

Notes

Manifold Assembly for the Convenient Polymerization of Ethylene Oxide and Butadiene

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Introduction

Working with gaseous compounds presents technical challenges not commonly encountered when using solutions and solids. Because of their volatility and potential toxicity, special equipment needs to be designed for safe handling of gaseous chemicals. Ethylene oxide (EO) and 1,3-butadiene (BD) are two examples of gaseous monomers at room temperature. Typically, these two gaseous monomers are handled in expensive high-pressure stainless steel reactors or under high vacuum using custom-made glassware.¹ Both monomers can be polymerized by “living” anionic polymerization to afford polymer with predictable molecular weight and low polydispersity (<1.1).^{1,2} Nevertheless, rigorous purification and quantitative measurement of molar amounts are required to make the polymerization truly controlled. Traditionally, anionic polymerization has been done using high-vacuum techniques.^{3,4} These techniques require extensive glass-blowing expertise and are time-consuming. Another limitation of high-vacuum technique is that only a few grams of sample can be synthesized per polymerization. To circumvent these issues, protocols based on Schlenk techniques have been used to perform living anionic polymerization.⁵ It is possible to synthesize tens of grams of polymer using Schlenk techniques in a single day.

Caution! Operating with 1,3-butadiene and ethylene oxide requires great care as they boil at -4.4 and 10.7 °C, respectively, and are toxic and flammable. Efficient thermostating at the temperatures reported is necessary when keeping or treating the monomers in glass containers or when it is transferred into the glass reactor. Failure to observe these precautions can lead to explosions and fire.

Ethylene oxide can be polymerized anionically to afford poly(ethylene oxide) (PEO) with controlled molecular weight and low polydispersity (below 1.1) and as a consequence has been widely used as a hydrophilic block in macromolecular amphiphiles because of its high polarity, ion transporting ability,^{6,7} and biocompatibility.⁸ 1,3-Butadiene is a major commodity chemical used in the manufacture of synthetic rubber and various plastics. Incorporation of poly(butadiene) into a material drastically modifies its mechanical properties. 1,3-Butadiene can be polymerized by radical, ionic, or metal-catalyzed polymerizations. Anionic polymerization enables excellent control over

molecular weight and polydispersity. A typical application of the anionic polymerization of 1,3-butadiene is found in the synthesis of styrene–butadiene–styrene rubber.⁹

Poly(butadiene-*b*-ethylene oxide) and more generally poly(alkane-*b*-ethylene oxide) have found applications in the biology arena. It has recently been shown that it is possible to self-assemble amphiphilic block copolymers into micelles which structurally mimic vesicles.¹⁰ These vesicles-forming block copolymers are potential candidates for entrapping biologically active molecules.¹¹ Also, vesicle-forming polymers offer fundamental insight into the natural design principles for biomembranes.¹²

As of today, only a few reports describing handling of gaseous monomers can be found.^{5,13} Herein, we describe the construction of a stainless steel manifold for the facile and safe handling and polymerization of ethylene oxide and 1,3-butadiene. Standard Schlenk glassware can be efficiently used as a reactor for the living polymerization of the two gaseous monomers, which makes the setup ideal for use in an academic laboratory. The gases are transferred by vacuum distillation and condensed at low temperature. Using this manifold, it is possible to run several experiments in a single day. The synthesis of a model poly(butadiene-*b*-ethylene oxide) by anionic polymerization will be described to illustrate a typical experimental protocol using the manifold.

Manifold Description. A representative diagram for the monomer tank farm is shown in Figure 1. A detailed listing of the quantity, part numbers, and manufacturers for all materials needed to construct the manifold can be found in the Supporting Information. The pressure regulators are connected to the gas cylinders of ethylene oxide, 1,3-butadiene, or nitrogen via flexible stainless steel tubing. A valve is placed after the regulator of each cylinder in order to shut off the supply line to the manifold and purge the regulator after replacing a cylinder. The nitrogen purification line is built identically to the butadiene purification line; columns of molecular sieves (3 Å), Selexsorb COS, and copper(II) oxide on alumina (oxygen scavenger) are placed in line to remove residual water, carbon dioxide, and oxygen impurities, respectively. The copper(II) oxide on alumina is reduced to copper(0) by passing a mixture of nitrogen/hydrogen 95/5% through the column at 200 °C until no further water is generated. Argon may be used as an inert gas instead of nitrogen. The purification column for the ethylene oxide line has only molecular sieves. It was observed that ethylene oxide will polymerize in contact with Selexorb and eventually clog the system. To maintain tank purity and laboratory safety, check valves are placed after the purification columns. Check valves with a relief pressure of 1/3 psig are used for the ethylene oxide and 1,3-butadiene supply while a check valve with a relief pressure of 10 psig is used for the nitrogen line. The lecture bottles of ethylene oxide and 1,3-butadiene are placed in a fume hood for safety purposes. All items have normal pipe thread (NPT) fittings and are connected with stainless steel tubing.

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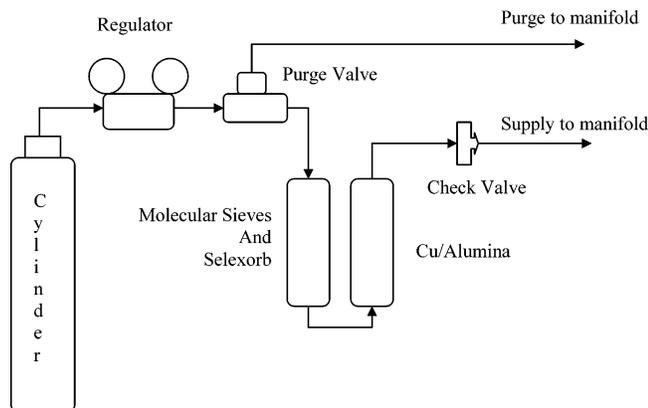


Figure 1. Tank farm schematic for 1,3-butadiene and nitrogen supply line. The purification column of the ethylene oxide line contains only molecular sieves.

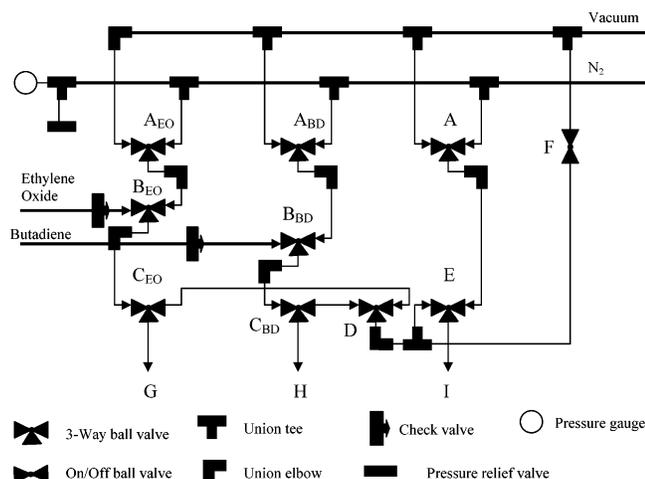


Figure 2. Manifold schematic. Ball valves and the pressure gauge are mounted in the faceplate with the plumbing behind the plate. Three-way ball valves are drawn such that the lower triangle represents the back of the valve.

A full diagram for the manifold is shown in Figure 2. The entire manifold is assembled on a 1.5 ft \times 2 ft \times 1/4 in. sheet of rolled aluminum in which the ball valves are mounted with the plumbing on the backside. Pressure gauges (0–15 psig) and pressure relief valves (set to 10 psi) are placed in the line with branch tees. Stainless steel tubing was bent, cut to length, and attached via Swagelok fittings. After construction, the manifold was tested for leaks by pressurizing with N₂ (50 psig) and monitoring for a pressure drop over a 24 h period. The assembled manifold was then mounted in a fume hood via lab feet bolted on the corners and the middle of the faceplate. Additionally, the manifold was stabilized with horizontal legs attached directly behind the plate (1 in. unistrut). Outlets G and H (Figure 2) have standard taper 14/20 ground glass joints connected to 1/4 in. glass tubing while outlet I has a standard taper 24/40 ground glass joint connected to 1/2 in. glass tubing. A glass-to-metal transition for the gas outlets G, H, and I were made by using either an Ultra-Torr Swagelok tube fitting union or a stainless steel union (1/4 in. for outlets G and H). In the latter case, stainless steel ferrules were replaced by Teflon ferrules to ensure a leak-free glass-to-metal transition. Outlet I was made with a reducing union (1/2 to 1/4 in.) in conjunction with 1/2 in. Teflon ferrule.

The vacuum line was custom-made, but any commercial vacuum manifold with Teflon plugs would work.⁵ A single-stage oil diffusion pump is used between the vacuum manifold

and the mechanical pump for improved vacuum. Two vacuum traps, in series, prevent the diffusion pump oil and the mechanical pump oil from being contaminated. The working vacuum is found to be between 5 and 10 mTorr. One outlet of the vacuum manifold is connected to the stainless steel manifold via heavy wall rubber tubing. Another outlet of the vacuum manifold is used to purge the ethylene oxide and 1,3-butadiene lines with nitrogen as described in the Experimental Procedure section.

Experimental Procedures

Materials. *sec*-Butyllithium (1.4 M), *n*-butyllithium (1.6 M), butadiene (99+%), ethylene oxide (99.5+%), styrene (99+%), tetrahydrofuran (THF, anhydrous, 99.9%), *N,N*-dimethylacetamide (99+%, spectrophotometric grade), and potassium (chunks in mineral oil, 98%) were purchased from Aldrich and used as received. Triphenylmethane was purchased from Aldrich and sublimed (103 °C, 6 mTorr) prior to use. *sec*-Butyllithium was titrated by the Gilman double titration method.¹⁴ Benzene (99+%) and chloroform were purchased from Fisher. Benzene was first stirred over sulfuric acid (100 mL of acid for 1 L of solvent) for 24 h, distilled over calcium hydride, and stored in a Schlenk flask containing a solution of *n*-butyllithium/styrene (5 mL of *n*-butyllithium and 0.5 mL of styrene per liter of solvent). Tetrahydrofuran was purified by distillation from a sodium/benzophenone mixture.

Triethylpotassium solution was prepared by mixing triphenylmethane (8 g, 32.7 mmol) and potassium (3 g, 76.73 mmol) in 100 mL of THF. After stirring overnight, the deep-red solution was filtered to remove excess potassium metal, and stored under an inert atmosphere. The solution can be stored in an air-free flask for months without degradation.

Instrumentation. Gel permeation chromatography (GPC) measurements of PBD-OH were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 pump with a K-2301 refractive index detector and K-2600 UV detector and a column bank consisting of two Polymer Labs PLGel Mixed D columns and one PLGel 50 Å column (1.5 \times 30 cm) at 35 °C. Molecular weights are reported relative to polystyrene standards (Polymer Labs, Inc.). GPC measurements of PBD-PEO were performed in a mixture of THF and *N,N*-dimethylacetamide (DMAc) (90:10 by vol) at 1 mL/min.¹⁵ A pump (HP series 1050) with a refractive index detector (HP 1047A) and two Polymer Labs ResiPore 3 μ m (300 \times 7.5 mm) columns were used. Molecular weights are reported relative to PEO standards (Polymer Labs, Inc.). ¹H NMR spectra were performed in CDCl₃ at room temperature on a Bruker 300 MHz.

Results and Discussion

The synthesis of a poly(butadiene-*b*-ethylene oxide) diblock copolymer by anionic polymerization is described to illustrate a typical experimental procedure using the manifold (Scheme 1). The results obtained are summarized in Table 1. The descriptions of the outlets and the various valves are referred to by a letter designation as shown in Figure 2. The manifold enables purification and measurement of a known amount of gaseous monomer (outlets G and H). Then, the desired amount of monomer is transferred to the reaction flask (outlet I).

Synthesis of Hydroxy-Terminated Polybutadiene by Anionic Polymerization. The manifold is first evacuated by opening valves A, A_{EO}, A_{BD}, B_{EO}, and B_{BD} to vacuum and opening valve F. Valves C_{EO}, C_{BD}, and E are kept closed. Valve D allows switching from one gas to the other and should be open to the monomer used first, 1,3-butadiene in this case. Even after passing through the purification columns, ethylene oxide and 1,3-butadiene are not pure enough to perform anionic polymerization. Additional purification steps are required. In a flame-dried 50 mL Schlenk flask, 3 mL of *n*-butyllithium (1.6

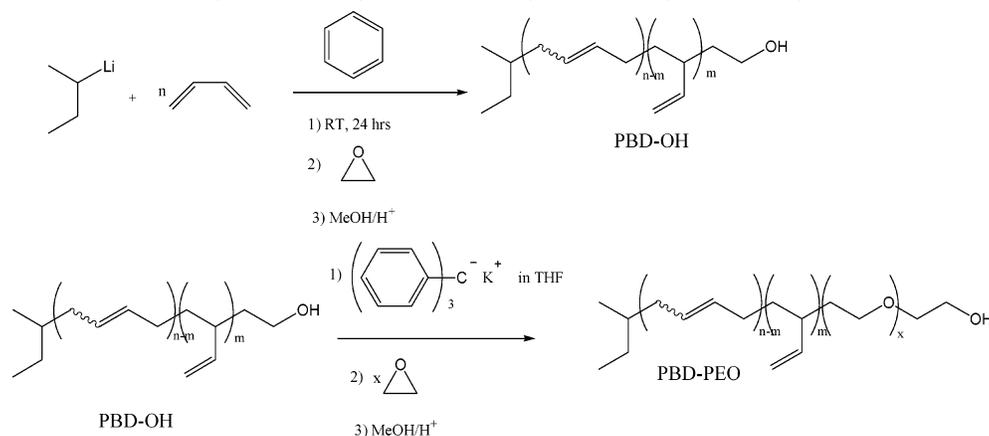
Scheme 1. Synthesis of Poly(butadiene-*b*-ethylene oxide) by Anionic Polymerization

Table 1. Summary of the Results of the Polymerization

entry	amount of monomer (vol at -78 °C, mol)	amount of initiator (or macroinitiator) (vol or mass, mol)	$M_{n,theo}$ (calcd, g/mol)	$M_{n,obs}^d$ (PDI)
PBD polymerization	butadiene (15 mL, 0.205 mol)	<i>sec</i> -butyllithium (0.92 mL, 1.29 mmol)	8596	8660 (1.03)
PEO polymerization	ethylene oxide (3.4 mL, 77.2 mmol)	PBD-OH (4 g, 0.462 mmol of OH)	7360	7260 (1.08)

^d For polybutadiene, $M_{n,obs}$ (number-average molecular weight observed) was measured by THF GPC vs polystyrene standard. A coefficient of 1.86 was applied to calculate the real polybutadiene molecular weight (Mark-Houwink parameters). The observed molecular weight for PEO was calculated from ¹H NMR.

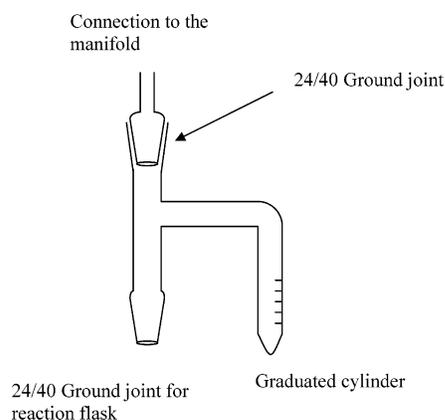


Figure 3. Graduated cylinder connected to outlet I.

M) is added via syringe under an inert atmosphere. Subsequently, the flask is attached to outlet H and the hexanes are removed under vacuum by opening valve C_{BD}. Then, valve A_{BD} is closed and valve B_{BD} is opened to the 1,3-butadiene line. The evacuated Schlenk flask attached to outlet H is cooled to -78 °C (acetone/dry ice mixture), and ~15 mL of 1,3-butadiene is condensed. This is then stirred at -10 °C (salt/ice mixture) for 1 h. Purified benzene (200 mL) is vacuum-distilled into a flame-dried Schlenk flask containing a glass stir bar and 0.92 mL of *sec*-BuLi (1.29 mmol). This Schlenk flask is connected to outlet I and is used as the reaction flask. Outlet I bears a sidearm with a graduated cylinder attached as depicted in Figure 3. Once the reaction flask is connected to outlet I, valve E is opened to vacuum and the sidearm is flame-dried while the reaction flask is kept closed. The density of butadiene is 0.74 g/mL at -78 °C.¹⁶ The purified 1,3-butadiene (15 mL, 0.205 mol) is then vacuum transferred into the sidearm cooled to -78 °C by closing valve A and valve F and turning valve C_{BD} the opposite way to connect the purified 1,3-butadiene to valve D. Valve E is opened to valve D. Finally, valve A, valve E, and the Schlenk flask containing the initiator are opened to nitrogen. The reactor is left under an inert atmosphere overnight. The 1,3-butadiene distills slowly into the reaction flask and is

consumed by the living polymer chain end. The pressure drop can be followed with the in-line pressure gauge.

After 24 h, the reaction flask is closed and the sidearm is evacuated again by opening valve A and valve E to vacuum. Ethylene oxide is also purified before being added to the reactor. Valve F is opened and then valve E is opened to ethylene oxide. In a flame-dried 25 mL Schlenk flask, 1 mL of *n*-butyllithium (1.6 M) was added by syringe, connected to outlet G, and the hexane was distilled off by opening valves A_{EO}, B_{EO}, and C_{EO} to the vacuum. Ethylene oxide (2 mL, 0.045 mol) is condensed in the Schlenk flask at -78 °C by opening valve B_{EO} to the ethylene oxide line. Ethylene oxide is stirred over *n*-BuLi for 1 h at 0 °C, and then 1 mL of ethylene oxide (0.027 mol) is subsequently condensed to a graduated cylinder connected to outlet I by opening valve C_{EO} to valve D and valve E to valve D. The ethylene oxide is subjected to three freeze-pump-thaw cycles, and valves A E and the reaction flask are opened to nitrogen. After 1 h, the polymer (PBD-OLi) was precipitated in acidic methanol. A number-average molecular weight (M_n) of 16 110 g/mol was obtained for the resultant PBD-OH by GPC using a THF mobile phase. A correction according to the Mark-Houwink equation resulted in a M_n of 8660 g/mol with a polydispersity index of 1.03.

Synthesis of Poly(butadiene-*b*-ethylene oxide) (PBD-PEO) by Anionic Polymerization. PBD-OH (4 g, 0.115 mmol) was first dried overnight in a vacuum oven at room temperature. Then, three consecutive azeotropic distillations from dried benzene at room temperature under reduced pressure (10 mTorr) were performed, and the polymer was left overnight under dynamic vacuum. Subsequently, 100 mL of tetrahydrofuran was distilled into the reaction flask. The hydroxyl group of PBD-OH was titrated with tritylpotassium to a 1:0.9 (hydroxyl group: tritylpotassium) ratio. Titrating to the equivalent point is not necessary, as the proton exchange rate between the hydroxyl end group of the polymer and the potassium alkoxide species generated by deprotonation proceeds at a much faster rate than the polymerization of ethylene oxide.^{17,18}

The reaction flask containing PBD-OK is connected to outlet I, and the manifold is evacuated by opening valves A_{EO}, A, F,

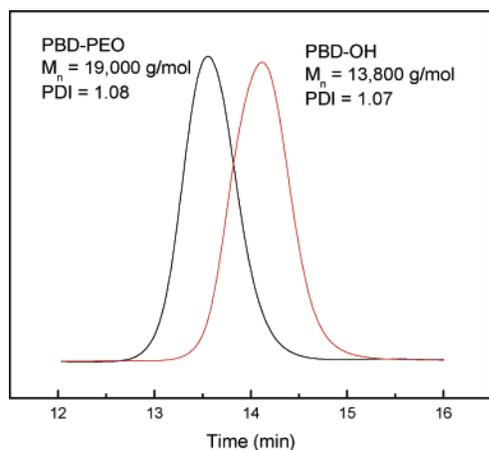


Figure 4. Overlays of PBD-OH and PBD-PEO traces obtained by GPC using a mixed THF/DMAc solvent phase.

B_{EO} , and E to vacuum. Valve D is opened to the ethylene oxide line. The same purification and transfer protocol that was used for the end-capping of the polybutadiene anion with ethylene oxide applies here. Ethylene oxide (3.4 mL, 77.2 mmol) was condensed in the graduated cylinder connected to outlet I. At this stage, ethylene oxide is slowly warmed to room temperature, enabling transfer to the reaction flask (valve A is open to nitrogen and the reaction flask is also open). Alternatively, it is possible to condense ethylene oxide directly in the reaction flask by cooling the THF solution in the reactor to 0 °C. Once all the monomer has been condensed in the THF solution, the flask can be closed and disconnected from the line. The reaction flask was left for 3 days with stirring at room temperature. The living polymer was terminated by adding one drop of acidic methanol into the THF solution. To purify the resulting PBD-PEO, flash chromatography with silica gel (50 g) using chloroform as a solvent was used. The block copolymer adsorbs to the silica gel because of the PEO block. After washing the starting material away from the final polymer with 300 mL of chloroform, the polymer is recovered by flushing the silica gel with a 9:1 chloroform:methanol mixture. The solvent is removed and the polymer dried overnight. Analysis by GPC using the solvent mixture THF:dimethylacetamide (90:10 v:v) gave $M_n = 19\,000$ g/mol and $PDI = 1.08$. The M_n of PEO calculated from the 1H NMR integrations was found to be equal to 7260 g/mol. An overlay of PBD-OH and PBD-PEO molecular weight traces obtained with the mixed solvent THF/DMAc GPC is shown in Figure 4.

Cleaning Procedure. It is important to maintain the system clean and free of impurities for the best results. After a monomer has been condensed and reacted, the corresponding purification columns are evacuated and kept under vacuum. For 1,3-butadiene, a Schlenk tube with a sidearm is connected to outlet H. Valves B_{BD} and C_{BD} are opened to the 1,3-butadiene purification train while vacuum is being pulled from the sidearm of the Schlenk flask. A similar procedure is repeated for ethylene oxide.

In summary, we have developed a convenient and safe way to handle and polymerize 1,3-butadiene and ethylene oxide. Using a stainless steel manifold, it is possible to perform several reactions a day on a multigram scale. The gaseous monomers are prepurified by passing through purification columns. It is possible to condense these gases at low temperature, enabling precise volume measurement of the monomers prior to addition into the reaction flask. Synthesis of a model poly(butadiene-*b*-ethylene oxide) was given as an example to illustrate the use

of the manifold. It is possible to run polymerizations on a scale of several tens of grams by using the appropriate flasks and solvent quantities. The molecular characterization of the final diblock copolymer is in agreement with results obtained by living anionic polymerization, thus demonstrating the utility of Schlenk techniques to successfully perform anionic polymerizations.

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Supporting Information Available: Parts lists for the manifold. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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