Block Copolymer Synthesis by a Miniemulsion Stable Free Radical Polymerization Process

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ABSTRACT: The ultimate success of living-radical polymerizations will depend on whether they can be used to make materials with unique properties in an economical and acceptable manufacturing process. We report a major step in this direction for the SFRP process by demonstrating that a miniemulsion process can be used to polymerize monomers to high conversion with a high degree of livingness and that this process can be used to synthesize block copolymers. The key to the polymerizations is the use of a nitroxide-terminated oligomer to initiate the miniemulsions. Miniemulsions are performed at 135 °C to greater than 99% conversion to give polystyrenes with polydispersities between 1.15 and 1.25. Chain extension studies show these materials to have a high degree of livingness. Reaction of these polystyrene latexes with *n*-butyl acrylate lead to the first block copolymers completely made under SFRP miniemulsion conditions.

In the late 1980s and early 1990s of the past century, the prevailing opinion about free radical polymerization was that it was a mature technology, and there was not much more to discover. Ten years later, free radical polymerization is one of the hottest research areas in polymer chemistry rejuvenated by the development of living-radical polymerization. A new way of looking and thinking about free radical polymerization has evolved. Three well-established living-free radical polymerization processes are now available: stable free radical polymerization (SFRP),[1] atom transfer radical polymerization (ATRP),[2] and reversible addition−fragmentation chain transfer (RAFT)[3] polymerization.

In the case of the SFRP process, the majority of the early work was performed under bulk conditions. While this was a useful system to develop the chemistry and understand the mechanism and kinetics of SFRP, there is little likelihood that it will be used in a manufacturing process. Therefore, in the past few years, attention has turned to developing an emulsion polymerization system, a process more amiable to large-scale synthesis. Clearly, prior to the advent of high-temperature living-radical polymerization, no one worried about performing emulsion polymerizations at temperatures above the boiling point of water. And, when work in this area was initiated, there was some question as to whether high-temperature emulsion polymerization would actually be possible. Some of the early emulsion SFRP literature strengthened these concerns. Bon et al.[4] first reported their valiant but unsuccessful attempts at developing a high-temperature SFRP emulsion process. This paper was followed by Marestin et al.,[5] who reported more success. However, the polydispersities of the polymers reported were broad, and no evidence for incremental increases in molecular weights were reported, a necessary requirement to prove a living system. While these initial results were not very encouraging, the authors in these two papers did do a very good job delineating some of the issues with performing a high-temperature SFRP emulsion. Results in two subsequent papers by Prodpran et al.[6] and MacLeod et al.[7] demonstrated that a high-temperature SFRP living-radical emulsion type process is indeed feasible, at least under miniemulsion conditions. In the former case, benzoyl peroxide was used as the initiator, and conversions were as high as 90% with polydispersities ranging from about 1.4 to 1.7. In the latter case, potassium persulfate was used as the initiator, and polydispersities were typically between 1.15 and 1.25 with conversions up to 85%. Fracet et al.[8] reported on SFRP miniemulsion results performed at temperatures below 100 °C using the nitroxide of *N*-*tert*-butyl-*N*-(diethylphosphono-2,2-dimethylpropyl). Experiments were run with azobis(isobutyronitrile) and potassium persulfate in combination with sodium metapersulfite, giving polydispersities of about 1.6 and greater than 2, respectively. A more recent paper by Butte et al.[9] concluded that the living-radical polymerization of choice for preserving high polymerization rates, based on compartmentalization arguments, is RAFT.

A successful SFRP miniemulsion process must satisfy a number of requirements. The miniemulsion must be stable under conditions of high temperature since SFRP polymerizations are typically performed at 135 °C. The system must be compatible with a variety of monomers, go to 100% conversion, and have short reaction times, typically 6 h or less. In addition, the polymers that are made must have a high degree of livingness so that their further modification will be possible.

Although the El-Aasser and Xerox groups were successful at demonstrating the feasibility of a high-temperature stable living-radical miniemulsion process, two major unresolved problems were evident in these papers. Both groups reported conversions of up to 90%. While these high conversions are commendable, for the purpose of manufacturing, where conversions approaching 100% are required, they are not acceptable. Furthermore, there were no indications in either paper as to the ability of the produced polystyrenes to reinitiate polymerization in the presence of more monomer. If these living-radical emulsion polymers are to be used to make block copolymers, an ultimate goal in our program, both these issues must be addressed. With that in mind we proceeded to further develop the SFRP miniemulsion process.

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In this paper we expand on the results of our earlier miniemulsion work[7] and report on a modified miniemulsion SFRP process in which a TEMPO-terminated polystyrene oligomer is used to initiate the polymerization. The modified miniemulsion process typically goes to 99.5% plus conversion and yields polymers that have a high degree of livingness as evidenced by chain extension experiments. In addition, we report the first example of the synthesis of a block copolymer under SFRP miniemulsion conditions.

Experimental Section

(a) Materials and Equipment. Nitroxides and monomers were used as received. Miniemulsion polymerizations were performed in a modified Parr bomb (300 mL) under a blanket of argon for typically 6 h or less at 135 °C. Samples for GPC and conversion analysis were removed through a tube, one end of which is in the reaction mixture and the other outside the reactor. Since the reaction mixture was typically under about 110 psi of pressure, the part of the tube that was outside the reactor filled with reaction mixture when a valve was opened. Molecular weights and polydispersities (PD) were estimated by gel permeation chromatography (GPC) using a Waters/Millipore liquid chromatograph equipped with a Waters model 510 pump, Ultrastyragel columns of pore size 10^4, 2×500, and 100 Å, a Waters model 410 differential refractometer (RI), and a Waters 486 tunable absorbance detector (UV). Polystyrene standards were used for calibration. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL $\min^{-1}$. GPC was performed on samples taken directly from the polymerization mixture without any prior precipitation that might remove low molecular weight chains. Excess monomer was removed by passing a flow of argon over the sample. Percentage conversions were determined by gas chromatography (GC) analysis of residual monomer using a Perkin-Elmer SIGMA 2000 gas chromatograph with a Perkin-Elmer LCI-100 laboratory computing integrator. The columns were Carbowax 20M purchased from Supelco. The conversions to polymer were calculated by difference. Miniemulsions were prepared using a Niro Sauvi Panda piston homogenizer. Reaction mixtures, which typically contain initiator, nitroxide, monomer, sodium dodecylbenzenesulfonate, hexadecane, and water, were passed through the homogonizer three times with a pressure of between 300 and 500 bar. Particle sizes were determined by dynamic light scattering on a Nicomp model 370 submicron particle sizer.

(b) SFRP Miniemulsion. To an aqueous solution (80 mL) of sodium dodecylbenzenesulfonate (1.28 g) and potassium persulfate (0.136 g, 0.0005 mol) was added a solution of styrene (22 mL, 0.19 mol) containing hexadecane (1.838 g) and TEMPO (0.177 g, 0.0011 mol). This was stirred for 1 min and then emulsified by three passes through a piston homogenizer at a pressure of 500 bar. The emulsion mixture was placed in a pressure reactor (modified PARR reactor, 300 mL capacity), and the reaction mixture was deoxygenated by 10 pressure and depressurizing sequences with argon gas over a period of one-half hour. The reactor was heated at 135 °C for 6 h and then cooled to afford a miniemulsion of particle size 142 nm. Conversion was calculated by GC to be 80%.

The above procedure was repeated at 145 °C for 6 h to provide a polymer that when chain extended according to the procedure described in section c gave Figure 5.

The above procedure was repeated at 135 °C for 17 h to provided a polymer that when chain extended according to the procedure described in section c gave Figure 6.

(c) Test for Livingness. A miniemulsion (100 mL) latex was precipitated in methanol (1 L) by dropwise addition with vigorous stirring. The resulting precipitate was filtered and then washed once with methanol (200 mL). The polystyrene was dried for 24 h under vacuum. A portion of the polymer precipitate (1.5 g) was dissolved in styrene (20 mL) in a three-necked 100 mL round-bottomed flask equipped with an argon inlet and water condensor. The solution was deoxygenated by bubbling argon through the solution for 20 min, and the reaction solution was heated by immersing the reaction flask in an oil bath preheated to 135 °C. The solution was heated for 90 min, and samples for molecular weight determinations were taken every one-half hour. If the miniemulsion polymers were living, an incremental increase in molecular weight was observed. The degree of livingness of the starting polymer determined whether the GPC distribution was mono- or multimodal. (See Results and Discussion section for details.)

(d) Modified Miniemulsion Polymerization. To a 100 mL round-bottom flask was added styrene (25 mL, 0.26 mol), TEMPO (0.195 g, 0.0013 mol), and benzoyl peroxide (0.242 g, 0.001 mol). The solution was deoxygenated by bubbling argon through the solution for 20 min and then heated by immersion in an oil bath preheated to 135 °C. The solution was maintained at temperature for 1 h and then cooled. Conversion was roughly 5%, and the number-average molecular weight (M_n) was 2000. The oligomeric mixture was added to a solution of sodium dodecylbenzenesulfonate (SDBS, 3.1 g) in water (100 mL). This was then passed through a piston homogenizer three times at a pressure of 500 psi. The resulting miniemulsion mixture was transferred to a Parr reactor and deoxygenated by pressurizing /depressurizing 10 times with argon gas. The reactor was then heated to 135 °C and maintained at that temperature for 6 h. Upon cooling, a stable polystyrene latex was isolated. The average particle size of the latex was about 200 nm. The polystyrene by GPC analysis had $M_n = 18\,789$, with a PD = 1.15. GC analysis of the residual styrene monomer showed it to be 700 ppm or about 0.3 wt %, giving a conversion of about 99.7 wt % based on the weight of monomer.

(e) Block Copolymer Synthesis. In a Parr reactor, to the polystyrene latex prepared above was added 10 mL of *n*-butyl acrylate. The latex was stirred at room temperature for 1 h while being purged with argon (10 cycles of pressurization followed by depressurization). The reactor was heated to 135 °C and maintained at temperature for 6 h. Upon cooling, a stable latex was obtained. GPC of the resulting product showed a shift to higher molecular weigtht $M_n = 34\,638$, while a very narrow polydispersity was maintained (PD = 1.18). GC analysis of residual monomer showed the product to contain 1400 ppm of *n*-butyl acrylate, giving a conversion of 99.4%.

Results and Discussion

The skepticism voiced by a number of polymer chemists concerning the feasibility of performing a high-temperature emulsion under SFRP conditions was well founded, and to date, it has remained an elusive goal.[10] However, performing the polymerizations under miniemulsion conditions has proven more successful. Stable miniemulsion can be achieved and maintained at high temperatures with the commonly used combination of sodium dodecylbenzenesulfonate and hexadecane.[11] Our first set of successful miniemulsion polymerizations employed potassium persulfate as the initiator and TEMPO as the nitroxide. The exact amount of nitroxide required was determined empirically because the initiator efficiency of potassium persulfate was unknown under these conditions. But even assuming 100% efficiency of the initiator, it still required more than 2 equiv of TEMPO, 2.2 to be exact, relative to potassium persulfate, to obtain narrow polydispersity polymers. Under these conditions, polymerizations proceed smoothly to provide polystyrenes whose molecular weights continue to grow with time (Figure 1) and have polydispersities between 1.10 and 1.25 (Table 1). As required for a living polymerization system, molecular weights increase in a linear fashion with conversion (Figure 2). Final conversions are generally about 80% as determined by GC analysis of residual monomer after 6 h. Longer reaction times do not provide any improvements.

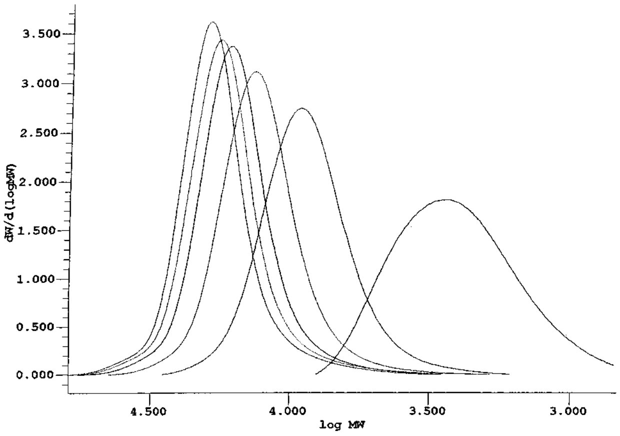

Figure 1. GPC plots showing the incremental increases in molecular weight over time for a miniemulsion styrene SFRP polymerization at 135 °C initiated with potassium persulfate.

Table 1. Molecular Weight, Polydispersity, and Conversion Data for a Styrene Miniemulsion Polymerization Performed at 135 °C

sample	time (h)	M_n	PD	conv (%)
i	1	2 283	1.25	8
ii	2	8 099	1.15	25
iii	3	11 993	1.13	40
iv	4	14 826	1.12	51
v	5	15 920	1.13	56
vi	6	17 396	1.12	61

No fouling of the reactor is evident, an indication of the stability of the miniemulsion. Particle sizes are generally about 150 nm. Although the particle size distributions are unimodal, they are also always broad.[12]

What should be noted about these polymerizations is that no additives, such as camphorsulfonic acid (CSA), are required to enable these polymerizations to proceed at a fast rate. CSA is added in bulk polymerizations to destroy the excess nitroxide that builds up in the reaction solution as a result of some termination that occurs.[13] CSA is not required under miniemulsion conditions because TEMPO is partially soluble in water and, therefore, partitions between the organic and aqueous phases.[14] It is hypothesized that enough excess TEMPO migrates to the aqueous phase to prevent any buildup in the organic phase, thus allowing the polymerization to proceed smoothly. The partial solubility of TEMPO in water also explains why a high TEMPO to potassium persulfate ratio is required to obtain narrow polydispersity polymers.

Unfortunately, even though the final polystyrene products have very narrow polydispersities, when they are isolated from the emulsion mixture and chain extended under bulk conditions to examine their livingness, bimodal molecular weight GPC distributions are always obtained (Figure 3). The lower molecular weight peak overlaps with the starting polystyrene, suggesting that the peak is due to dead chains in the starting material. It is conceivable that dead chains form during the course of the miniemulsion process, but it is also possible they form during the isolation procedure or during the chain extension process. Our suspicion was that the dead chains were forming in the latter part of the polymerization. To determine whether this is the case, a miniemulsion was performed for a shorter reaction time (3 h as opposed to 6 h), and the lower conversion (50% as opposed to 85%) polymer was isolated. Chain extension of this material with styrene under bulk conditions proceeded smoothly, and as indicated in Figure 4, the peak associated with the starting polystyrene completely disappears. This result not only substantiates our suspicion as to when the dead chains are forming but also confirms that the polymer isolation and chain extension procedures do not contribute to the dead chains.

Early attempts to push the conversion to 100%, by manipulating reaction parameters and the miniemulsion formulation, were uniformly unsuccessful. Not only was complete conversion never achieved, but also longer reaction times, 14 h instead of 6 h, and higher temperatures, 145 °C instead of 135 °C, resulted in polystyrene polymers that showed extensive amounts of dead chains when chain extended (Figures 5 and 6). Because the

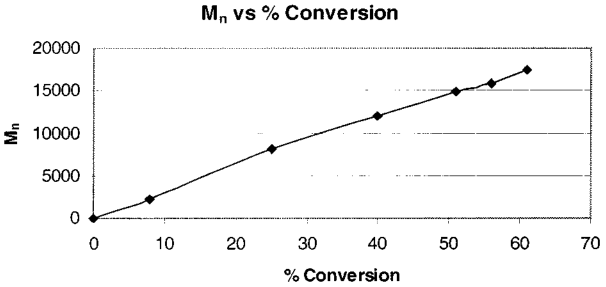

Figure 2. Plot of molecular weight vs conversion for the data in Table 1.

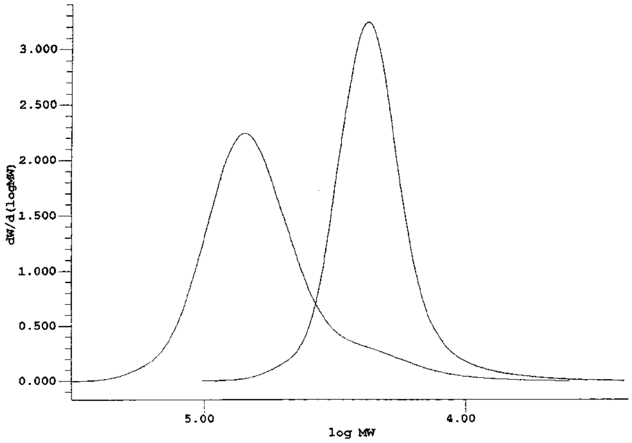

Figure 3. GPC plots showing a chain extension of polystyrene prepared by a miniemulsion styrene SFRP polymerization at 135 °C initiated with potassium persulfate.

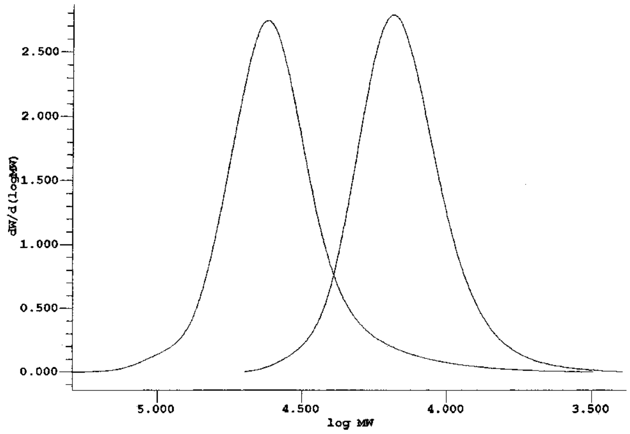

Figure 4. GPC plots showing a chain extension of a low conversion (50%) polystyrene prepared by a miniemulsion styrene SFRP polymerization at 135 °C over 3 h initiated with potassium persulfate.

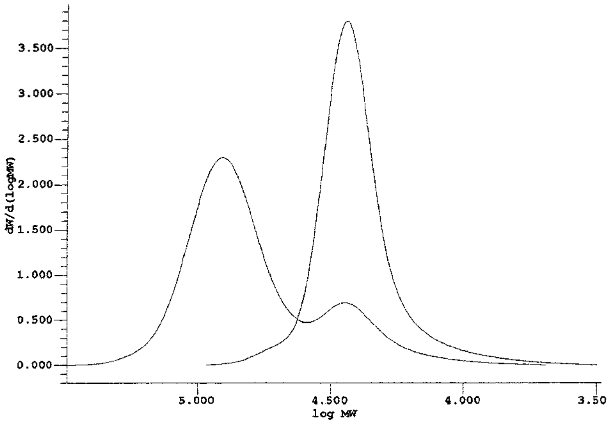

Figure 5. GPC plots showing a chain extension of a polystyrene prepared by a miniemulsion styrene SFRP polymerization at 145 °C over 6 h initiated with potassium persulfate taken to 67% conversion.

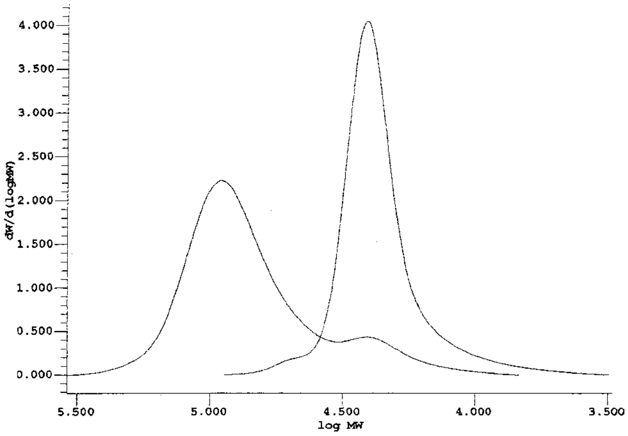

Figure 6. GPC plots showing a chain extension of a polystyrene prepared by a miniemulsion styrene SFRP polymerization at 135 °C over 17 h initiated with potassium persulfate taken to 92% conversion.

magnitude of a GPC molecular weight distribution is related to the amount of sample by weight that is present, the lower molecular weight peaks, while relatively small, contain a disproportionate larger number of chains relative to the higher molecular weight distributions. Thus, these smaller low molecular weight distribution peaks may contain a significant number of chains. Increasing the reaction rates to shorten the reaction time by using less nitroxide was equally unsuccessful. Polymers were obtained that gave high molecular weight peaks in the GPC plots suggestive of a population of uncapped polymer chains acting in a conventional free radical polymerization manner.

During the course of all of this work we were concerned about the initiation step. In the case of a conventional free radical polymerization at temperatures of less than 100 °C, initiation typically occurs over a few hours. At any given time in the polymerization, relative to the actual amount of initiator used, only small amounts of primary radical ($R^•$), radical plus monomer ($RM^•$), and oligomers ($RM_n^•$) are present in the aqueous phase, allowing the system to deal with them in a more or less controlled fashion. However, in the case of the SFRP process, all the initiator dissociates in a few minutes or less. This has the effect of overwhelming the system minutes into the polymerization because a large portion of the nitroxide, which controls the initiation step, is in the organic layer and unavailable to react with the primary radicals forming in the aqueous layer.

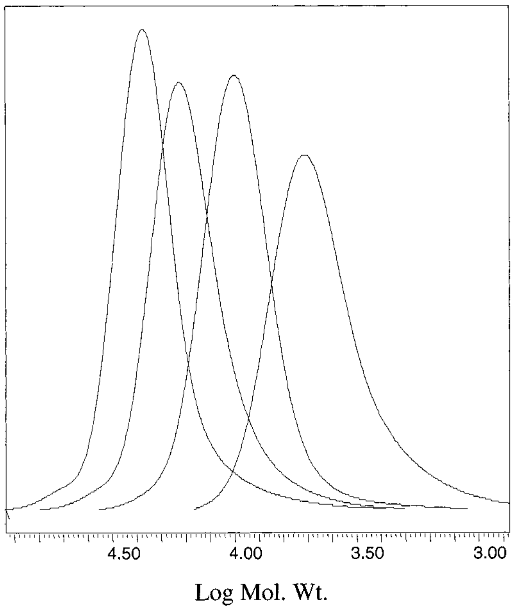

Figure 7. GPC plots showing the incremental increases in molecular weight over time for a miniemulsion styrene SFRP polymerization at 135 °C initiated with TEMPO-terminated polystyrene oligomer.

Table 2. Molecular Weight and Polydispersity Data for a Styrene Miniemulsion Polymerization Performed at 135 °C with TEMPO-Terminated Polystyrene as the Initiator

sample	time (h)	M_n	PD
i	1	3 933	1.25
ii	2	8 891	1.15
iii	3.5	13 889	1.18
iv	6	20 197	1.17

In addition, in a conventional free radical polymerization, high molecular weight polymers are formed almost immediately which, in the case of an emulsion or miniemulsion polymerization, can further help to stabilize the miniemulsion droplets. In the case of a living-free radical polymerization process, since the rate of chain growth is slower, early in the polymerization the system has only small molecule and very small oligomeric material present. This again leaves the system less stable. To address these problems, we decided to take advantage of the fact that a TEMPO-terminated polystyrene oligomer could serve as the initiator to enable polymerization. Two advantages of using these oligomers are immediately evident. First, the initial fast disruptive initiation step described above can be avoided. Second, since the TEMPO-terminated polystyrene is water insoluble, it can act as a cosurfactant to stabilize the system removing the need for hexadecane. This could prove beneficial sometime in an application where hexadecane is undesirable.

To prepare the TEMPO-terminated polystyrene oligomer, an SFRP bulk polymerization was performed under standard conditions to about 5% conversion, with benzoyl peroxide as the initiator. The molecular weights of these oligomers are typically in the range of M_n 1500–2500. The resulting reaction mixture is subsequently emulsified as described in the Experimental Section. Upon heating to 135 °C, polymerization occurs, and the polystyrene is seen to increase in molecular weight as the reaction continues (Figure 7 and Table 2). Very narrow polydispersed polymers are obtained.

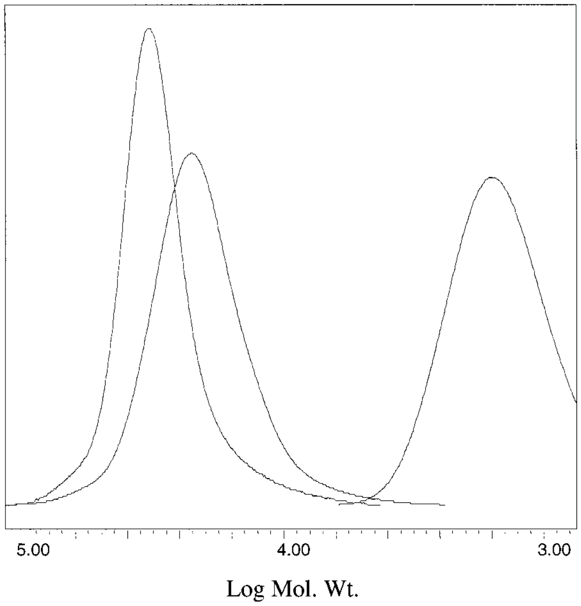

Figure 8. GPC plots showing the chain extension of polystyrene with *n*-butyl acrylate under miniemulsion conditions to form a block copolymer of styrene and *n*-butyl acrylate.

What is very interesting about these polymerizations is conversions are typically 99.5% plus, much higher than what is obtained in our previous system where initiation was achieved using potassium persulfate. We can speculate on the reason for the high conversion based on some earlier work performed in a conventional miniemulsion system. It has been shown that in the presence of 1% of a high molecular weight polymer all miniemulsion monomer droplets become nucleated.[15] In the absence of such a polymer only 5% of particles become nucleated, the rest of the particles serve as monomer reservoirs. It may, therefore, be reasonable to assume that the starting TEMPO-terminated oligomer, present in a concentration of about 5%, enables all the miniemulsion droplets to be nucleated. As such, more of the monomer is in the vicinity of propagating chains, and fewer particles are left to act as monomer reservoirs. This enables the polymerization to be more efficient at consuming monomer. Or it is possible that since all the miniemulsion droplets are nucleated, there are fewer TEMPO-terminated chains per droplet and, therefore, the possibility of a large buildup in free nitroxide is less, enabling the polymerization to proceed in an efficient manner.

When the final polystyrene products are isolated and reacted with more styrene monomer under bulk conditions, they chain extend in a manner suggesting that the vast majority of the chains are still living. GPC results are similar to those illustrated in Figure 3. Work has been initiated to determine why this modified miniemulsion system gives polymer chains with a higher degree of livingness than under our initial miniemulsion conditions. It may be related to the more even distribution of polymer chains throughout all the miniemulsion droplets, thus reducing the actual number of chains in each droplet. However, before a reasonable explanation can be proposed, the mechanism of termination needs to be determined.

The molecular weights (M_n) that have been achieved to date under these miniemulsion conditions have varied between 10 000 and 35 000 with polydispersities of 1.25 or less. This is not to suggest these are limiting molecular weights. Studies are underway to determine the maximum molecular weight that can be obtained while maintaining a high degree of livingness.

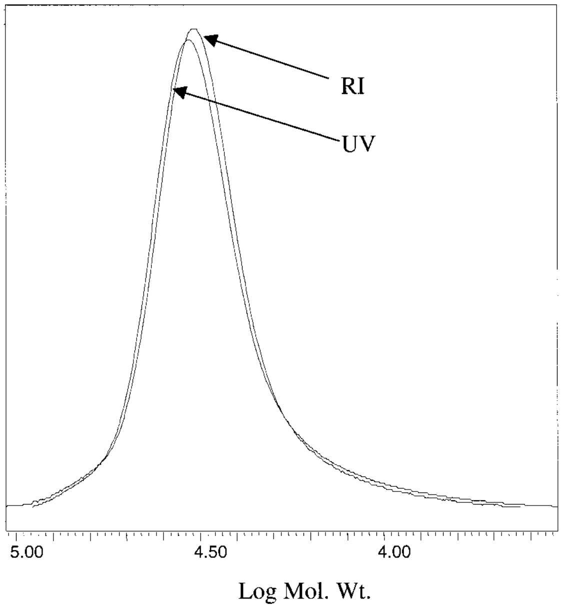

Figure 9. RI and UV GPC overlay for the poly(styrene-*b*-*n*-butyl acrylate) prepared by a miniemulsion process.

Table 3. Molecular Weight and Polydispersity Data for a Block Copolymer of Styrene and *n*-butyl Acrylate Compared to the Starting Polystyrene

sample	M_n	PD	conv (%)
oligomer	1 476	1.25	
polystyrene	18 789	1.15	99.6
poly(S-*b*-*n*-BuAc)	34 638	1.18	99.4

Since the polystyrene polymers prepared by the modified miniemulsion exhibited a higher degree of livingness, it remained to be seen whether block copolymers could be made with these materials under miniemulsion conditions. To that end, *n*-butyl acrylate was added to a polystyrene latex (M_n = 18 789, PD = 1.15) and taken to 99.6% conversion. The reaction mixture was allowed to stir for 1 h and then heated to 135 °C under argon for 6 h. GPC analysis of the final product showed a distinct shift of the molecular weight distribution to higher molecular weight (Figure 8). As well, the RI and UV GPC distributions of the product were very similar (Figure 9), a necessary, although not necessarily sufficient, condition for a block copolymer of high purity. The M_n of the product was 34 638 with a PD of 1.18, and conversion, as determined by GC analysis of residual *n*-butyl acrylate, was 99.4% (Table 3). It should be noted that the *n*-butyl acrylate polymerized even though the nitroxide that is on the chain ends is TEMPO. This is a very interesting result since polymerization of acrylates with TEMPO to high conversion has proven to be problematic over the years.[16] The significance of this result will be expanded upon in a future publication, but suffice to say it opens the possibility of polymerizing acrylates under miniemulsion conditions using TEMPO or some other readily available commercial nitroxide.

Summary

The living-radical polymerization area has been very successful from a fundamental study point of view. However, its ultimate success will depend on whether new materials can be made by them that will have unique properties and whether, once these materials have been identified, they can be produced in an economical and acceptable manufacturing process. To that end efforts are being made to develop living-radical processes that can be readily scalable and can be used to synthesize unique materials. We report a major step in this direction for the SFRP process by demonstrating that a miniemulsion process can be used to polymerize monomers to high conversion with a high degree of livingness and that this process can be used to synthesize block copolymers. Ten years ago, a suggestion that block copolymers might be synthesized by a free radical polymerization process and under miniemulsion conditions would have seemed far fetched. Today, it is close to being a reality. Work is continuing to see how well this system can be scaled up[17] and to see whether other monomers are compatible with the system, in particular, acrylate monomers.[18] As well, while we have speculated as to why the use of a TEMPO-terminated polystyrene as the initiator in SFRP miniemulsions leads to a higher degree of livingness and enables the polymerizations to proceed to higher conversions, studies have been initiated to understand these results in more detail.

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(17) Initial work by us on the scale-up work has been very encouraging. It is not unusual that larger scale polymerizations are more reproducible primarily because reaction parameters such as heating, cooling, and heat transfer are better controlled.

(18) A manuscript is in preparation dealing with our work to polymerize acrylates under miniemulsion conditions.

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