Narrow-Polydispersity Diblock and Triblock Copolymers of Alkyl Acrylates by a "Living" Stable Free Radical Polymerization

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"Living" free radical polymerization has undergone tremendous advancement in the past few years, particularly in the area of nitroxide-mediated free radical polymerization. In 1993, Georges et al.[1] first reported that narrow molecular weight distribution polystyrene could be produced by a stable free radical polymerization (SFRP) process. The mechanism involves reversible capping of the growing chain by a counter stable free radical such as TEMPO (2,2,6,6-tetramethyl-1-piperidinoxyl). In the early eighties, Solomon and Rizzardo[2] had applied a similar concept to the synthesis of methyl acrylate oligomers. The potential of reversible capping for the development of a new "living" free radical polymerization was not realized since high molecular weights and narrow polydispersities were not achieved in their early work. In fact, recent attempts to obtain high molecular weight polyacrylates in a "living" reproducible fashion by SFRP have been notably unsuccessful. These results are even more surprising in light of the fact that high molecular weight random copolymers of styrene/acrylates have been synthesized by this technique by ourselves[3] and others.[4]

A "living" free radical polymerization offers an alternative to anionic polymerization as the method of choice for synthesis of block copolymers. Work carried out in our laboratory[5] has demonstrated that stable free radical block copolymerization of styrenic and diene monomers is feasible in "living" fashion. Currently, the only commercially available block copolymers containing poly(meth)acrylates are produced via group transfer polymerization (GTP).[6] GTP is considered by many to be an enolate-initiated anionic polymerization[7] and as such has the same stringent purity requirements as does anionic polymerization. In addition, GTP is not applicable to styrenic and diene monomers, eliminating the possibility of synthesizing block copolymers from disparate monomers.

Anionic polymerization, using the methods developed by Teyssie et al.,[8] is suitable for the synthesis of block copolymers containing styrene and alkyl acrylates, but the monomer purity and low temperatures required have made large-scale production by such processes impractical. In addition, the order of monomer addition in a sequential anionic polymerization is determined by the stability of the resulting anion. Anionic polymerization can only occur if the electroaffinity of the monomer introduced is comparable to, or greater than, the electroaffinity of the initiating anionic chain end. Therefore, if a block copolymer containing styrene and an alkyl acrylate is desired, the styrene block must be introduced first and once the more stable acrylate anion has been generated, it is not possible to incorporate an additional block of styrene. In the nitroxide-mediated polymerization system described herein, cross-initiation should be possible between any two monomers which are known to copolymerize in a conventional free radical polymerization.

Table 1. Polymerization of *n*-Butyl Acrylate (4-oxo-TEMPO/AIBN = 1.58/1)

sample	reacn time (h)	M_n	M_w	M_w/M_n
1	3	4752	6120	1.29
2	6	8280	11628	1.40
3	9	10504	16105	1.53

We now report the successful synthesis of polyacrylate homopolymers as well as polystyrene/polyacrylate diblocks, polyacrylate/polyacrylate diblocks, and polyacrylate/polyacrylate/polyacrylate triblocks, all via nitroxide-mediated "living" polymerization. In addition, cross-initiation of styrene and *n*-butyl acrylate has also been demonstrated, which could enable the commercial availability of block copolymers which were previously inaccessible.

n-Butyl acrylate (45 mL), 4-oxo-TEMPO (4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxyl) (246 mg), and AIBN (150 mg) were combined, stirred, and flushed thoroughly with argon gas. The reaction mixture was then submerged in an oil bath which had been preheated to 105 °C, and the temperature was raised to 155 °C over 30 min. After 3 h, the reaction mixture was cooled to room temperature and a portion of the mixture was removed for characterization and subsequent use as a macroinitiator in an extension to a block copolymer. This process was repeated after 6 and 9 h of polymerization time. Molecular weight values were determined by gel permeation chromatography (GPC) employing four Waters Ultrastyragel columns (100, 500, 10^3, and 10^4 Å) and tetrahydrofuran as the eluent, at 1.0 mL $\min^{-1}$, and are reported relative to polystyrene standards. The GPC results given in Table 1 show an incremental increase in molecular weight with time, which indicates that poly(*n*-butyl acrylate)-4-oxo-TEMPO was obtained by a "living" free radical polymerization. The polydispersity (PD = M_w/M_n) broadened slightly with reaction time but remained narrow compared to conventional free radical polymerization. Molecular weights as high as 27 000 have been obtained for homopolymers synthesized by the SFRP process.

Each of the aliquots removed from the reaction described above were employed as macroinitiators. The poly(*n*-butyl acrylate) polymer chain was extended with styrene monomer to verify that these materials retained the "living" end group. These reactions proceeded smoothly and the polydispersity of the resulting block copolymers narrowed with increasing styrene content. Figure 1 shows the GPC chromatogram of a poly(*n*-butyl acrylate) starting material (**4**), the block copolymer resulting from chain extension with styrene (**5**), and finally a high molecular weight, narrow-polydispersity block copolymer (**6**) (M_w = 119K, PD = 1.38), resulting from a second chain extension with styrene. This work represents the first successful synthesis of poly(*n*-butyl acrylate)-*b*-polystyrene copolymers, by a nitroxide-mediated polymerization, where both blocks were produced in a well-controlled "living" manner.

To demonstrate cross-initiation, a TEMPO-terminated polystyrene oligomer (**7**) was chain extended with *n*-butyl acrylate monomer to yield diblock copolymer (**8**) (M_w = 16K), as shown in Figure 2. The polystyrene-*b*-poly(*n*-butyl acrylate)-TEMPO diblock (**8**) was washed with methanol to remove excess TEMPO and subjected to a second chain extension with *n*-butyl acrylate to give diblock **9**. The M_n, M_w, and polydispersity results for each of these chromatograms are given in Table 2.

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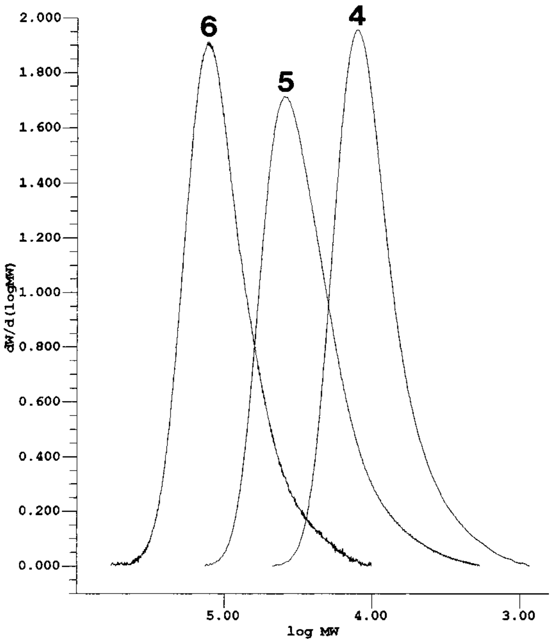

Figure 1. Comparison of the GPC chromatograms of poly(*n*-BuA)-4-oxo-TEMPO starting material (**4**), diblock copolymer P(*n*-BuA)-*b*-PS (**5**) resulting from chain extension of **4**, and P(*n*-BuA)-*b*-PS-*b*-PS (**6**) resulting from chain extension of **5**.

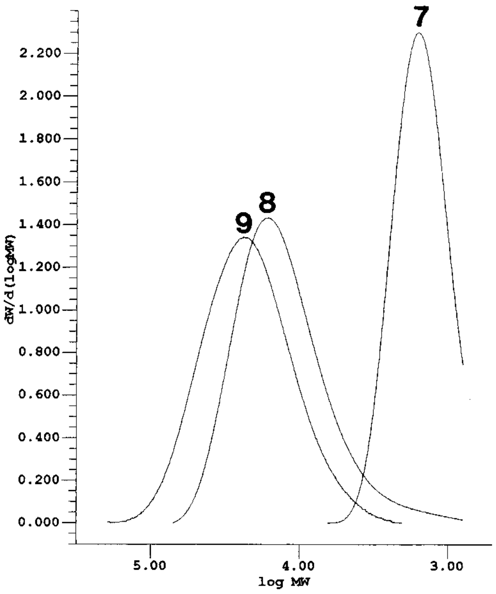

Figure 2. Comparison of the GPC chromatograms of polystyrene-TEMPO starting material (**7**), diblock copolymer PS-*b*-(*n*-BuA) (**8**) resulting from chain extension of **7**, and PS-*b*-P(*n*-BuA)-*b*-P(*n*-BuA) (**9**) resulting from chain extension of **8**.

Table 2. Chain Extension of PS-TEMPO with *n*-Butyl Acrylate Monomer at 145 °C

sample	reacn time (h)	M_n	M_w	M_w/M_n
7	1	1514	1728	1.14
8	2.5	9671	16173	1.67
9	1	17352	27473	1.58

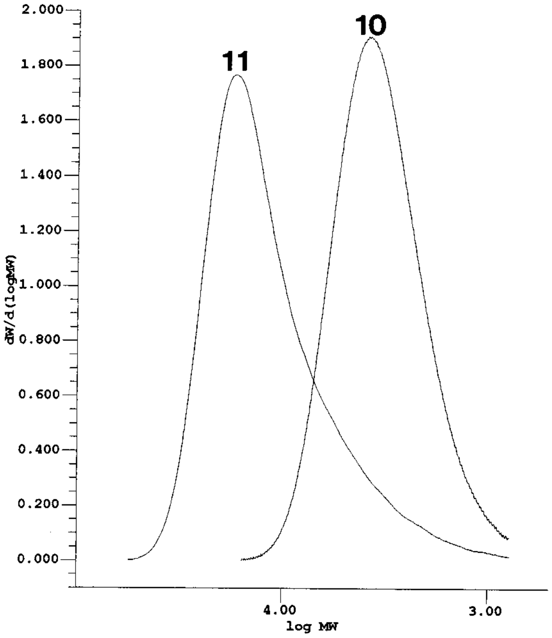

Figure 3. Comparison of the GPC chromatograms of poly(*n*-BuA)-4-oxo-TEMPO starting material (**10**) and diblock copolymer poly(*n*-BuA)-*b*-poly(*tert*-BuA) (**11**) resulting from chain extension of **10**.

Poly(*n*-butyl acrylate) homopolymers (**10**) were also chain extended with *tert*-butyl acrylate monomer to give a mixed polyacrylate diblock (**11**) as shown in Figure 3. This diblock was then further chain extended to give a poly(*n*-butyl acrylate)-*b*-poly(*tert*-butyl acrylate)-*b*-poly(*n*-butyl acrylate) triblock with block lengths of 4K, 10K, and 2.5K, respectively. Chain extension with poly(*tert*-butyl acrylate) was carried out under pressure in a Parr reactor to achieve the required polymerization temperature of 145 °C. Each of these chain extensions proceeded by a "living" mechanism.

In summary, we have demonstrated the application of the SFRP process to acrylates to produce high molecular weight homopolymers, mixed acrylate di- and triblock copolymers, and acrylate/styrene diblock copolymers. Controlled propagation with retention of the "living" end group, and cross-initiation of alkyl acrylates and styrene have also been demonstrated. Polyacrylates and block copolymers containing polyacrylates are an important class of materials, and this work broadens the application of nitroxide-mediated polymerizations substantially.

References and Notes

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