) offered some degree of control over the polymerization of styrene, methyl methacrylate, and *N*,*N*-(dimethylamino)ethyl methacrylate.[10] Although broad molecular weight distributions were obtained ($M_w/M_n > 1.6$ at high conversions), the "livingness" of the system was demonstrated by the ability to chain extend triazolinyl-terminated polystyrenes. Greater control over the SFRP of styrene was achieved with the use of a spirotriazolinyl radical (1′,3′-diphenylspiro[9*H*-fluorene-9,5′-[$\Delta^3$-1,2,4-triazolin]-2-yl, $M_w/M_n = 1.3 - 1.4$).[11] However, the attempted polymerization of methyl methacrylate in the presence of this radical was not successful.

Yamada reported the polymerization of various monomers moderated by the 1,3,5-triphenylverdazyl radical **2**.[12,13] At 60 °C polymerization of styrene did not occur while the homopolymerization of methyl methacrylate proceeded to conversions of only 3−9% over 30−40 h.[12] When the polymerization of styrene was repeated at 110 °C, first-order kinetics were observed; however, the polydispersity indices ($M_w/M_n$) of the resulting polystyrenes were typically greater than 2, and end-group analysis showed that ∼60% of the chains were the product of bimolecular termination reactions.[13] It was concluded by the authors that a pure "living" radical polymerization could not be mediated under these conditions.



**1** R = Ph



**2** R = Ph

Despite the meager success obtained in these previous studies, we felt verdazyls possess features that make them worthy of further investigation for application in SFRP. Verdazyls are inherently very stable radicals and lend themselves to a myriad of structural modifications, providing the opportunity to perform extensive studies on the relationship of their structure to their ability to control living-radical polymerizations. Furthermore, there exists an extensive body of literature relating to their syntheses that continues to be developed, providing relatively easy access to these molecules.[14] For these reasons, a study was initiated to determine whether oxo-verdazyls with various R and R′ substitutents (**3**) could successfully mediate a SFRP process.

The current work aims to improve on the previous results of verdazyl-mediated SFRP reported by Yamada, proving the SFRP

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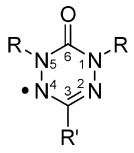
process amenable to expansion through the use of other families of stable radicals. In this paper we report our initial findings and demonstrate that living-radical polymerizations of styrene and *n*-butyl acrylate can be mediated by verdazyl radicals when the R substitutents are methyl groups and the R′ substitutent is either phenyl, ethyl, or hydrogen. We further show, with illustrative examples, that the homopolymers made by this technique can be chain extended to give well-defined diblock copolymers.



**3a** R, R' = Ph
**3b** R = Me; R' = Ph
**3c** R = Me; R' = Et
**3d** R = Me; R' = H

## Experimental Section

**(a) Materials and Equipment.** Benzoyl peroxide (BPO, Aldrich, 70% solids content in water) was purified by recrystallization from methanol. 1,1′-Azobis(cyclohexanecarbonitrile) (Aldrich, 98%) was used as received. The BST unimer **4** (2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-oxy)ethyl benzoate) was prepared according to the literature and recrystallized from isopropanol.[15] Benzoic acid 2-bromo-2-phenylethyl ester was prepared following standard benzylic bromination conditions,[16] as described in a recent publication.[17] *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine (Aldrich, 99%), $Cu^0$ (Aldrich, 99%), $CuBr_2$ (Aldrich, 99.999%), and all solvents (Aldrich) used in the various reactions were used without further purification. Verdazyl radicals were synthesized according to published procedures.[14] Verdazyl-stabilized *n*-butyl acrylate was prepared by passing *n*-butyl acrylate (Aldrich, ≥99%) through a 4-methoxyphenol inhibitor removal column (Aldrich) and adding verdazyl radical at a concentration of 1 mg per 40 mL of *n*-butyl acrylate. In a similar manner, inhibitor was removed from styrene (Aldrich, ≥99%) using a 4-*tert*-butylcatechol inhibitor removal column and the monomer stabilized with verdazyl radical at a concentration of 1 mg per 40 mL of styrene. (The specific verdazyl radical used to stabilize the monomer was the same as the verdazyl radical used for that particular polymerization.)

Elemental analysis was performed on a Perkin-Elmer Series II model 2400 CHNS/O analyzer equipped with a Mettler MT5 micro analytical balance, operating in the CHN mode. Samples were calibrated against an internal standard, acetanilide (C, 71.09; H, 6.71; N, 10.3), before and after running samples.

Polymer molecular weights and polydispersity indices were estimated by size exclusion chromatography (SEC) using a Waters 2690 separations module equipped with a Waters model 410 differential refractometer (RI) detector and Styragel HR4 (7.8 × 300 mm, effective MW range 5000−600 000), HR2 (4.6 × 300 mm, effective MW range 500−20 000), and HR1 (4.6 × 300 mm, effective M*W* range 100−5000) columns calibrated with polystyrene standards in the range $M_n$ = 400−188 000 g mol$^{-1}$.[18] THF was used as eluent at 40 °C and a flow rate of 0.35 mL min$^{-1}$. SEC was performed on samples taken directly from the reaction mixture without any prior precipitation that may remove low molecular weight chains. Excess monomer was removed by evaporation with a stream of air before SEC analysis. Percentage conversions were determined gravimetrically.

**(b) Styrene Polymerizations with BPO in the Presence of Verdazyl Radicals 3a or 3b.** In a typical experiment, styrene (10 mL, 8.7 × 10$^{-2}$ mol), BPO (28 mg, 1.2 × 10$^{-4}$ mol), and verdazyl radical **3a** (86 mg, 2.6 × 10$^{-4}$ mol) were placed in a 50 mL three-necked round-bottom flask fitted with a thermometer, a condenser equipped with a gas outlet adapter, and a septum, through which argon was introduced and samples were removed via syringe. The solution was purged with argon for 30 min and then heated to 110 °C under a slow stream of argon for 2 h. After 1 h, conversion was 25%, $M_n$ = 28 700 g mol$^{-1}$, and $M_w/M_n$ = 1.7. After 2 h, conversion was 26%, $M_n$ = 29 200 g mol$^{-1}$, and $M_w/M_n$ = 1.6. Repeating the polymerization with a larger amount of verdazyl radical (0.10 g, 3.1 × 10$^{-4}$ mol) resulted in a conversion of 21% after 2 h, $M_n$ = 24 000 g mol$^{-1}$ and $M_w/M_n$ = 1.7. Similar results were obtained with **3b**.

**(c) Styrene Polymerizations with 1,1′-Azobis(cyclohexanecarbonitrile) in the Presence of Verdazyl Radicals 3a or 3b.** Using the same experimental procedure described in experimental section (b) a solution of styrene (10 mL, 8.7 × 10$^{-2}$ mol), azobis(cyclohexanecarbonitrile) (17 mg, 7.0 × 10$^{-5}$ mol), and verdazyl radical **3a** (0.10 g, 3.12 × 10$^{-4}$ mol) was heated to 110 °C. After 1 h, conversion was 10%, $M_n$ = 13 900 g mol$^{-1}$, and $M_w/M_n$ = 2.0. After 2 h, conversion was 13%, $M_n$ = 14 000 g mol$^{-1}$ and $M_w/M_n$ = 2.0. Similar results were obtained with **3b**.

**(d) Exchange Reactions of 4 with Verdazyl Radicals 3a−c.** In a typical reaction, exemplified with verdazyl **3a**, argon was bubbled through a solution of **4** (0.75 g, 2.0 × 10$^{-3}$ mol) and **3a** (1.3 g, 4.0 × 10$^{-3}$ mol) in chlorobenzene for 30 min, after which the solution was heated under argon at 120 °C for 2 h. The solvent was evaporated, and the resulting oil was passed though a silica gel column, with 30% ethyl acetate in hexane as the eluent, to give the verdazyl unimer (**5a**) (0.99 g, 90%). In solution the unimer exists as two conformers (C−N rotamers). 2-Phenyl-2-(1,3,5-triphenyl-6-oxoverdazyl)ethyl benzoate (**5a**), recrystallized from isopropanol to give a white crystalline product, mp143−144 °C. A numbering scheme for NMR assignments of **5a**−**c** is provided as Supporting Information. $^1$H NMR (acetone-$d_6$, 0 °C): major conformer (92%), $\delta$ 4.50 (dd, $J$ = 11.7, 3.9 Hz, 1H8), 4.78 (dd, $J$ = 11.7, 10.6 Hz, 1H8), 4.86 (dd, $J$ = 10.6, 3.9 Hz, 1H7), 6.9−8.2 (m, 25H aromatic); minor conformer (8%), $\delta$ 4.52 (dd, $J$ = 12.0, 4.1 Hz, 1H8), 4.80 (dd, $J$ = 12.0, 10.3 Hz, 1H8), 5.00 (dd, $J$ = 10.3, 4.1 Hz, 1H7), 6.9−8.2 (m, 25H aromatic). $^{13}$C NMR ($CDCl_3$, 20 °C): major conformer, $\delta$ 62.28 (C8), 65.61 (C7), 120−144 (30C aromatic), 149.02 (C6), 152.79 (C3), 165.81 (C10); minor conformer, $\delta$ 63.71 (C8), 67.48 (C7), 120−144 (30C aromatic), 149.64 (C6), 152.94 (C3), 165.92 (C10). Anal. Calcd for $C_{35}H_{28}N_4O_3$ (552.62): C, 76.07; H, 5.11; N, 10.14. Found: C, 76.08; H, 5.47; N, 10.30.

2-Phenyl-2-(1,5-dimethyl-3-phenyl-6-oxoverdazyl)ethyl benzoate unimer (**5b**), recrystallized from isopropanol to give a white crystalline product, 30% yield, mp 97−98 °C. $^1$H NMR ($CDCl_3$, −20 °C): major conformer (78%), $\delta$ 2.65 (s, 3H12), 3.34 (s, 3H11), 4.50 (dd, $J$ = 10.8, 4.1 Hz, 1H7), 4.63 (dd, $J$ = 11.9, 4.1 Hz, 1H8), 5.04 (dd, $J$ = 11.9, 10.8 Hz, 1H8), 7.2−8.2 (m, 15H aromatic); minor conformer (22%), $\delta$ 2.71 (s, 3H11), 3.05 (s, 3H12), 4.53 (dd, $J$ = 11.6, 3.8 Hz, 1H8), 4.77 (dd, $J$ = 10.3, 3.8 Hz, 1H7), 5.08 (dd, $J$ = 11.6, 10.3 Hz, 1H8), 7.2−8.2 (m, 15H aromatic). $^{13}$C NMR ($CDCl_3$, −20 °C): major conformer, $\delta$ 35.55 (C12), 40.39 (C11), 62.15 (C8), 64.26 (C7), 127−135 (18C aromatic), 147.21 (C6), 157.17 (C3), 166.11 (C10); minor conformer, $\delta$ 36.70 (C12), 40.02 (C11), 63.22 (C8), 63.84 (C7), 127−136 (18C aromatic), 149.22 (C6), 159.38 (C3), 165.99 (C10). Anal. Calcd for $C_{25}H_{24}N_4O_3$ (428.48): C 70.08; H, 5.65; N, 13.08. Found: C, 70.06; H, 5.55: N, 13.08.

2-Phenyl-2-(1,5-dimethyl-3-ethyl-6-oxoverdazyl)ethyl benzoate unimer (**5c**), recrystallized from isopropanol to give a white crystalline product, 38% yield, mp 78−80 °C. The coupling products were determined by $^1$H NMR (−40 °C, $CDCl_3$) to be a 1.8:1 mixture of diastereomers, as indicated by integration of the methyl hydrogens at $\delta$ 2.96 (s, 3H12, minor diastereomer) and 3.17 (s, 3H11, major diastereomer). $^1$H NMR (55 °C, $CDCl_3$, diastereomers are in fast exchange): $\delta$ 1.16 (t, $J$ = 7.4 Hz, 3H14), 2.35 (q, $J$ = 7.5 Hz, 2H13), 2.78 (s, 3H12), 2.92 (s, 3H11), 4.88, 4.69, 4.66 (ABC spin system, $^2J$ = −11.8, $^3J$ = 9.1, 5.2, 1H7, 2H8), 7.31−8.0 (m, 10H aromatic). $^{13}$C NMR (55 °C, $CDCl_3$, fast exchange): $\delta$ 11.27 (C14), 25.17 (C13), 35.73 (C12), 39.57 (C11), 63.30 (C8), 63.69 (C7), 128−136 (12C aromatic), 151.60 (C6), 157.84 (C3), 166.21 (C10). Anal. Calcd for $C_{21}H_{24}N_4O_3$ (380.44): C 66.30; H 6.36; N 14.73. Found: C 66.44; H 6.26; N 14.88.

**(e) Synthesis of Verdazyl Unimer 5d.** A modified version of a reaction originally reported by Matyjaszewski was used for the preparation of unimer **5d**.[19] 1,5-Dimethyl-6-oxoverdazyl (**3d)** (0.5 g, $3.9 \times 10^{-3}$ mol), benzoic acid 2-bromo-2-phenyl-ethyl ester (1.07 g, $3.5 \times 10^{-3}$ mol), and pentamethyldiethylenetriamine (0.12 g, $7.0 \times 10^{-4}$ mol) were dissolved in 15 mL of toluene in a three-necked round-bottom flask equipped with a reflux condenser, a septum, and a thermometer. Argon was bubbled through the solution for 30 min before the addition of copper powder ($Cu^0$) (0.22 g, $3.5 \times 10^{-3}$ mol) and $CuBr_2$ (16 mg, $7.0 \times 10^{-5}$ mol). The reaction was carried out at 60 °C for 40 h. The reaction mixture was filtered to remove solid copper residues, and the solvent was removed. The crude product was redissolved in methylene chloride, washed three times with water, dried over sodium sulfate, and filtered. The solvent was evaporated, and the resulting oil was passed though a silica gel column, with 30% ethyl acetate in hexane as the eluent. 2-Phenyl-2-(1,5-dimethyl-6-oxoverdazyl)ethyl benzoate unimer (**5d**), recrystallized from hexanes/isopropanol (90:10 v/v) to give a white crystalline product, 44% yield. $^1$H NMR (20 °C, $CDCl_3$): $\delta$ 2.91 (s, 3H12), 3.01 (s, 3H11), 4.91, 4.73, 4.60 (ABC spin system, $^2J = -11.8$, $^3J = 9.1$, 5.2, 1H7, 2H8), 6.78 (s, 1H3), 7.34−8.06 (m, 10H aromatic). $^{13}$C NMR (20 °C, $CDCl_3$): $\delta$ 36.20 (C12), 38.49 (C11), 62.79 (C8), 64.79 (C7), 128−138 (12C aromatic), 134.45 (C6), 156.93 (C6), 166.12 (C10). Anal. Calcd for $C_{19}H_{20}N_4O_3$ (352.15): C 64.76; H 5.72; N 15.90. Found: C 65.01; H 5.90; N 15.69.

**(f) Polymerizations of Styrene with Verdazyl Unimer 5a.** Using the same experimental procedure described in experimental section (b), a solution of styrene (10 mL, $8.7 \times 10^{-2}$ mol) and verdazyl unimer **5a** (0.10 g, $1.8 \times 10^{-4}$ mol) was heated to 130 °C. The results are summarized in Table 1.

**(g) Polymerizations of Styrene with Verdazyl Unimer 5b.** Using the same experimental procedure described in experimental section (b), a solution of styrene (10 mL, $8.7 \times 10^{-2}$ mol) and verdazyl unimer **5b** (0.10 g, $2.3 \times 10^{-4}$ mol) was heated at 125 °C for 6 h. The results are summarized in Table 2. Polymerizations with unimer **5c** and **5d** were performed in a similar manner. Polystyrene products used as macroinitiators for the block copolymer synthesis were isolated by precipitation in methanol after dissolution in a minimal amount of THF. This precipitation was performed three times before the polymer was dried under vacuum to constant weight.

**(h) Polymerizations of *n*-Butyl Acrylate with Verdazyl Unimer 5b.** Using the same experimental procedure described in experimental section (b), a solution of *n*-butyl acrylate (15 mL, $1.0 \times 10^{-1}$ mol) and verdazyl unimer **5b** (0.10 g, $2.3 \times 10^{-4}$ mol) was heated to 130 °C for 28 h. The results are summarized in Table 3. Polymerizations with unimers **5c** and **5d** were performed in a similar manner. Poly(*n*-butyl acrylate) products used as macroinitiators for the block copolymer synthesis were isolated by precipitation in 80/20 methanol/water after dissolution in a minimal amount of $CH_2Cl_2$. This precipitation was performed three times before the polymer was dried under vacuum to constant weight.

**(i) General Procedure for Block Copolymer Formation: Preparation of Poly(*n*-butyl acrylate)-*b*-polystyrene from Poly(*n*-butyl acrylate) Macroinitiator.** A solution of styrene (10 mL, 87 mmol) and 1,5-dimethyl-3-ethyl-6-oxoverdazyl-terminated poly(*n*-butyl acrylate) ($M_n = 10\,700$, $M_w/M_n = 1.14$, 2.49 g, 0.23 mmol) was degassed by sparging with argon for 1 h and heated at 125 °C for 6.5 h. The resultant diblock copolymer had $M_n = 20\,800$ g mol$^{-1}$ and $M_w/M_n = 1.22$.

**(j) General Procedure for Block Copolymer Formation: Preparation of Polystyrene-*b*-poly(*n*-butyl acrylate) from Polystyrene Macroinitiator.** A solution of *n*-butyl acrylate (4.5 g, 35 mmol) and 1,5-dimethyl-3-ethyl-6-oxoverdazyl-terminated polystyrene ($M_n = 6890$ g/ mol$^{-1}$, $M_w/M_n = 1.09$, 1.62 g, 0.24 mmol) was degassed by sparging with argon for 1 h and heated at 135 °C for 7 h. The resultant diblock copolymer had $M_n = 10\,800$ g mol$^{-1}$ and $M_w/M_n = 1.16$.

**Table 1. Results for the Polymerization of Styrene (10 mL, $8.7 \times 10^{-2}$ mol) at 130 °C Initiated with Verdazyl Unimer 5a (0.1 g, $1.8 \times 10^{-4}$ mol)**

| rxn time (h) | $M_n$[a] | $M_n^{TH}$[b] | $M_w/M_n$[a] | convn (%)[c] |
|---|---|---|---|---|
| 0.5 | 17400 | 1000 | 1.7 | 2 |
| 1.5 | 25100 | 4500 | 1.8 | 9 |
| 4 | 30500 | 11100 | 1.7 | 22 |
| 6 | 32700 | 20000 | 1.6 | 39 |

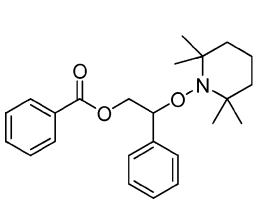
[a] Determined by SEC analysis calibrated with linear polystyrene standards. [b] Theoretical molecular weight calculated on the basis of monomer conversion. [c] Conversions determined gravimetrically.

**Table 2. Results for the Polymerization of Styrene (10 mL, $8.7 \times 10^{-2}$ mol) at 125 °C Initiated with Verdazyl Unimer 5b (0.1 g, $2.34 \times 10^{-4}$ mol)**

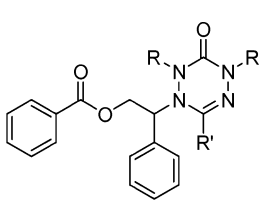
| rxn time (h) | $M_n$ | $M_n^{TH}$ | $M_w/M_n$ | convn (%) |
|---|---|---|---|---|
| 1 | 4200 | 4600 | 1.13 | 12 |
| 2 | 7700 | 8900 | 1.14 | 23 |
| 3 | 9800 | 11600 | 1.19 | 30 |
| 4 | 11200 | 13500 | 1.22 | 35 |
| 5 | 12100 | 15500 | 1.22 | 40 |

## Results and Discussion

The first attempts at verdazyl-mediated polymerizations were performed using a bimolecular initiating system, consisting of heating a conventional free radical initiator in the presence of the verdazyl radicals. BPO-initiated styrene polymerizations performed in the presence of verdazyl radicals **3a** or **3b** were uniformly unsuccessful. For example, a polymerization with verdazyl radical **3a** and BPO (molar ratio 2.2:1) resulted in a 25% conversion after 1 h with no further increase (26%) after 2 h. The $M_w/M_n$ values of the resulting polymers were in the range of 1.7, much higher than would be expected for a living-radical polymerization process. The high conversion in the first hour suggested the rate of polymerization was too fast to achieve a controlled polymerization. Increasing the verdazyl radical to BPO molar ratio to 2.7:1 resulted in a slower rate of polymerization (21% conversion after 2 h); however, no improvement in $M_w/M_n$ was observed. In a similar manner, polymerizations initiated with 1,1′-azobis(cyclohexanecarbonitrile) gave polymers with high polydispersity indices. Manipulating the initiator to verdazyl ratio to give relatively slow rates of conversion (13%/h) still resulted in $M_w/M_n$ values in the range of 2.0. It was speculated these reactions failed due to the inability of the verdazyls to control a radical polymerization or due to the use of the wrong stoichiometry between BPO and the verdazyl radical. Since the verdazyl radicals were initially in short supply, it was deemed prudent to attempt these polymerizations using verdazyl unimolecular initiators (unimers **5a**−**d**), the verdazyl analogues of **4** employed extensively in nitroxide-mediated polymerizations.



**4**



**5a** R, R' = Ph
**5b** R = Me; R' = Ph
**5c** R = Me; R' = Et
**5d** R = Me; R' = H

Verdazyl unimers **5a**−**c** were prepared by an exchange reaction with BST, by heating 1 equiv of **4** with 2 equiv of the verdazyl radical in chlorobenzene for 2 h. The verdazyl unimers were purified by silica gel column chromatography to give

**Table 3. Polymerization of *n*-Butyl Acrylate (15 mL, $1.0 \times 10^{-1}$ mol) at 130 °C Initiated with Verdazyl Unimer 5b (0.1 g, $2.33 \times 10^{-4}$ mol)**

| rxn time (h) | $M_n$ | $M_n^{TH}$ | $M_w/M_n$ | convn (%) |
|---|---|---|---|---|
| 2.5 | 3000 | 3600 | 1.58 | 5.9 |
| 3.5 | 3900 | 4600 | 1.49 | 8.1 |
| 5.5 | 5900 | 6900 | 1.36 | 12 |
| 8.5 | 7900 | 9800 | 1.29 | 17 |
| 12 | 9600 | 14400 | 1.27 | 25 |
| 18 | 12200 | 18500 | 1.22 | 32 |
| 28 | 14300 | 23000 | 1.20 | 40 |

**Table 4. Polymerization of *n*-Butyl Acrylate (8 mL, $5.6 \times 10^{-2}$ mol) at 132 °C Initiated with Verdazyl Unimer 5c (0.075 g, $1.97 \times 10^{-4}$ mol) in the Presence of Ascorbic Acid (0.020 g, $1.0 \times 10^{-4}$)**

| rxn time (h) | $M_n$ | $M_n^{TH}$ | $M_w/M_n$ | convn (%) |
|---|---|---|---|---|
| 1 | 5600 | 5800 | 1.53 | 16 |
| 4 | 8100 | 8900 | 1.39 | 20 |
| 5.5 | 10300 | 11400 | 1.23 | 31 |
| 27 | 13100 | 18700 | 1.21 | 53 |

**Table 5. Polymerization of Styrene (10 mL, $8.7 \times 10^{-2}$ mol) at 123 °C Initiated with Verdazyl Unimer 5d (0.082 g, $2.33 \times 10^{-4}$ mol)**

| rxn time (h) | $M_n$ | $M_n^{TH}$ | $M_w/M_n$ | convn (%) |
|---|---|---|---|---|
| 1 | 1720 | 2160 | 1.11 | 5.6 |
| 2 | 5220 | 5850 | 1.09 | 15 |
| 3 | 10300 | 12100 | 1.08 | 31 |
| 5 | 15200 | 16700 | 1.09 | 43 |
| 7 | 19900 | 23000 | 1.09 | 59 |

crystalline materials, which individually exist as conformational isomers in solution, which can interchange by rotation around the C−N bond between the verdazyl and styryl unit. While the exchange reaction with **5a** was almost quantitative, giving an indication of the high stability of the verdazyl−benzyl bond, the exchange reaction with **5b** only proceeded to 33% conversion. In an effort to increase the yield of verdazyl unimer ascorbic acid, known to react quickly and quantitatively with nitroxides to form hydroxyamines, was added to the exchange reactions.[20] Ascorbic acid is also known to react with verdazyls;[21] however, this reaction appears to be slower on the basis of qualitative observations of the rates of reaction of verdazyl radicals **5a**−**c** and TEMPO with ascorbic acid: whereas the color associated with TEMPO disappears almost immediately with an excess of ascorbic acid at room temperature, the color associated with the verdazyl radical persists for hours. Therefore, it was anticipated that adding ascorbic acid to the exchange reactions between **4** and verdazyl radicals would result in a preferential destruction of TEMPO, allowing a higher yield of the verdazyl unimer. This was indeed the case and a roughly 50% improvement in yield was realized by performing the exchange reaction in the presence of ascorbic acid.

Attempts to prepare unimer **5d** through an exchange reaction with BST were unsuccessful at temperatures ranging from 100 to 120 °C, as the yellow color associated with the verdazyl radical quickly disappeared upon heating and no verdazyl unimer was detected by $^1$H NMR. This suggests a decreased stability of the verdazyl radical **3d** at elevated temperatures and a significantly weaker verdazyl−benzyl bond. Verdazyl unimer **5d** was eventually prepared by an atom transfer radical addition (ATRA) reaction involving a halogen transfer reaction between an organic halide/copper complex in the presence of verdazyl radical **3d**,[19] giving a 44% yield after purification.

The polymerization of styrene in the presence of verdazyl unimer **5a** at 130 °C gave similar results to those previously obtained by Yamada (Table 1).[13] High molecular weight was obtained early in the reaction mixture with some increase over time; however, there was poor correlation between actual and theoretical molecular weights. While the polydispersity values remained relatively low, these results clearly demonstrate these polymerizations do not proceed in a controlled manner. A significant amount of unimer was observed in the reaction mixture by SEC analysis of early samples (Figure 1) and was not completely consumed even after 6 h polymerization, indicating a slow initiation process at 130 °C. It appears that a slow dissociation of the triphenylverdazyl−styrene bond within the verdazyl unimer **5a** is occurring at the polymerization temperature, and this will be verified by measurement of the dissociation kinetics for the various verdazyl unimers in a future research study. Once initiated, however, the polymerization proceeds very quickly, achieving high molecular weights even at low monomer conversions. This is assumed to be a result of a slow recombination of verdazyl **3a** with the propagating chain end due to steric hindrance imposed by the bulky phenyl substituents, resulting in a loss of control over the polymerization. This behavior is quite different from that observed previously for nitroxide-mediated SFRP and may result from the chemical and structural differences of the nitrogen-centered verdazyl radicals.

In contrast, a well-controlled polymerization of styrene was achieved with verdazyl unimer **5b** at 125 °C under similar reaction conditions (Table 2). An overlay of the SEC distributions for the samples listed in Table 2 is provided as Supporting Information (Figure S2). A fast dissociation of the styrene−verdazyl bond allows the polymerization to proceed in a controlled fashion, as the unimer is observed by SEC analysis to be completely consumed during the first 30 min of the polymerization. In addition, the recombination reaction of the verdazyl with the propagating radical is sufficiently fast to allow control over the polymerization, likely a result of the decreased steric bulk of the 1,5-dimethyl-substituted verdazyl **3b**, as compared to the 1,5-diphenyl-substituted verdazyl **3a**. It is therefore apparent that a change in substituent at the 1- and 5-positions on the verdazyl ring from phenyl to methyl groups allows verdazyl **3b** to effectively mediate the free-radical polymerization of styrene.

The polymerization of *n*-butyl acrylate also proceeded under controlled conditions with verdazyl unimer **5b** (Table 3). An overlay of the SEC distributions for the samples listed in Table 3 is shown in Figure 2. Despite the relatively long reaction times (40% conversion after 28 h), it is noteworthy that the distributions remain uniform throughout the course of the polymerization, and no significant tailing is observed in the later samples at the low molecular weight end of the distributions, which would indicate chain termination reactions.

While changing the verdazyl substituents at the 1- and 5-positions from phenyl to methyl groups allowed the successful polymerization of the styrene and *n*-butyl acrylate, a change in substituent at the 3-position can also affected the ability of the verdazyl to mediate radical polymerizations to various extents with different monomers. A change from phenyl (verdazyl **3b**) to ethyl (**3c**) substituent resulted in a decreased rate of polymerization for styrene. For example, a polymerization initiated with verdazyl unimer **5c** proceeded to only 30% conversion after 5 h, in comparison to 40% conversion achieved with verdazyl unimer **5b** under the same reaction conditions. However, the $M_w/M_n$ of the polymer produced using **5c** was noticeably smaller than with **5b,** typically remaining in the area of 1.10 throughout the 5 h polymerization.

In contrast, the rate of polymerization of *n*-butyl acrylate was virtually identical when comparing verdazyl unimer **5c** to **5b**,

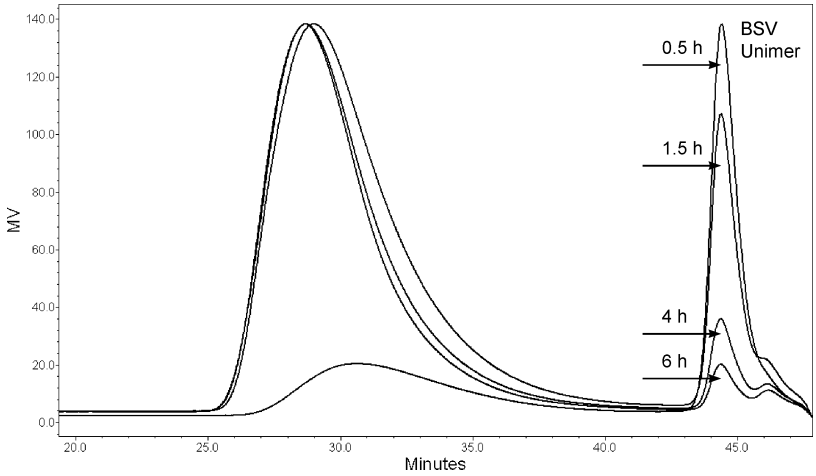



**Figure 1.** Size exclusion chromatographs of the polymer distributions for styrene polymerization mediated with verdazyl unimer **5a** for the samples listed in Table 1.

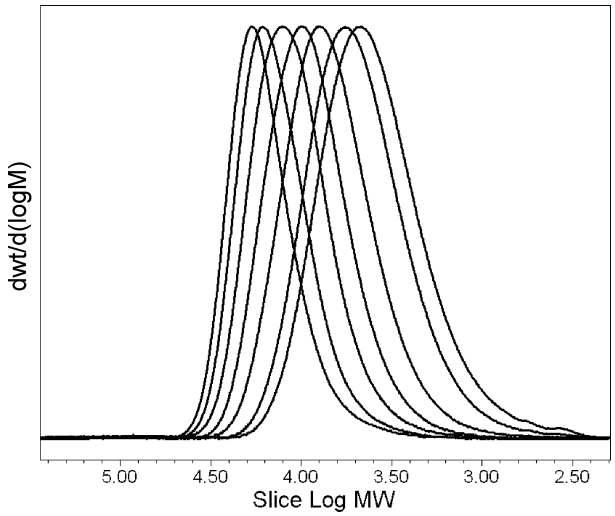



**Figure 2.** Size exclusion chromatographs of the polymer distributions for *n*-butyl acrylate polymerization mediated with verdazyl unimer **5b** for the samples listed in Table 3.

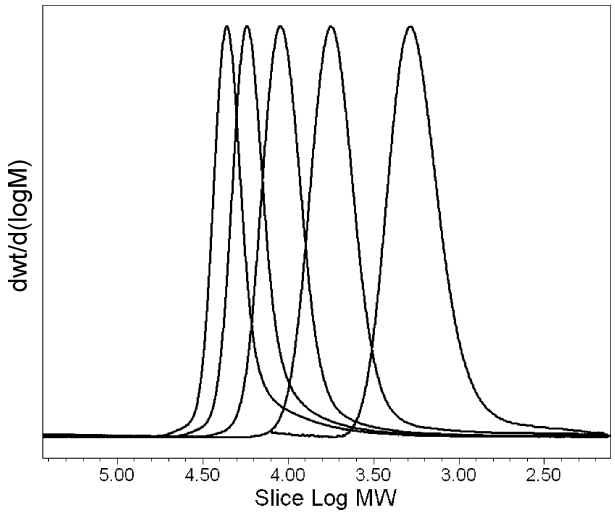



**Figure 3.** Size exclusion chromatograph overlay of the polymer distributions for a styrene polymerization mediated with verdazyl unimer **5d,** as listed in Table 5.

with typical conversions being about 40% after 24 h. However, the rate of polymerization was increased significantly with the addition of a small amount of ascorbic acid to the reaction mixture, which serves to react with excess free verdazyl radical which accumulates during the polymerization due to unavoidable termination reactions. This concept was previously applied to the TEMPO-mediated polymerization of *n*-butyl acrylate, as the continuous addition of a solution of an ascorbic acid derivative (ascorbic acid 6-palmitate) resulted in high conversions at short reaction times while maintaining good control over the polymerization.[22] Pure ascorbic acid was used in the present work, which has only a minimal solubility in *n*-butyl acrylate. Despite this limitation, conversions of over 50% were achieved in about 25 h while maintaining control over the polymerization (Table 4). It is expected that further optimization of the polymerization rate through the use of an ascorbic acid derivative with a greater solubility in *n*-butyl acrylate is possible and will be investigated in the future.

**Table 6. Polymerization of *n*-Butyl Acrylate (10 mL, $7.0 \times 10^{-2}$ mol) at 125 °C Initiated with Verdazyl Unimer 5d (0.087 g, $2.50 \times 10^{-4}$ mol)**

| rxn time (h) | $M_n$ | $M_n^{TH}$ | $M_w/M_n$ | convn (%) |
|---|---|---|---|---|
| 1 | 1550 | 2530 | 2.53 | 7.1 |
| 2 | 2460 | 3570 | 2.20 | 10 |
| 4 | 10800 | 11000 | 1.96 | 31 |
| 8 | 23200 | 24300 | 1.54 | 68 |

An incremental increase in molecular weight with conversion was observed for the verdazyl-mediated radical polymerizations of styrene and *n*-butyl acrylate initiated with unimers **5b** and **5c**, illustrating the living character of the reactions. The rate of reaction tended to slow over time, presumably due to the accumulation of free verdazyl radical due to unavoidable termination reactions, which serves to inhibit the polymerization. This effect was most noticeable in the polymerization of *n*-butyl acrylate, which lacks the autoinitiation mechanism of styrene polymerizations known to control the concentration of mediating radicals and allow high monomer conversions to be reached.[22,23] The fact that the polymerization of *n*-butyl acrylate does proceed, albeit rather slowly, indicates that the radical concentration is being controlled in some fashion, presumably by slow decomposition of the verdazyl. Indeed, the polymerization of acrylates with highly stable nitroxides with no decomposition mechanism were previously observed to proceed to only low conversions (<10%) before stopping.[17,22] Despite the controlled nature of the reactions, poor agreement was found between the experimental molecular weight measured by SEC and the theoretical molecular weight calculated on the basis of monomer conversion for the polymerization of styrene (Table 2) and more obviously for the polymerization of acrylate (Table 3). The observed molecular weight was consistently smaller than the

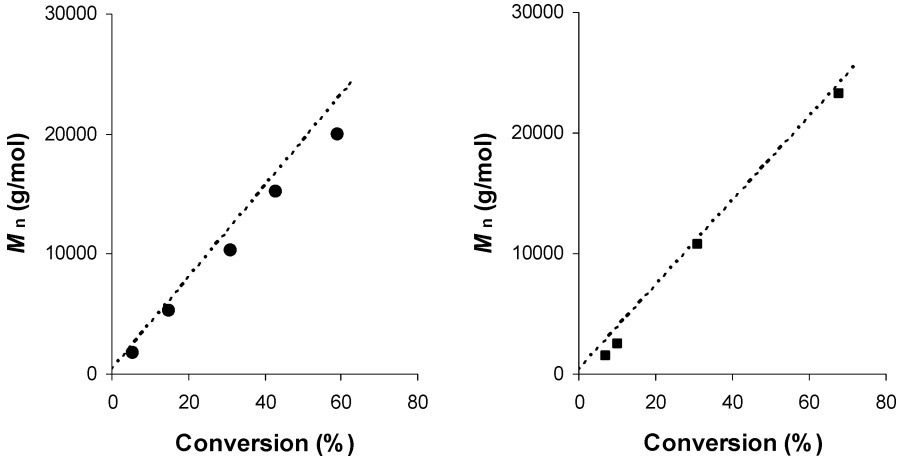



**Figure 4.** Demonstration of the linear dependence of the molar mass on monomer conversion for styrene (○) and *n*-butyl acrylate (■) polymerizations at 125 °C, respectively, initiated with verdazyl unimer **5d**, showing the theoretical molar mass (---) calculated from the conversion. [Styrene]/[BSV **5d**]: $8.7 \times 10^{-2}/2.3 \times 10^{-4}$; [*n*-butyl acrylate]/[BSV **5d**]: $7.0 \times 10^{-2}/2.5 \times 10^{-4}$.

predicted molecular weight, by as much as 40% in the case of acrylate polymerizations. The molecular weight deviations were believed to result from monomer evaporation from the polymerization reactor under a constant low flow of argon gas, particularly for acrylate polymerizations taking place over ~30 h. In response to a referee's concerns, and in order to verify that the molecular weight discrepancies were due to monomer losses, an acrylate polymerization was carried out with unimer **5b** in a sealed glass ampule (10 mL of *n*-butyl acrylate, $7.0 \times 10^{-2}$ mol; 100 mg of **5b**, $2.3 \times 10^{-4}$ mol). SEC analysis of the polymer after 40 h polymerization time at 130 °C found $M_n = 12\,900$ and $M_w/M_n = 1.22$, in excellent agreement with the theoretical molecular weight calculated on the basis of monomer conversion of 34% ($M_n^{TH} = 13\,200$).

Since the rate of polymerization with verdazyls **5b** and **5c** was observed to be quite slow, it was deemed prudent to move on and address the experimental problem of monomer loss with a different verdazyl which displays a higher rate of polymerization. In order to minimize the loss of monomer during the polymerization, the flow of argon through the reaction vessel was reduced, providing a much better agreement of theoretical and experimental molecular weights as illustrated in the results presented in the following paragraphs.

A faster rate of styrene polymerization was achieved with verdazyl unimer **5d**, which contains no substituent at the 3-position in the verdazyl structure, reaching 60% conversion in 7 h at 123 °C (Table 5). The $M_w/M_n$ values for the samples were lower than those observed with either unimer **5b** or **5c**, remaining below 1.10 throughout the polymerization. An overlay of the SEC distributions for the samples listed in Table 5 is shown in Figure 3, displaying less tailing at the low molecular weight end of the distribution than polystyrene samples produced from unimers **5b** or **5c**, indicating a reduction in the amount of termination occurring during the reaction.

The polymerization of *n*-butyl acrylate with verdazyl unimer **5d** was first attempted at 133 °C and resulted in a very fast and uncontrolled reaction. When the temperature was reduced to 125 °C, the polymerization proceeded in a more controlled manner, reaching 68% conversion in 8 h (Table 6). Although the polydispersity values at early times are quite high, the distributions did narrow throughout the reaction, reaching a final value of $M_w/M_n = 1.54$. A further reduction in the temperature to 115 °C resulted in broad molecular weight distributions, and some unimer was still detected in the SEC chromatographs even after several hours of heating. Indeed, even at 125 °C some unimer was still observed after 30 min of heating, which may account for the broad polydispersities observed at early times in the reaction. Clearly, initiation of the *n*-butyl acrylate polymerization with the styrene-based verdazyl unimer **5d** is problematic, presumably due to difficulties with the crossover reaction. It is expected that an acylate-based unimer would initiate the polymerization more efficiently, resulting in an improved polymerization of *n*-butyl acrylate. We are currently preparing acrylate-based verdazyl unimers in an effort to improve on these preliminary results.

For verdazyl unimers **5b** and **5c** a change from phenyl to ethyl substitution at the 3-position in the verdazyl structure had a small effect on the rate of styrene polymerization and no effect on the polymerization of *n*-butyl acrylate. However, it is obvious that the absence of a substituent at the 3-position (**3d**) provides an enhancement in the rate of styrene polymerization and more significantly *n*-butyl acrylate. This is presumably due to an increased rate of decomposition of the verdazyl, which prevents the accumulation of free verdazyl during the polymerization allowing higher conversions to be reached. We are currently investigating this decomposition mechanism and will present the findings in an upcoming paper. The living character of the styrene and *n*-butyl acrylate polymerizations performed with verdazyl unimer **5d** is illustrated in plots of the molecular weight against monomer conversion in Figure 4. An incremental increase in molecular weight is observed with conversion, and the molecular weights measured by SEC are in good agreement with theoretical values for both polymerization systems.

The presence of verdazyl terminal groups was verified by $^1$H NMR spectroscopy, using a polystyrene oligomer prepared from unimer **5c** ($M_n = 1050$, $M_w/M_n = 1.23$). Peaks for the verdazyl terminal group are clearly seen in the spectrum (Figure S3, provided as Supporting Information). By integration of the peaks in the $^1$H NMR spectrum corresponding to the benzoyl initiating groups and verdazyl terminal groups, it was calculated that over 90% of the chains contained a verdazyl terminus.

To further demonstrate the living character of verdazyl-mediated SFRP, a series of chain extensions were performed with the homopolymers prepared from verdazyl unimer **5c**. The polystyrene and poly(*n*-butyl acrylate) macroinitiators were purified by several precipitation cycles prior to extension, performed carefully to avoid the removal of any low molecular weight fractions. This was confirmed by SEC analysis of each homopolymer before and after precipitation, displaying identical distributions (Figures S4 and S5 in the Supporting Information).

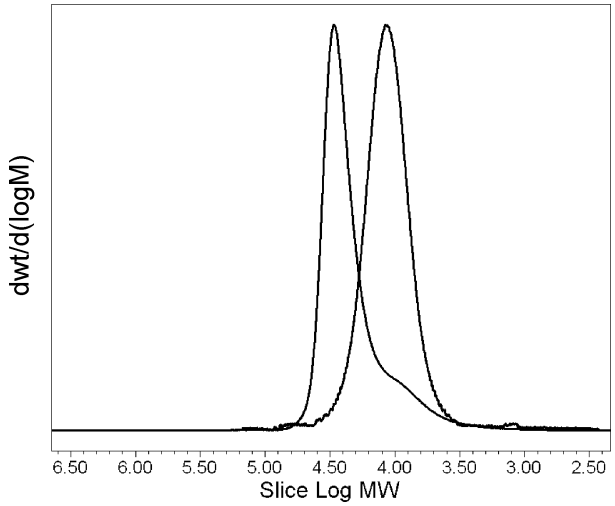



**Figure 5.** Poly(*n*-butyl acrylate)-*b*-styrene diblock formation mediated with verdazyl **3b**. Right: poly(*n*-butyl acrylate), $M_n$ 10 700 g mol$^{-1}$, $M_w/M_n$ 1.14. Left: poly(*n*-butyl acrylate)-*b*-styrene, $M_n$ 20 800 g mol$^{-1}$, $M_w/M_n$ 1.19 (26% styrene monomer conversion, $M_n^{TH} = 21\,000$).

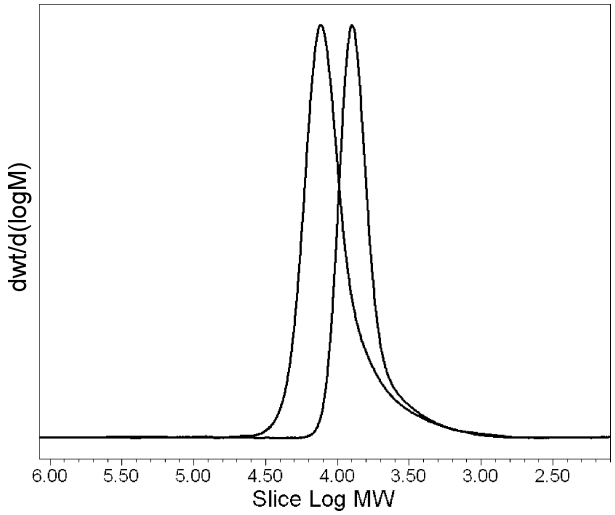



**Figure 6.** Polystyrene-*b*-(*n*-butyl acrylate) diblock formation mediated with verdazyl **3c**. Right: polystyrene, $M_n$ 6890 g mol$^{-1}$, $M_w/M_n$ 1.09. Left: polystyrene-*b*-(*n*-butyl acrylate), $M_n$ 10 800 g mol$^{-1}$, $M_w/M_n$ 1.16.

SEC distributions depicting the synthesis of poly(*n*-butyl acrylate)-*block*-polystyrene and polystyrene-*block*-poly(*n*-butyl acrylate) diblocks are illustrated in Figure 5 and Figure 6, respectively. A clean chain extension of poly(*n*-butyl acrylate) with styrene was achieved, with only a small shoulder due to unreacted or terminated starting block observable (Figure 5). The molecular weight of the diblock copolymer is nearly double that of the starting block and agreed well with the theoretical value calculated on the basis of styrene conversion. For the chain extension of polystyrene with *n*-butyl acrylate in Figure 6, the presence of homopolymer contamination in the diblock copolymers by either unreacted or terminated starting block cannot be ruled out due to the lack of baseline separation. It is clear, however, that controlled growth of a second poly(*n*-butyl acrylate) block was achieved as a significant increase in molecular weight was observed while maintaining a low polydispersity.

## Summary

The polymerization of styrene or *n*-butyl acrylate has been shown to proceed under living-radical polymerization conditions in the presence of verdazyl unimers **5b**, **5c**, and **5d** to give polymers that can be readily extended to form block copolymers. The fact that verdazyl unimer **5a** was unsuccessful in achieving the same results demonstrates that the structure of the verdazyl is critical to the success of these polymerizations. One might argue on the basis of results presented in this paper that the ability of verdazyl radicals to control radical polymerizations is related to their inherent instability under the reaction conditions, but more data are required to affirm this statement. However, these promising initial results open a new front in the development of living-radical polymerization processes, and the ability to manipulate the verdazyl structure offers the opportunity to further control and modify this process. Other verdazyl radicals are presently under investigation to develop fundamental understanding into the relationship between verdazyl radical structure and activity and to expand the family of monomers that can be polymerized with this system. In addition, we recently reported the use of $^1$H NMR to determine the bond dissociation constants of model alkoxyamines,[24] and we are in the process of extending this methodology to the verdazyl unimers to provide bond dissociation constants for the verdazyl systems reported herein.

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**Supporting Information Available:** Numbering scheme for NMR assignments of **3a**−**c**, SEC overlay distribution plot for the results summarized in Table 2, $^1$H NMR spectra of verdazyl-terminated polystyrene oligomer, and SEC distribution plots for the polystyrene and poly(*n*-butyl acrylate) macroinitiators used for block copolymer synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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