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Dual Living Free Radical and Ring Opening Polymerizations from a Double-Headed Initiator

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ABSTRACT: The concept of performing dual living polymerizations from a single initiating molecule with no intermediate activation, or transformation, steps is presented. The compatibility of "living", or controlled free radical procedures, either nitroxide mediated or atom transfer radical polymerization (ATRP), with the living ring opening polymerization of ϵ-caprolactone, and vice versa, is demonstrated by the synthesis of a variety of well-defined block copolymers. For example, from a hydroxy-functionalized alkoxyamine, either the living ring opening polymerization of ϵ-caprolactone, or the "living" free radical polymerization of styrene can be performed leading to narrow polydispersity polymeric initiators. These polymeric initiators can then be used to initiate the living polymerization of the other monomer system without the need for intermediate steps. In a similar way, hydroxy-functionalized ATRP initiators can be used as bifunctional initiators for the polymerization of both ϵ-caprolactone and a variety of other vinyl monomers. The novel block copolymers that are obtained were shown to have low polydispersities and controllable molecular weights for both of the blocks.

The desire to control polymer properties through the synthesis of block copolymers and complex macromolecular architectures is a continuing theme throughout polymer chemistry.[1] Traditionally, block copolymers are prepared by the sequential polymerization of different monomer units using the same chemistry (i.e., two anionic procedures)[2] or by the coupling of preformed functional polymers.[3] While this is successful, it does not address the issue of dissimilar monomer systems which are polymerized by fundamentally different chemistries (i.e., anionic ring opening and free radical procedures). To solve this difficulty a number of workers[4] have examined the polymerization of dissimilar monomers by the initial living polymerization of one monomer followed by a sequence of transformation reactions to convert the propagating center from the first polymerization to the second type of living polymerization (i.e., anionic to cationic). These transformation steps are necessary since initiating centers for one polymerization are essentially always incompatible with the reaction conditions of other living polymerizations.

A large body of work has recently been published on the polymerization of vinyl monomers by "living" free radical procedures.[5] Two main approaches have been developed, the first involves mediation of the free radical process by stable nitroxide free radicals,[6] while the second was developed from the Kharasch reaction, and a variety of metal complexes have been employed.[7] In both cases, one of the major advantages of "living" free radical chemistry, when compared to other living procedures for the polymerization of vinyl monomers, is the stability of the initiating, or propagating, centers.[8] This has enabled the development of a wide variety of functionalized unimolecular initiators for the synthesis of well-defined linear polymers,[9] block copolymers,[10] and other complex macromolecular architectures.[11] The chemical stability of these unimolecular initiators therefore opens up the possibility of combining "living" free radical procedures with a wide variety of other living polymerizations. A fundamental advantage of such a strategy is that the novel block copolymers are prepared under mild conditions in the minimum number of steps with no intermediate functionalization reactions. While

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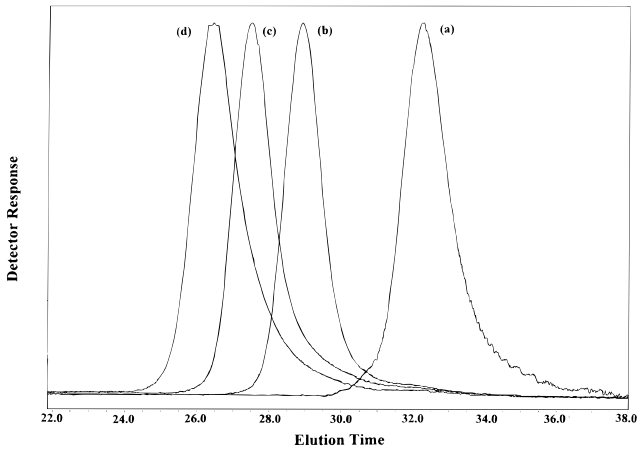
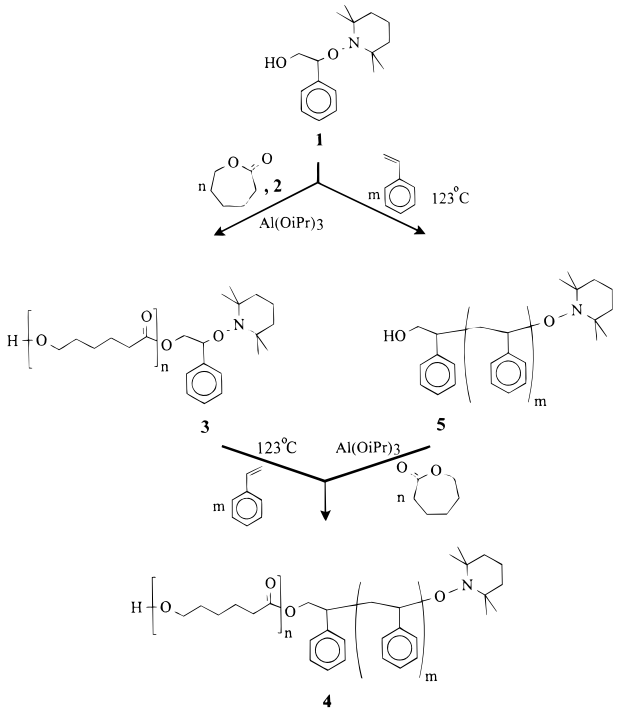


Figure 1. Comparison of GPC traces for (a) the functionalized poly(caprolactone) initiator, **3a**, and the block copolymers obtained from reaction with varying amounts of styrene (Table 1), (b) block copolymer, **4c**, (c) block copolymer, **4e**, and (d) block copolymer, **4g**.

Scheme 1



this paper was in preparation, initial efforts in developing such systems were presented independently by Matyjaszewski[12] and Sogah.[13] In this report, the development of a dual living polymerization strategy in which two different functional groups on a single initiator are used to initiate living ring opening and "living" free radical polymerizations is presented.

Results and Discussion

Nitroxide-Mediated "Living" Free Radical Polymerizations. The basic outline for this strategy is shown in Scheme 1 for the nitroxide-mediated case involving functionalized alkoxyamine initiators. The dual, or double headed initiator, **1**, contains a single primary alcohol which is used as the initiating center for the living ring opening polymerization of cyclic lactones, as well as a secondary benzylic group which is an efficient initiator for the nitroxide-mediated "living" free radical polymerization of vinyl monomers. Initially, it was decided to grow a well-defined polycaprolactone chain from the hydroxy group of **1** and, without further chemical transformations, use the chain end functionalized polycaprolactone as a polymeric initiator for the controlled polymerization of vinyl monomers. To demonstrate this strategy, the living ring opening polymerization of ϵ-caprolactone, **2**, by **1** as the initiator was studied using a catalytic amount of aluminum tris(isopropoxide) as a promoter.[14] The compatibility of the alkoxyamine with the polymerization conditions was evidenced by the fact that the polycaprolactones, **3**, obtained using this procedure had extremely low polydispersities and controllable molecular weights.[15] For example, polymerization of 70 equiv of **2** by **1** gave polycaprolactone **3b** (Table 1) with a polydispersity of 1.04 and a degree of polymerization of 74 as determined by ^{1}H NMR spectroscopy. More importantly, resonances for the alkoxyamine group could be observed at 0.6, 4.2−4.8, and 7.27 ppm, and integration confirmed the single alkoxyamine chain end per macromolecule.

Table 1. Molecular Weight Characteristics of Block Copolymers Prepared by Nitroxide-Mediated "Living" Free Radical Procedures

block copolymer	polymeric initiator[a]	M_n SEC	M_n calc[b]	PD
4a	**3a**	17 500	19 000	1.07
4b	**5**	24 000	26 000	1.08
4c	**3a**	29 000	31 000	1.07
4d	**3b**	37 000	34 000	1.09
4e	**3a**	49 500	54 000	1.12
4f	**3b**	61 500	65 000	1.11
4g	**3a**	85 000	91 000	1.19
4h	**3b**	99 000	96 000	1.20
4i	**3b**	135 000	147 000	1.29
4j	**3b**	149 000	175 000	1.41
4k	**3b**[c]	85 000	98 000	1.32
4l	**3b**[d]	54 000	58 000	1.15

[a] Mn and PD of polymeric initiator is given in text. [b] Polystyrene equivalent molecular weights; for calculation method see ref 23. [c] Monomer feed ratio was a 75/25 mixture of styrene and MMA. [d] Monomer feed ratio was a 90/10 mixture of styrene and MMA.

The polycaprolactone, **3**, could then be used to initiate the polymerization of vinyl monomers, such as styrene or a mixture of styrene and methyl methacrylate, to give a block copolymer, **4**, with no intermediate steps. As shown in Figure 1, the molecular weight of the block copolymer increased in a systematic way with increasing amounts of styrene and gel permeation chromatography (GPC) analysis could not detect any unreacted polycaprolactone in the block copolymers. For example, polymerization of 275 equiv of styrene with polycaprolactone, **3b**, having a molecular weight of 8500 gave the block copolymer, **4d**, which was shown to have a number average molecular weight of 37 000 and a polydispersity (PD) of 1.09. This agrees favorably with the theoretical molecular weight of 34 000.[16,23] As can be seen from Table 1, the low polydispersity and the molecular weight control of the block copolymer are maintained up to molecular weights of 150 000, and the degree of control is significantly better than for small molecule unimolecular initiators, such as **1**. It should also be noted that well-defined random copolymer blocks of various styrene/methyl methacrylate ratios can be grown from the poly(caprolactone) initiators.

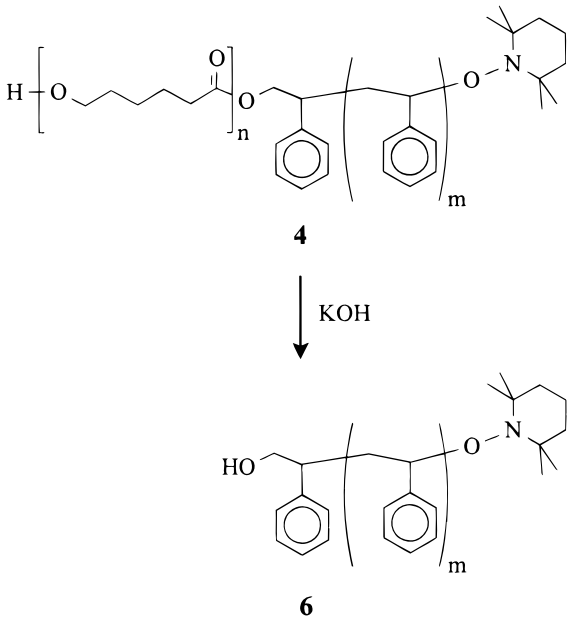
These results, coupled with the observation that the polymerization of styrene using **3** reaches 90% conver-

sion in 8 h when compared to 48 h for **1,** suggests that the attachment of an alkoxyamine initiating center to the polycaprolactone chain significantly increases its reactivity and leads to greater control over the "living" free radical process. To investigate whether this is simply a polarity effect due to the added polycaprolactone or is a direct result of covalent attachment, the polymerization of styrene (1250, 1000, and 750 equiv) by **1** in the presence of nonfunctionalized polycaprolactone was studied under the same conditions.[17] In each case, the molecular weight of the polystyrene obtained was significantly lower and the polydispersity higher when compared to the same polymerization using the functionalized polycaprolactone, **3**. For example, polymerization of **1** with 1000 equiv of styrene gave a homopolystyrene derivative with $M_n = 79\,000$ and PD = 1.40, which is significantly different from the polymerization of **3** with 1000 equiv of styrene which leads to the block copolymer, **4h** ($M_n = 99\,000$ and PD = 1.20). This suggests that attachment of the alkoxyamine group to the chain end of a dissimilar polymer chain, such as polycaprolactone, may significantly enhance the rate of polymerization, thus avoiding complications due to excessive amounts of autopolymerization, while at the same time possibly decreasing the initial amount of termination reactions.[18]

The versatility of using functionalized unimolecular initiators as dual initiating species was further examined by reversing the growth strategy. In this case, a polystyrene block was initially grown from the double-headed initiator, **1**, to give a hydroxy-terminated polystyrene chain, **5**, with a M_n of 4500 and a polydispersity of 1.09. The hydroxy chain end of **5** could then be used to initiate the living ring opening polymerization of ϵ-caprolactone, **2**, again without any intermediate transformation steps. As for the previous strategy, the molecular weight of the block copolymer, **4b**, could be controlled by monomer ratio, and low polydispersity materials were obtained (Scheme 1). For example, polymerization of **2** with **5** in the presence of $Al(O^iPr)_3$ gave the block copolymer, **4b**, in 85% yield which was shown to have a molecular weight of 24 000 and a polydispersity of 1.08. This ability to prepare well-defined block copolymers, **4**, from a single molecule, **1**, by the controlled growth of both chains in either sequence and with no intermediate steps demonstrates the versatility of this double-headed initiator strategy. It should also be noted that this strategy can also be used to place functionality at the junction point between the two blocks, similar to the concept of "link-functionalized" polymers recently proposed by Novak.[19]

Confirmation of the block copolymer structure was accomplished by a number of different techniques. ^1H, ^{13}C NMR and infrared spectra of the block copolymers showed resonances correlating to both the polycaprolactone and polystyrene segments while GPC analysis showed the expected increase in molecular weights in each case. To gain further insight into the formation of the copolymers and to conclusively demonstrate the block structure, hydrolysis of **4** with potassium hydroxide was investigated (Scheme 2). Analysis of the reaction sequence by ^1H NMR clearly shows the starting poly(caprolactone), **3b**, containing minor resonances for the alkoxyamine terminal group. Polymerization of styrene then gives the block copolymer, **4d**, which reveals resonances for both the polystyrene and poly(caprolactone) blocks while on hydrolysis the peaks due

Scheme 2



to the poly(caprolactone) disappear and a spectrum for polystyrene, **6**, is observed (Figure 2). GPC analysis of **4d** and **6** also showed the expected decrease in molecular weight on hydrolysis (Figure 3). Interestingly, the molecular weight of **6**, obtained by hydrolysis of **4**, correlated with the theoretical molecular weight and in all cases the polydispersities were low (1.10−1.15). This is fully consistent with both the synthetic strategy and the production of only negligible amounts of autopolymerized homopolystyrene during the "living" free radical portion of this dual living polymerization strategy. The lack of homopolymer contamination was further confirmed by the optical clarity of thin films formed from the block copolymers.

Atom Transfer "Living" Free Radical Polymerizations. In examination of the atom transfer radical process, a wide range of potential double-headed initiators, containing the required primary alcohol initiating group and an initiating functionality for ATRP, are possible. However due to its commercial availability and relatively low cost, 2,2,2-tribromoethanol, **7**, was selected as our initial dual functional initiator. Initially the efficiency of **7** to initiate the controlled free radical polymerization of vinyl monomers was investigated. Under standard conditions,[20] using CuBr/bipy as the metal complex, the homopolymerization of styrene with **7** was shown to be a living process with the molecular weight of the product, **8**, being controlled by the initiator to monomer ratio, while polydispersities were low (1.2−1.3). Similarly, the homopolymerization of methyl methacrylate using **7** and $NiBr_2(PPh_3)_2$, or $RhBr(PPh_3)_3$, as metal catalysts[21] was observed to be a living process leading to low polydispersity, controlled molecular weight materials with one polymer chain being initiated per tribromoethanol molecule (Table 2). These results suggest that 2,2,2-tribromoethanol, **7**, is an efficient initiator for the controlled atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate which is in agreement with recent work on the use of polyhalogenated initiators, such as CCl_4, in ATRP.[22]

Having demonstrated that **7** is an efficient initiator for the "living" free radical polymerization of vinyl monomers, the use of **7** as an initiator for the living ring

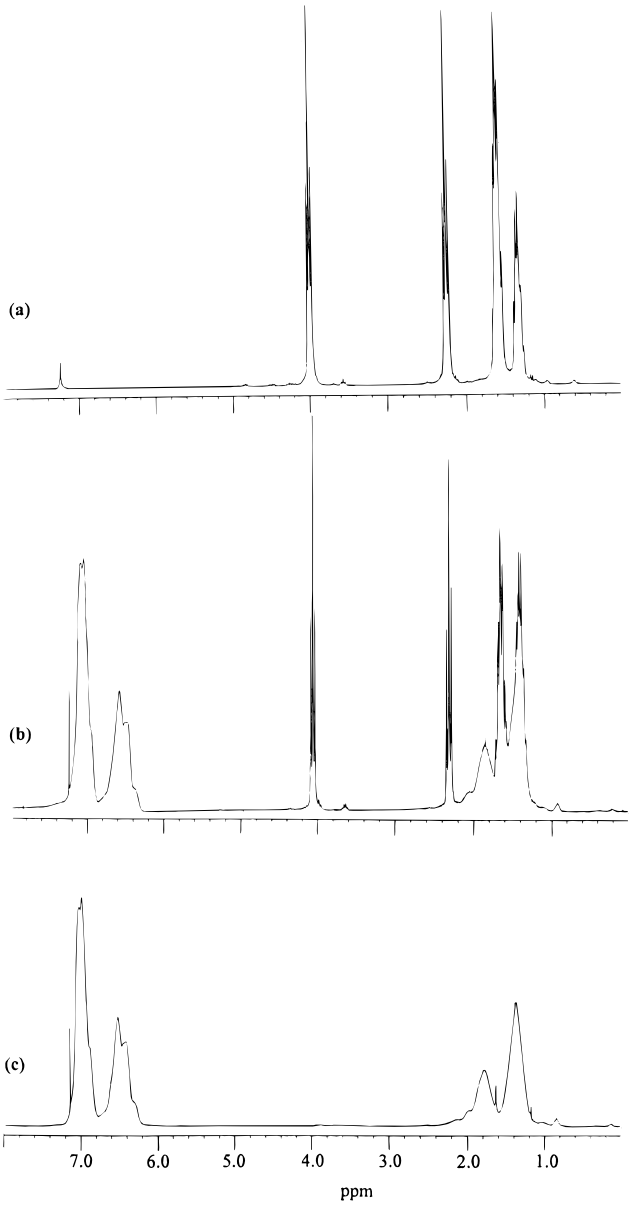


Figure 2. Comparison of ^{1}H NMR spectra for (a) the functionalized poly(caprolactone) initiator, **3b**, (b) the block copolymer, **4d**, and (c) the product obtained after hydrolysis, **5**.

opening polymerization of ϵ-caprolactone was studied in detail. Aluminum tris(isopropoxide) was reacted with 4 equiv of **7** and then added to a solution of ϵ-caprolactone in toluene and polymerization conducted at room temperature for 1 h. The poly(caprolactone) derivatives, **9**, that were obtained gave experimental molecular weights which were similar to the theoretical molecular weights while polydispersities were low (1.09−1.15) (Table 2). Significantly, the ^{1}H NMR spectrum of **9** showed a minor resonance at 4.24 ppm which can be attributed to the methylene protons of the tribromoethoxy end group. Integration of this signal and comparison with the caprolactone resonance at 4.10 ppm gave a molecular weight, M_n, of 2500, which is essentially the same as that determined from theory and confirms that **7** is an efficient initiator for the living ring opening polymerization of ϵ-caprolactone and leads to materials with a single tribromoethyl chain end.

The opportunity now exists to combine these two results into a novel synthetic strategy for the synthesis of a wide variety of block copolymers from a readily

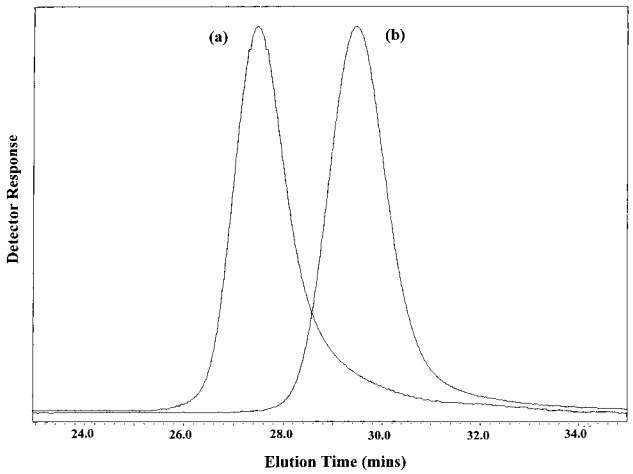


Figure 3. Comparison of GPC traces for (a) the block copolymers, **4d**, and (b) the product, **6**, obtained after hydrolysis of **4d** (Table 1).

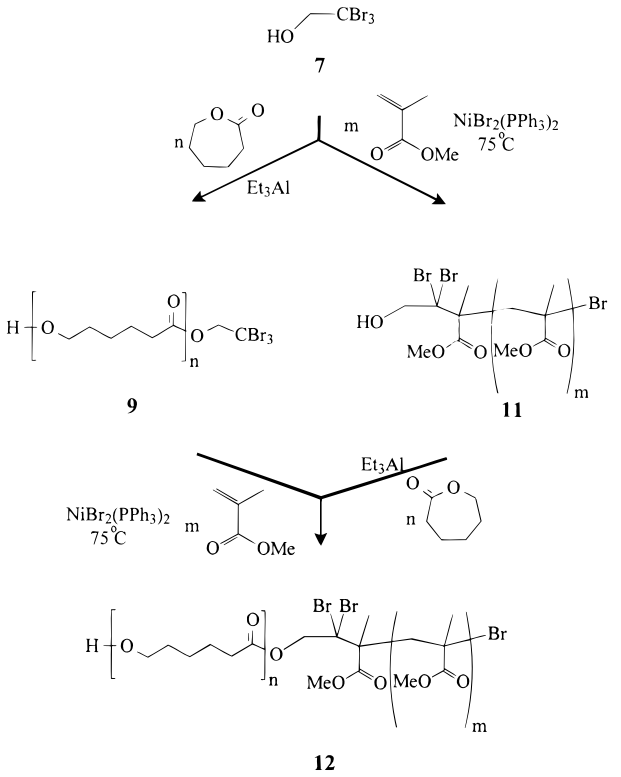
Table 2. Molecular Weight Characteristics of Starting Telechelic Polymers Prepared by Atom Transfer Radical Procedures

monomer	metal system	M_n SEC	M_n calc	PD
styrene	CuBr/bipy	2200	1700	1.21
styrene	CuBr/di-*n*-bipy	9000	8500	1.10
MMA	$RhBr(PPh_3)_3$	3100	2700	1.30
MMA	$NiBr_2(PPh_3)_2$	2900	2900	1.32
MMA	$NiBr_2(PPh_3)_2$	37000	31000	1.34
CL	$Al(O^iPr)_3$	2500	2600	1.15
CL	$Al(O^iPr)_3$	5800	6000	1.09

available double-headed initiator using ATRP. As demonstrated for the alkoxyamine initiator, **1**, the same concept of sequential vinyl/ring opening polymerization is applicable for the ATRP-based system. Initially, a short polystyrene block was grown from **7** under standard ATRP conditions to give a monohydroxy-terminated polystyrene derivative, **8** (M_n = 2 250, PD = 1.21). With no intermediate transformation steps, **8** could then be used to initiate the living ring-opening polymerization of ϵ-caprolactone. Reaction of **8** with triethylaluminum at room temperature for 2.5 h gave the activated alkoxide derivative, which after addition of caprolactone, leads to the desired polystyrene-*b*-poly(caprolactone) block copolymer, **10** (M_n = 44 500, PD = 1.17). The structure of the block copolymer was confirmed by a variety of techniques. The elution peak for **10** is shifted to higher values when compared to the starting polystyrene block, **8**, while the low polydispersity is maintained and no significant amount of unreacted **8** is observed. Furthermore, dual detection size exclusion chromatography (SEC) gave superimposable traces for both the refractive index and 254 nm UV detection, which suggests that the polystyrene macroinitiator is homogeneously incorporated into the block copolymer structure.

To illustrate the versatility of this approach for other vinyl monomers, hydroxy-terminated poly(methyl methacrylate), **11** (M_n = 44 500, PD = 1.17), was prepared by ATRP and again reacted with triethylaluminum followed by ϵ-caprolactone to give the block copolymer, **12**, in 75% yield after purification (Scheme 3). In this case, GPC analysis again showed the expected increase in molecular weight with little, or no, evidence of unreacted starting material, **11**. Significantly, ^{1}H NMR of **12** showed resonances for both the caprolactone and methyl methacrylate blocks and integration of these

Scheme 3



resonances reveals that the molar composition of caprolactone in **12** ($F_{CL} = 0.7$) is in close agreement with the feed ratio and conversion ($f_{CL} = 0.67$).

The reverse strategy, polymerization of caprolactone followed by polymerization of the vinyl monomer, was then examined. As detailed previously, initiation of caprolactone polymerization from 2,2,2-tribromoethanol, **7**, gives well-defined telechelic macromolecules with a single tribromoethyl chain end, **9**. Reaction of **9** with methyl methacrylate in the presence of $NiBr_2(PPh_3)_2$ at 75 °C for 14 h in THF gave the desired diblock copolymer, **13**, in 95% yield after purification (Scheme 3). Analysis of **13** by NMR spectroscopy showed the expected resonances for both blocks, while comparison of the GPC traces for **9** and **13** revealed a narrow polydispersity, unimodal peak for **13** with no unreacted starting macroinitiator. Similar results were obtained for the synthesis of polystyrene block copolymers from **9** using CuBr and 2,2′-bipyridine.

An added benefit of living free radical procedures is the presence of dormant initiating groups at the chain ends of the block copolymers. This permits the growth of additional blocks by reactivation of the living free radical process which allows the preparation of novel multiblock copolymers. To demonstrate this principle an ABC triblock copolymer was prepared starting from the polycaprolactone macroinitiator, **9**, by initial ATRP polymerization of *n*-butyl acrylate to give the block copolymer, **14**. Following isolation and purification of the polycaprolactone-*b*-poly(*n*-butyl acrylate) copolymer, **14**, a third block was formed by polymerization of methyl methacrylate, again under ATRP conditions. This gave the desired ABC triblock copolymer, **15**, which was shown by a combination of spectroscopic and chromatographic techniques to have the correct structure. Interestingly, a broadening of the molecular weight distribution is observed by GPC on going from **9** to **14** to **15**, which is probably due to a combination of minor amounts of termination and incomplete initiation occurring during the ATRP steps.

In conclusion, we have demonstrated that a single difunctional molecule can be used as a dual initiator for the living polymerization of dissimilar monomers without the need for intermediate functionalization steps. Hydroxy and alkoxyamine, or tribromo, initiating groups were found to be fully compatible with the reaction conditions for both the living ring opening polymerization of ϵ-caprolactone and nitroxide-mediated, or atom transfer "living" free radical, polymerizations. This permits novel well-defined block copolymers to be readily prepared in the minimum number of steps under synthetically nondemanding conditions. Future work will describe the extension of this novel technique to other living polymerization systems and monomer combinations.

Experimental Section

Materials. 2,2,2-Tribromoethanol (97%), $NiBr_2(PPh_3)_2$ (99%), $RhBr(PPh_3)_3$ (99%), and 2,2′-bipyridine (99%) were purchased from Aldrich and used as received. Triphenylphosphine (Aldrich) was purified by recrystallization in methanol. Methyl methacrylate (99% Aldrich), *n*-butyl acrylate (99% Aldrich), styrene (99% Aldrich) and ϵ-caprolactone (99% Janssen) were dried over CaH_2 for 24 h and distilled under high vacuum before use. Hydroxyethyl methacrylate (98%, Aldrich) was dried over molecular sieves and distilled just before reaction. THF and toluene were dried by refluxing over sodium benzophenone and degassed by bubbling nitrogen for 15 min just before use. $Al(O^iPr)_3$ (Aldrich) (sublimed two times) and $Al(Et)_3$ (Fluka) were dissolved in dry toluene being the concentration measured by complexometric titration using a standard solution of ethylenediametetraacetate (EDTA). The molecular weight distributions were determined at 25 °C in THF using refractive index and UV detectors with poly(methyl methacrylate) (PMMA) or polystyrene (PS) standard samples as calibration. ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS for reference on a Bruker AM 400 apparatus at room temperature.

1-Benzoyloxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane, 16. To a solution of benzoyl peroxide (4.0 g, 12.4 mmol) in distilled styrene (160 mL) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (5.68 g, 36.4 mmol) and the solution heated at 80 °C under nitrogen for 20 h. After cooling the solution was evaporated to dryness and the reaction mixture prepurified by flash chromatography eluting with hexane gradually increasing to 1:1 hexane/dichloromethane then to dichloromethane. This gave fractions highly enriched in the desired product which was then combined and purified by a second flash chromatography column eluting with 1:1 hexane/dichloromethane gradually increasing to 1:9 hexane/dichloromethane to give the modified TEMPO initiator, **16**, as a pale yellow oil (2.64 g, 42%): IR (neat) 3100−2850, 1720, and 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75, 1.07, 1.21, 1.37 (each br s, 12H, CH_3), 1.38−1.52 (m, 6H, CH_2); 4.53 (ABq, J = 6 Hz, 1 H, C*H*H), 4.83 (ABq, J = 6 Hz, 1 H, CH*H*), 5.06 (ABq, J = 3 Hz, 1 H, C***H***), 7.25−7.56 (m, 8 H, Ar*H*) and 7.91 (B of ABq, J = 6 Hz, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 17.09, 20.31, 34.00, 40.36, 60.01, 66.68, 83.90, 127.54, 127.97, 128.18, 129.48, 130.14, 132.72, 140.61, and 166.20; mass spectrum (EI) m/z 381; Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.6; H, 8.19; N, 3.67. Found: C, 76.0; H, 7.97; N, 3.86

1-Hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)ethane, 1. To a solution of the benzyl ester, **16** (3.2 g, 8.4 mmol), in ethanol (100 mL) was added aqueous sodium hydroxide (10 mL of a 1 N solution, 10.0 mmol) and the solution heated at reflux under nitrogen for 2 h. After cooling, the solution was evaporated to dryness and partitioned between water (200 mL) and dichloromethane (200 mL), and the aqueous layer extracted with dichloromethane (2 × 100 mL). The combined organic layers were dried with magnesium sulfate evaporated to dryness, and the crude product was

purified by flash chromatography eluting with 1:4 hexane/dichloromethane, gradually increasing to 1:9 hexane/dichloromethane to give the hydroxy derivative, **1**, as a pale yellow oil (2.01 g, 87%): ^{1}H NMR ($CDCl_3$) δ 1.14, 1.21, 1.33, 1.50 (each br s, 12H, CH_3), 1.38−1.72 (m, 6H, CH_2); 3.71 (br d, J = 9 Hz, 1 H, CHH), 4.21 (d of d, J = 2 and 6 Hz, 1 H, CHH), 5.29 (d of d, J = 2 and 3 Hz, 1 H, CH), 5.88 (br s, OH), and 7.25−7.56 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.15, 20.41, 20.73, 32.76, 34.61, 40.23, 40.41, 60.38, 61.69, 69.73, 83.59, 126.20, 127.89, 128.34, and 138.92; mass spectrum (EI) m/z 277. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.6; H, 9.81; N, 5.05. Found: C, 73.8; H, 10.05; N, 5.08.

Alkoxyamine-Terminated Poly(caprolactone), 3. To a solution of the alcohol, **1** (277 mg, 1.0 mmol), in dry toluene (10 mL) was added aluminum tris(isopropoxide) (0.18 mL, 0.06 mmol, 0.3 M solution in toluene), and the reaction mixture was stirred at room temperature under argon for 5 min and then evaporated to dryness. This procedure was then repeated twice. To the reaction mixture was then added dry toluene (50 mL) followed by ϵ-caprolactone (5.0 g, 43.9 mmol) and the polymerization stirred at 25 °C for 16 h under argon. Acetic acid (0.5 mL) was then added and the polymers precipitated into hexane to give the crude polymer as a white solid. This was then redissolved in tetrahydrofuran and precipitated into hexane, or methanol, to give the purified polymer, 3 (4.64 g, 88%): IR 3000−2850, 1720, 1440, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.60 and 0.95 (each br s, tempo-CH_3), 1.20−1.70 (complex m, CH_2), 2.24 (t, J = 8 Hz, COCH_2), 4.03 (t, J = 8 Hz, OCH_2), 4.22, 4.48, and 4.83 (br m, minor alkoxyamine resonances), and 7.25 (s, ArH); ^{13}C NMR ($CDCl_3$) δ 24.57, 25.53, 28.35, 34.11, 64.14, 173.53, and very minor resonances for alkoxyamine.

Hydroxy-Terminated Polystyrene, 5. To the initiator, **1** (277 mg, 1.0 mmol), was added styrene (7.80 g, 75 mmol) and the polymerization mixture heated at 125 °C for 24 h under argon. The solidified reaction mixture was then redissolved in methylene chloride and precipitated into methanol, followed by reprecipitation into a mixture of acetone/2-propanol. The purified polymer was obtained as a white solid, **5** (5.85 g, 75%): IR 3000−2850, 1720, 1440, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20−2.05 (complex m) and 6.40−7.22 (complex m); ^{13}C NMR ($CDCl_3$) δ 40.20, 40.35−45.0 (broad multiplet), 125.40, 127.62, 127.98, and 144.50−145.5 (br).

Polystyrene-*b*-poly(caprolactone), 4a. To the alkoxyamine-terminated poly(caprolactone), **3a** (2.0 g), was added styrene (4.50 g, 43 mmol), and the polymerization mixture was heated at 125 °C for 8 h under argon. The solidified reaction mixture was then redissolved in methylene chloride and precipitated into methanol, followed by reprecipitation into a mixture of acetone/2-propanol. The purified polymer was obtained as a white solid, **4a** (5.91 g, 91%): IR 3200−2850, 1720, 1605, 1470, and 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25−2.10 (complex m, PCl−CH_2 and PSt−CH/CH_2), 2.28 (t, J = 8 Hz, COCH_2), 4.05 (t, J = 8 Hz, OCH_2), and 6.4−7.2 (br m, PSt−ArH); ^{13}C NMR ($CDCl_3$) δ 24.65, 25.50, 28.41, 34.15, 40.2, 40.3−45.0 (br), 125.45, 127.60, 128.02, 144.5−145.5 (br), and 173.50.

Polystyrene-*b*-poly(caprolactone), 4b. To a solution of the alcohol, **5** (2.0 g, 0.44 mmol), in dry toluene (10 mL) was added aluminum tris(isopropoxide) (0.06 mL, 0.02 mmol, 0.3 M solution in toluene) and the reaction mixture stirred at room temperature under argon for 5 min and then evaporated to dryness. This procedure was then repeated twice. To the reaction mixture was then added dry toluene (50 mL) followed by ϵ-caprolactone (5.0 g, 43.9 mmol), and the polymerization was stirred at 25 °C for 16 h under argon. Acetic acid (0.5 mL) was then added and the polymers precipitated into hexane to give the crude polymer as a white solid. This was then redissolved in tetrahydrofuran and precipitated into hexane, or methanol, to give the purified block copolymer, **4b** (6.02 g, 86%): IR 3200−2850, 1720, 1605, 1470, and 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25−2.10 (complex m, PCl−CH_2 and PSt−CH/CH_2), 2.28 (t, J = 8 Hz, COCH_2), 4.05 (t, J = 8 Hz, OCH_2), and 6.4−7.2 (br m, PSt−ArH); ^{13}C NMR ($CDCl_3$) δ 24.60, 25.52, 28.35, 34.13, 40.2, 40.3−45.0 (br), 125.45, 127.60, 127.95, 144.5−145.5 (br), and 173.50.

Tribromoethoxy End Functionalized Polycaprolactone, 9. Aluminum tris(2,2,2-tribromoethoxide) was synthesized by the reaction of Al(O^{i}Pr)$_3$ (6.0 mL, 0.3 mol·L^{-1} in toluene) with 4 equiv of 2,2,2-tribromoethanol, **7** (2.26 g, 8.0 mmol), previously dried by two toluene azeotropic distillations in a carefully dried and nitrogen-purged distillation apparatus. The toluene/isopropyl alcohol azeotrope was continuously distilled off (three times 10 mL of toluene), which favorably displaced the reaction equilibrium. Then toluene was added to adjust the initiator concentration. Polymerization was carried out under stirring in toluene in a previously flamed and nitrogen-purged glass reactor. Toluene (30 mL), ϵ-caprolactone (5.00 g, 43.8 mmol) and the desired amount of initiator solution were successively added through a rubber septum with a syringe or a stainless steel capillary. Reactions were carried out at 25 °C for 1 h. Then an excess with respect to the initiator of a 0.1 M solution of HCl was added and the polymers precipitated in heptane (yields are typically 85−95%): IR 3000−2850, 1720, 1440, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20−1.70 (complex m, CH_2), 2.24 (t, J = 8 Hz, COCH_2), 4.03 (t, J = 8 Hz, OCH_2), and 5.2 (br m, CH_2CBr$_3$); ^{13}C NMR ($CDCl_3$) δ 24.55, 25.50, 28.35, 34.10, 64.15, 173.50.

General Procedures for ATRP. All experiments were performed by using Schlenck method. In a typical experience, the different solids are introduced in a glass tube. The tube is then closed with a three-way stopcock and a cycle of vacuum-nitrogen is repeated three times to remove the oxygen. The liquids are then added via a syringe in the following order: solvent, monomer, initiator, and catalyst solutions (toluene). When high temperature or long time reaction are required, the tubes are sealed under vacuum. PMMA and PS conversions were determined gravimetrically by precipitation in respectively heptane or methanol after dissolution in THF. For the Pn−BuA, solvent and residual monomer were evaporated and dried under high vacuum at 80 °C.

Poly(methyl methacrylate)-*b*-poly(caprolactone), 12. Hydroxyl end functionalized poly(methyl methacrylate), **11** (0.15 g), was dried by three toluene azeotropic distillations, dry THF (30 mL) was added and the reaction mixture was cooled to −78 °C. Triethylaluminum (2.7 mL, 0.22 mmol, 0.08 M solution) was added, the reaction was strirred at room temperature for 2.5 h, and then ϵ-caprolactone (2.0 g, 17.5 mmol) was added. After 48 h, the polymerization was stopped by addition of an excess (relative to the initiator) of diluted HCl solution. The solvent was removed by evaporation, and the crude polymer was redissolved in 5 mL of THF and purified by precipitation into cold methanol (2.09 g, 93% yield): IR 3000−2850, 1720, 1475, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6−1.1 (br m, PMMA−CH_3); 1.3−2.10 (complex m, PCl−CH_2 and PMMA−CH_2), 2.30 (t, J = 8 Hz, COCH_2), 3.60 (s, PMMA−OCH_3), and 4.05 (t, J = 8 Hz, OCH_2).

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(15) Two poly(caprolactone) initiators were prepared, **3a** was shown to have a DP of 35 and a polydispersity of 1.09 while **3b** was found to have a DP of 74 and a polydispersity of 1.04.
(16) Theoretical molecular weights for the "living" free radical polymerizations are calculated by assuming that one alkoxyamine initiating group leads to a single polymer chain, the degree of polymerization of which is governed by the ratio of styrene to initiator, and the polymerizations are run to 90% conversion.
(17) The nonfunctionalized polycaprolactone was of approximately the same DP, 40, and polydispersity, 1.06, as the polymeric initiator samples. The weight percentage of nonfunctionalized polycaprolactone was also the same as for the polymeric initiator cases.
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(23) The calculated polystyrene equivalent molecular weights for the block copolymers were determined by assuming a 95% conversion for the caprolactone polymerization and a PSt equivalent molecular weight of a poly(caprolactone) homopolymer, or block, being ca. 2.0 times that of the actual molecular weight. Therefore for copolymer **4b**, 43.9 mmol of caprolactone is polymerized with 0.44 mmol of initiator to 95% conversion. This gives a DP of 95 and a molecular weight of 10 750. The PSt equivalent molecular weight is then 21 500, and together with the molecular weight of the starting block (4500) gives a total calculated polystyrene equivalent molecular weight of ca. 26 000.

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