

A Modified Glass Reactor for the Preparation of Linear and Star-Branched Block Copolymers via Living Anionic Polymerization

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ABSTRACT: A modular high-vacuum system for large-scale anionic polymerization reactions was designed that utilizes mechanical agitation in place of magnetic stirring, Teflon Rotoflo stopcocks in place of glass breakseals, and spherical o-ring joints in place of direct glass seals. A standard reactor body was used, and depending upon reactor design, it was fitted with appropriate reactant ampules, volumetric charging cylinders, etc., to facilitate polymerization, blocking reactions, and linking reactions with minimal effort. To demonstrate the efficacy of the system a number of linear and three-arm star-block copolymers comprised of oligostyrene outer blocks and polybutadiene inner blocks were synthesized. The block copolymers were characterized by narrow molecular weight dispersity, and the star polymers showed greater than 95% linking efficiency. The polybutadiene blocks contained approximately 40% 1,2-enchainment and were exhaustively hydrogenated using H₂ and a nickel octoate/triethyl aluminum catalyst. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 151–159, 1997

Key words: anionic polymerization; styrene/butadiene; block copolymer; star polymer; hydrogenation

INTRODUCTION

Anionic polymerization is frequently the method of choice for preparation of model polymers where precise control of parameters such as molecular weight, molecular weight distribution, microarchitecture, etc., is desired.^{1–5} The use of rigorous high-vacuum anionic polymerization techniques,

as outlined in detail by Morton and Fetters,^{6–10} provides nearly monodisperse polymers of predetermined molecular weight and microarchitecture. For careful kinetic measurements or mechanistic elucidations these procedures remain the method of choice. Classical high-vacuum techniques are, however, characterized by time-consuming solvent and monomer preparation and tedious reactor and ampule construction, often requiring the efforts of a skilled glassblower. In addition, it is often difficult to continuously sample the composition of the reactor, to make adjustment to the polymer composition during the polymerization process, or to synthesize sufficient quantities of polymer necessary for mechanical tensile and melt rheological testing. To circumvent many of these difficulties associated with classical anionic syntheses, McGrath and coworkers

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ers¹¹ have designed a low-pressure, inert-atmosphere reactor system based on stainless steel or glass reactors, and column purification of monomers and solvents over activated alumina and molecular sieves. Ndoni and coworkers have also reported a similar reaction system based on an inert atmosphere and reusable glassware.¹² These systems do allow for the production of large quantities of materials with less effort and in a shorter time; however, it may often be inadequate for certain inherently problematic procedures such as, for example, linking of living arms to form star-branched polymers.

To bridge the gap between classical anionic syntheses and the semiproduction methods of McGrath et al., we have designed a new modular high-vacuum system that utilizes mechanical agitation in place of magnetic stirring, Teflon Rotoflo stopcocks in place of glass breakseals, and spherical o-ring joints in place of direct glass seals. In this way, a standard reactor body is used, and depending upon reactor design, it is fitted with appropriate reactant ampoules, volumetric charging cylinders, etc., to facilitate polymerization, blocking reactions, and linking reactions with minimal effort.

In a previous article¹³ we described the synthesis using classical high-vacuum techniques, of star-branched block copolymers that served as precursors to unique block copolymer ionomers. *sec*-Butyllithium was used to oligomerize styrene, followed by sequential polymerization of butadiene to form a living diblock "arm," that was next linked using methyltrichlorosilane to afford a three-arm star-branched polymer. Butadiene, styrene, *sec*-butyllithium, and chlorosilanes were all purified and delivered to an all-glass reactor via ampoules equipped with glass breakseals. We were able to effectively polymerize 50–75 g batches varying in molecular weight from 7–30 K, with linking efficiencies greater than 90%. Polymers that were less than 90% linked were fractionated with significant loss of yield.

This article describes the modifications of our original techniques, which allow for the preparation of higher molecular weight polymers with higher linking efficiencies. By construction of a high-vacuum reactor that allows mechanical stirring, narrow molecular weight distributions have been preserved, even under conditions of increased polymerization solution viscosity. The design and implementation of a new linking ampoule has also improved the synthesis of star-branched

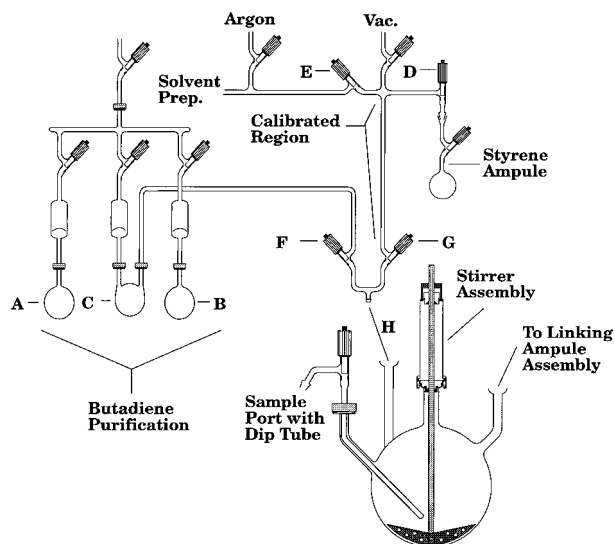


Figure 1 Modular high-vacuum system for large-scale anionic polymerization reactions: (A and B) 1,3-butadiene purification flasks; (C) 1,3-butadiene storage ampule; (D) isolation valve for styrene ampule; (E) isolation valve for solvent purification section; (F) 1,3-butadiene addition control valve; (G) styrene addition control valve; (H) 28/15 spherical o-ring joint for reactor attachment.

polymers by permitting more accurate additions of linking agents, leading to higher linking efficiencies.

EXPERIMENTAL

Materials

Benzene (J. T. Baker, reagent grade) was stirred over concentrated sulfuric acid for 2 weeks, transferred onto a vacuum line, and stirred over calcium hydride for a minimum of 1 week. The benzene was then distilled onto sodium dispersion and stirred (approximately 3 days) until sodium platelets had formed and the solution was clear. The benzene was next distilled onto living oligostyryllithium, and stirred for a minimum of 48 h, with formation of a characteristic deep red color, indicating the purification process was complete. As shown in Figure 1, butadiene (Aldrich, 99+%) was condensed into a 1 L flask **A** equipped with a 28/15 spherical o-ring joint; the flask was then attached to a vacuum line using a union-type screw clamp. Next, the butadiene was distilled onto neat *n*-butyllithium contained in flask **B**, and stirred for 6–8 h at -20°C . The purification

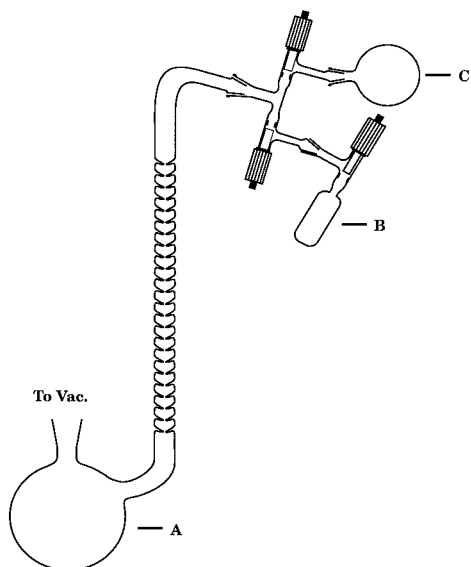


Figure 2 Chlorosilane purification assembly: (A) distilling flask; (B) storage ampule; (C) forecut receiving flask.

process was deemed complete when the butadiene had changed from a clear water white to a light straw yellow color, indicating a living solution. Occasionally, a living solution was not attained after 6–8 h; in these cases it was necessary to repeat the process until a living solution was obtained. The purified monomer was next distilled into a storage vessel **C** equipped with rotoflo stopcocks, degassed, and stored at -78°C . Styrene (Aldrich, 99%) was stirred in a flask on a vacuum line over freshly ground calcium hydride for a minimum of 3 days, degassed, and distilled onto neat dibutylmagnesium. After the styrene solution had turned yellow, indicating a living solution, the styrene was distilled into a storage ampule equipped with a Rotoflo stopcock and 14/20 joint and stored under vacuum at -10°C . Triethylamine (Aldrich, 99%) was stirred over freshly ground calcium hydride for 1 week, degassed, and stored in a flask on the vacuum line. An appropriate amount of the triethylamine was then distilled onto neat *n*-butyllithium and allowed to stir for a minimum of 1 day before use. Methyltrichlorosilane (Aldrich, 99%) was transferred to a purification assembly (Fig. 2), attached to a vacuum line, and degassed using a minimum of three freeze–pump–thaw cycles. A forecut of approximately 30–40% of the silane linking agent was then fractionally distilled from **A** into **C**, and then isolated from the system by closing the Rotoflo

valve. The next 30% fraction was distilled directly into the receiving vessel **B**. The ampule was then closed, covered with aluminum foil, and stored at -10°C until used. *sec*-Butyllithium (12 wt % solution in cyclohexane, Lithium Corp. of America) was analyzed for active carbon–lithium content by titrating a known quantity of 2,5-dimethoxybenzyl alcohol using the as-received solution¹⁴; the commercial solution concentration was then converted to molarity. Nickel octoate (8% Ni content, in mineral spirits, Pfaltz & Bauer) and triethyl aluminum (1.0M solution in hexanes, Aldrich Chemical Co.) were used as received.

Vacuum Line and Reactor Design

The vacuum line and polymerization reactor are represented in Figure 1. The vacuum line was constructed from 15 mm borosilicate glass tubing and 0–10 mm Teflon Rotoflo stopcocks (Fisher Scientific). Flasks used in the purification and storage of butadiene, and the reactor body were attached to the vacuum line using 28/15 spherical o-ring joints and screw type union clamps (Ace Glass Co.). Similar joints and unions were also used to attach the stirrer, sample removal port, and linking ampule assemblies to the reactor body. The sample removal port consisted of a Teflon needle valve fitted with a 14/20 joint and a flexible Teflon dip-tube. Additional details for the mechanical stirrer and linking agent/initiation ampule assembly are found in Figures 3 and 4, respectively.

Mechanical Stirrer

The stirrer assembly was custom fabricated and, as shown in Figure 3, was composed of a stationary Teflon body **E** equipped with fluorocarbon elastomer o-ring seals **D** and a highly polished 9.5 mm diameter 316 stainless steel (SS) shaft **F**. The lower end of the stir shaft was fitted with two Teflon paddles held in place with a small screw threaded into the stir shaft. A Teflon compression nut **B** (3/4"-16 UNF thread) compressed the upper o-ring, forming a vacuum-tight seal between the shaft and stirrer body, while a brass thrust bearing assembly **A** with brass thrust washers **C**, prevented the shaft from being drawn into the evacuated flask and abrading the Teflon body. The thrust bearing assembly was held in place with a set screw and adjusted to prevent the lower end of the stir shaft from wearing on the bottom of the reactor flask. Additional sealing was provided

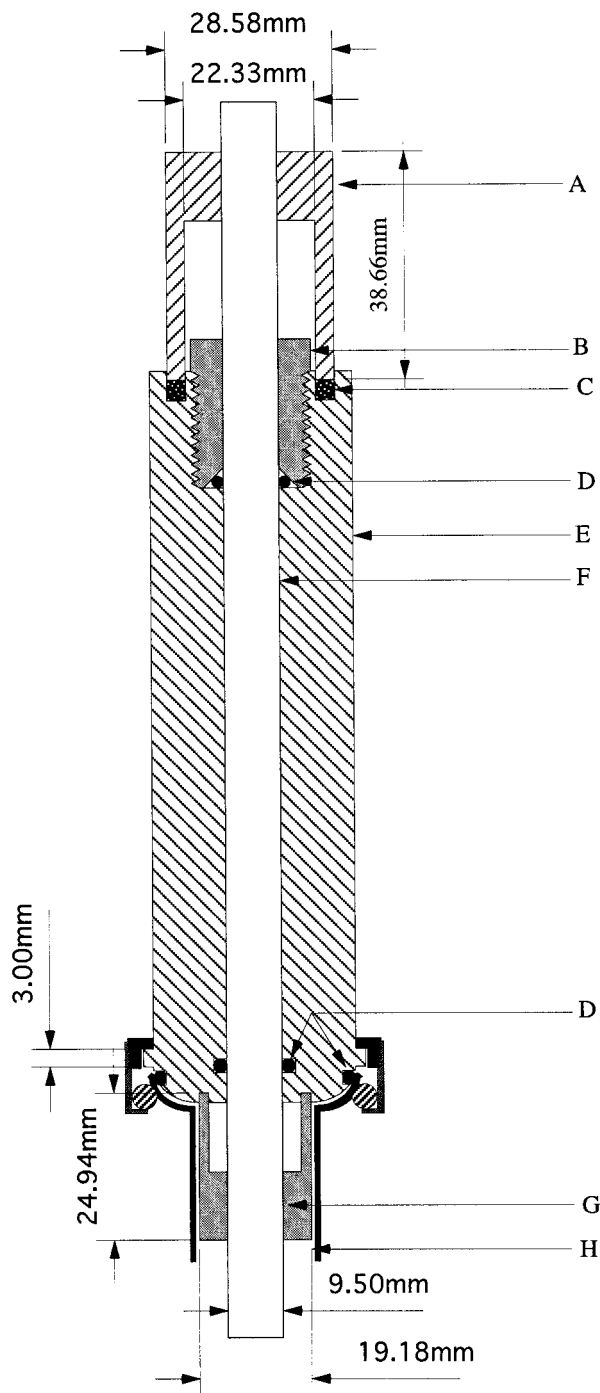


Figure 3 Mechanical stirrer assembly: (A) brass thrust assembly; (B) Teflon compression nut; (C) thrust washers; (D) o-ring; (E) Teflon body; (F) 316 stainless steel shaft; (G) grease cup; (H) reactor neck.

by a second lower o-ring, and by packing the space between the two o-rings with a high-quality hydrocarbon vacuum grease. To prevent possible

contamination of the reactor, a small grease cup **G** was press-fitted to the shaft and held in place with a small set screw to catch any grease that worked past the lower o-ring. The complete assembly was attached to the reactor body **H** using a 35/25 spherical o-ring joint and a screw-type union clamp. Stirring torque was supplied via a flexible shaft (Ace Glass Co.) from a variable-speed gearhead motor operating from 10–90 rpm.

Linking Agent/Initiation Assembly

The linking agent/initiation assembly, shown schematically in Figure 4, was composed of three essential parts: a storage ampule **D**, a calibrated delivery ampule **C**, made from a 1 mL pipet sealed at the bottom, and a metering valve **A**. Stopcocks **A**, **B**, and **C** were Teflon Rotoflo valves; vacuum was supplied to the ampule assembly via a greased ground glass stopcock. To facilitate initiation of the reaction with butyllithium, a greased stopcock and septum **F** was added to the linking ampule assembly.

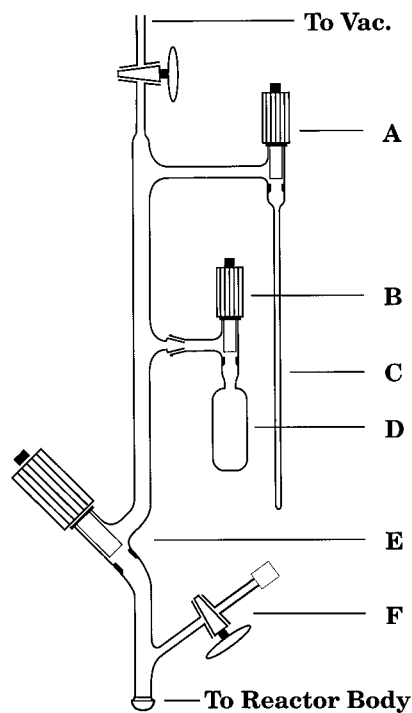


Figure 4 Linking agent/initiation assembly: (A) metering valve; (B) chlorosilane storage ampule valve; (C) 1 mL calibrated delivery ampule; (D) chlorosilane storage ampule; (E) isolation valve for the linking agent assembly; (F) greased stopcock and septum assembly for introduction of the initiator.

Polymer Synthesis

Star-branched block copolymers composed of oligostyrene outer blocks and polybutadiene inner block were synthesized using a 3 L glass reactor (Fig. 1) equipped with three female 28/15 spherical joints to accept the linking agent ampule and sample removal assemblies, and to attach the reactor to the vacuum line. A single 35/25 female joint was attached to the center of the flask to accept the stirrer assembly. The reactor was assembled, attached to the vacuum line using screw-type union clamps, and flamed under high vacuum using an oxy/propane hand torch intermittently over a period of 6 h to remove surface moisture. The following procedure was used to produce a three-arm star-block copolymer with overall molecular weight (MW) of 105,000 g/mol: approximately 1 L of purified benzene was distilled into the reactor, followed by the addition of 7.3 mL of 1.25 M *sec*-butyllithium in cyclohexane. Addition of the initiator was accomplished by first adding dry argon gas to the reactor to establish positive pressure inside the reactor, followed by injection via syringe using a 25-cm needle that was fitted through the septum and greased stopcock assembly **F** (Fig. 4). (A long needle was used to permit injection directly into the reactor, preventing contamination by the greased stopcock. In addition, this prevented polymerization of butadiene on the reactor port from residual initiator left on the inside of the linking ampule assembly.) After removing the needle, the stopcock was closed, the argon was removed by applying a vacuum, and the mechanical stirrer was activated. A styrene ampule containing the freshly distilled monomer and equipped with a Teflon stopcock and 14/20 joint was then attached to the high vacuum line (Fig. 1), and the space between **D** and the ampule was evacuated and flamed down. Next, 8.3 mL (73 mmol) of styrene was distilled into the calibrated region above the reactor. The reactor was chilled to approximately 5°C using an ice water bath, and then stopcock **G** was opened to allow the styrene monomer to drain into the reactor. A deep red color was observed, indicating initiation of the styryl oligomers. Residual styrene in the calibrated region was then washed into the reactor by distilling an additional 500 mL of benzene into the reactor. Mechanical stirring was maintained at approximately 20 rpm, and the oligomers were allowed to form for 12 h at 5°C and then slowly warm to room temperature. After

24 h the styrene oligomerization was complete, and 56 mL of purified triethylamine was distilled into the reactor through **E** and **G**, with a subsequent color change to deep purple. The reactor was again chilled to 5°C, and then approximately 500 mL (5.74 mol) of butadiene was allowed to slowly distill into the reactor from **C** through **F**. Immediately upon addition of butadiene the color changed to pale yellow. At this point, stirring speed was increased to 85 rpm, and butadiene polymerization was allowed to proceed for 12 h at 5°C and then slowly warm to room temperature. After 24 h the butadiene polymerization was complete, and the reaction mixture was quite viscous. The "arm" was sampled at this time by attaching a flask to the sample port (Fig. 1), evacuating it, and opening the rotoflo valve to permit living polymer solution to travel through the dip-tube into the evacuated flask.

Linking of the living arms to form a three-arm star was accomplished in the following manner: with stopcock **E** closed (Fig. 4), the linking agent apparatus was evacuated. Next, 0.35 mL (2.98 mmol) of methyl trichlorosilane was distilled from storage flask **D** into calibrated pipet **C**. Stopcocks **A** and **B** were then closed, and the vacuum momentarily applied to remove any residual chlorosilane from the linking ampule. The reactor was heated to 45°C and allowed to stir at the maximum possible rate. Three aliquots of the silane, 0.31 (2.98 mmol, 90% of the theoretical requirement), 0.02 (0.15 mmol, 5% of theoretical requirement), and 0.02 mL, were then distilled into the reactor at 1-h intervals. After 4 h had elapsed from the time of first addition of the linking agent, the polymer was precipitated into methanol, redissolved in hexanes, and stored under nitrogen until hydrogenation.

Linear triblock polymers were prepared in a similar manner. Styrene was oligomerized to form the initial outer block; butadiene was polymerized sequentially to form the center block; a second addition of styrene was sequentially oligomerized to form the final outer block. The living polymer was then terminated with degassed methanol and subjected to the same work-up procedure described above.

Hydrogenation

Hydrogenation of the olefinic unsaturations was performed using low pressure H₂ and a nickel-based catalyst.¹⁵ To hydrogenate 325 g of polymer,

a quantity of nickel octoate catalyst was prepared as follows: to a clean, dry 250-mL Erlenmeyer flask equipped with a magnetic stir-bar were charged 40 mL freshly distilled cyclohexane and 6.0 mmol nickel octoate in mineral spirits. The flask was then sealed with a rubber septum and fitted with a nitrogen purge. While stirring, 15 mmol of triethyl aluminum was added dropwise. After addition of a few drops, the solution turned from a light green to a dark black color. After addition was complete, the solution was allowed to stir for 30 min, and was then transferred immediately to the hydrogenation reactor.

The hydrogenation reactor, containing 325 g block copolymer dissolved in 1.7 L hexanes and 4 L cyclohexane, and the freshly prepared catalyst solution, was heated to 50°C and stirred under 50 psi of hydrogen for a period of 24 h. The reactor was then cooled, vented, and the contents were freed of catalyst in the following manner: The hydrogenation solution was transferred to two 5 L three-neck flasks, each fitted with a gas dispersion stone and magnetic stir-bar. The black solutions were allowed to stir for a period of 24 h under a constant oxygen purge. The dispersion stones were then removed, and 1 L of 10% phosphoric acid was added to each flask and stirred until the black color had completely disappeared. The top organic layer was then decanted, and the purified polymer recovered by precipitation into methanol. Proton NMR was used to insure that no residual unsaturations remained.

Hydrogenations were performed using a low-pressure 12-L reactor of our own design, as shown in Figure 5. The main reactor consisted of a standard 3-gallon 316 SS soda keg **I** with the following modifications: (a) a heating/cooling coil **J** constructed from 6 m of 1/4" stainless steel tubing was silver soldered directly to the reactor and attached with flexible lines to a constant temperature circulator **L**, which used water as the heat transfer fluid; (b) inlet **A** and outlet **H** were modified to allow pressurization and venting of hydrogen; (c) the top access door of the keg was fitted with a post that was positioned within a needle-bearing assembly that was pressed into the flywheel **G**, at a point 3 cm from the center of rotation of drive shaft **C**. In this way, operation of the electric motor **F** imposed an eccentric motion to the top of the keg, which caused the contents to be vortexed.

The reactor was designed to operate at a maximum of 125 psi and 100°C. Approximately 8 L of

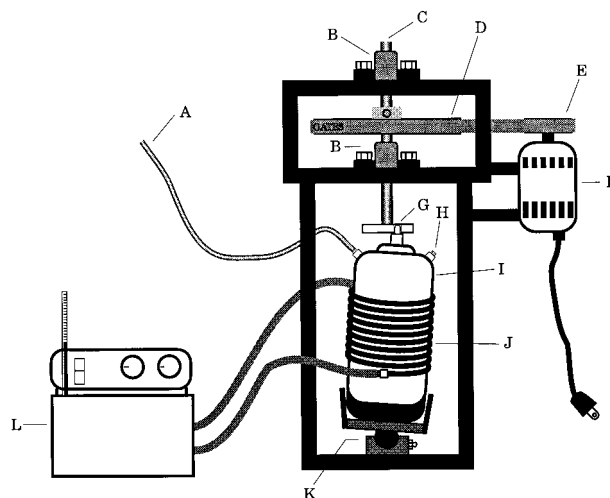


Figure 5 Low-pressure hydrogenation reactor: (A) hydrogen inlet line; (B) pillow-block roller bearing; (C) 5/8" drive shaft; (D) 16" pulley; (E) 2" pulley; (F) 1/4 hp ac motor; (G) flywheel and needle bearing assembly; (H) hydrogen vent; (I) 3 gal SS soda keg reactor; (J) heating cooling coil; (K) ball and socket bearing; (L) thermal bath/circulator.

polymer solution could be effectively hydrogenated in a single batch.

Molecular Weight and Structural Characterization

Gel permeation chromatography (GPC) data were obtained using a Waters Associates system equipped with a Rheodyne injector, Model 6000A solvent delivery module, four Ultrastayragel columns of nominal pore sizes 100, 500, 10^4 , and 10^5 Å or a bank of two PL-Gel Mixed-D 300×7.5 mm (length \times i.d.) columns by Polymer Laboratories, Ltd., and a Waters Model 410 differential refractometer detector operating at 33°C. THF, freshly distilled from calcium hydride, was the eluting solvent and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 0.25% (w/w) in THF. Solutions were filtered using 0.45 μ m Teflon filters, and the injection volume was 50 μ L. Number and weight-average molecular weights and molecular weight distributions were analyzed using ADALAB software with GPC Chromatochart enhancement.

^1H - and ^{13}C -NMR spectroscopy was performed at room temperature using a Bruker AC-300 spectrometer. The spectra of polymers were acquired using 5–10% (w/w) CDCl_3 solutions, and chemical shifts were measured relative to an internal reference (0 ppm) of TMS.

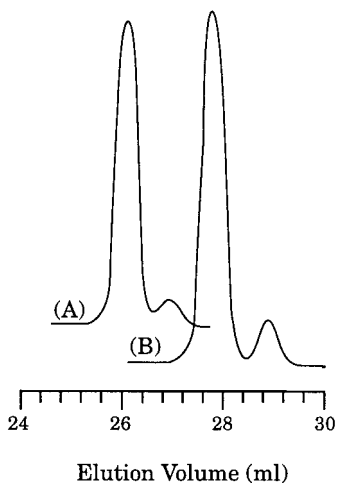


Figure 6 GPC chromatograms of three-arm star radial, styrene/butadiene block copolymers: (A) synthesized using the described techniques; (B) synthesized earlier using rigorous high-vacuum techniques.

RESULTS AND DISCUSSION

Using the vacuum line and reactor system described above, a number of star-branched copolymers of various molecular weights were synthesized. Typical GPC chromatograms for several of these polymers are shown in Figures 6 and 7. Figure 6(A) demonstrates the preservation of narrow polydispersity of a three-arm star radial-block copolymer produced using the described techniques, compared to a similar star polymer, shown in Figure 6(B), synthesized earlier using rigorous high

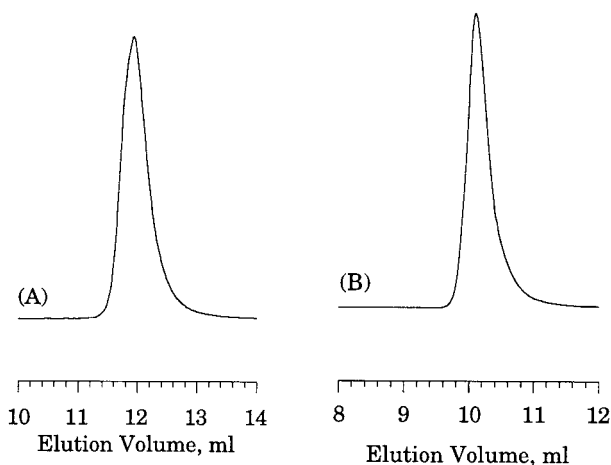


Figure 7 GPC chromatograms of styrene/butadiene/styrene triblock copolymers: (A) 25,000 g/mol; (B) 75,000 g/mol.

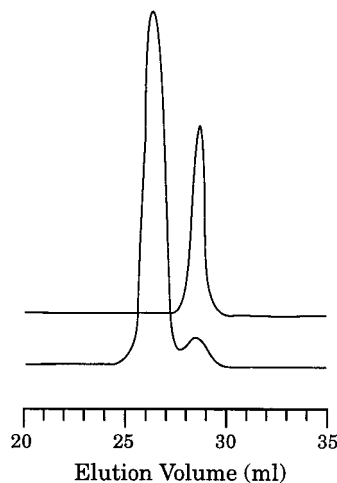


Figure 8 GPC chromatograms demonstrating linking efficiency greater than 97% for a three-arm star radial, styrene/butadiene block copolymer (120,000 g/mol): (lower trace) star block copolymer; (upper trace) precursor arm.

vacuum techniques. Figure 7 demonstrates the effectiveness of these techniques for the preparation of linear triblock copolymers synthesized by sequential addition. The GPC chromatograms show no significant difference between polymers obtained using classical techniques vs. the new modular techniques.

The use of mechanical stirring increased the percent solids that could be used in the polymerizations from less than 10% (for MWs greater than 50,000 g/mol, 5% was typical) to approximately 25%, with no increase in polymer polydispersity. This is an improvement over classical techniques that require magnetic stirring and where either higher molecular weight or concentration often lead to broadening of the molecular weight distribution. Thus, mechanical stirring allowed 325 g batch sizes with no sacrifice in polymer quality compared to 40–50 g using magnetic stirring.

Significant improvement in linking efficiencies was realized using the new linking ampule assembly. The metering valve allowed precise addition of the linking agent in quantities as small as 0.01 mL, leading to linking efficiencies as high as 97% (Fig. 8). In an earlier work, we reported the use of “microampules” of the linking agent, in conjunction with GPC to monitor the progress of linking. These experiences showed that the window of opportunity for linking the living arms lasted approximately 3 to 4 h after the first addition of

the linker; after this time little additional linking occurred. Unfortunately, much of this available linking time was consumed during GPC analysis of aliquots, which was necessary to identify the appropriate ampules to use. Thus, the earlier method was cumbersome and yielded linking efficiencies of only 83–85%. To attain greater linking efficiency, the new method involved a precisely controlled “blind” titration of the living arms (meaning that no GPC monitor was used), performed as quickly as possible and in stages, involving an initial large aliquot of linking agent followed by several smaller aliquots. The strategy was based on the fact that the linking reaction is irreversible. The negative consequences of adding a cumulative amount of the linker that is too great were lessened, provided that the stoichiometric excess was added only after the vast majority of the chains had already been irreversibly linked. Thus, additions were designed such that the first aliquot of the linker would be as close as possible to the theoretical quantity of the linker required, without being in excess, and subsequent additions of the linker would be made only after all previously added linkers had been consumed. (An excess linker on the first addition would have resulted in the formation of diarm polymers.) To insure that the first aliquot of the linker was not in excess, it contained only 90–95% of the theoretically required amount. The second and third additions of the linker contained 2–5% of the theoretical amount. The increase in linking efficiency resulted because the exactly required volume of coupling agent was always added, compared with the previously reported microampule technique, where the closest volume was chosen from a group of previously prepared microampules.

The use of spherical o-ring joints to join the reactor to the vacuum line and the ampules to the reactor provided a quick and effective way to construct polymerization reactors. These joints provided significant advantages over blown glass seals. They allowed each part of the reactor to be reusable, without additional glassblowing, and they reduced the chance of breakage during handling of the reactor. Additionally, the spherical union-type clamp allowed the joint to operate under positive pressure (10–15 psi), and also allowed for some misalignment in the component pieces. The presence of a flexible o-ring in the joint also imparted further flexibility to the joint.

Hydrogenation of the polybutadiene block was readily accomplished on a relatively large scale us-

ing H_2 and a nickel octoate/triethyl aluminum catalyst/cocatalyst system. The ratio of nickel octoate to triethyl aluminum was critical; if the ratio of nickel to aluminum was too high, the catalyst became unselective, resulting in hydrogenation of the outer oligostyrene blocks. Complete removal of olefinic unsaturations was observed by 1H -NMR.

CONCLUSIONS

While rigorous high-vacuum anionic polymerization techniques provide extremely narrow molecular weight distribution polymers in the absence of measurable termination, these techniques are often not practical in large-scale preparations. The use of a modular vacuum line and reactor system, as detailed herein, overcomes this limitation, without significant sacrifice in polymer quality.

The efficacy of these techniques was demonstrated through the synthesis of star-branched block copolymers. GPC chromatograms showed no significant differences in molecular weight distributions, compared to results obtained for the synthesis of similar polymers using classical techniques. In fact, narrow distributions were maintained under conditions of high solution viscosity caused by high molecular weight and/or polymer concentration.

An improved method for linking living polymer arms was also demonstrated. Although this procedure is inherently problematic, the use of a calibrated ampule capable of delivering a prescribed volume of the linker enabled significantly better linking efficiency. Careful titration of the living arms achieved better results than previously possible, even after polymer fractionation.

The replacement of blown glass seals with o-ring joints and union clamps, glass ampules with resealable ones, and microampules with variable volume ampules, reduced the time required to prepare for multi-step anionic syntheses. It also facilitated problematic procedures, such as linking, and provided reliable efficient mechanical agitation, without any change in molecular weight distributions. These techniques have been shown to be an effective alternative to classical anionic techniques, especially when solution viscosities are high.

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