

Schlenk Techniques for Anionic Polymerization

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Abstract Anionic polymerization-high vacuum techniques (HVTs) are doubtlessly the most prominent and reliable experimental tools to prepare polymer samples with well-defined and, in many cases, complex macromolecular architectures. Due to the high demands for time and skilled technical personnel, HVTs are currently used in only a few research laboratories worldwide. Instead, most researchers in this field are attracted to more facile Schlenk techniques. The basic principle of this technique followed in all laboratories is substantially the same, i.e. the use of alternate vacuum and inert gas atmosphere in glass apparatus for the purification/charging of monomer, solvents, additives, and for the manipulation of air-sensitive compounds such as alkyl metal initiators, organometallic or organic catalysts. However, it is executed quite differently in each research group in terms of the structure of Schlenk apparatus (manifolds, connections, purification/storage flasks, reactors, etc.), the use of small supplementary devices (soft tubing, cannulas, stopcocks, etc.) and experimental procedures. The operational methods are partly purpose-oriented while also featured by a high flexibility, which makes it impossible to describe in detail each specific one. In this chapter we will briefly exemplify the application of Schlenk techniques for anionic polymerization by describing the performance of a few experiments from our own work.

Keywords Schlenk techniques • Vacuum gas manifold • Anionic polymerization • Living polymerization

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1 Introduction

Wilhelm Johann Schlenk (22 March 1879 – 29 April 1943) was a German organic chemist who discovered organolithium compounds around 1917 [1]. He was born and studied chemistry in Munich and later in 1919 he succeeded Hermann Emil Fischer at the University of Berlin. He also discovered (together with his son) that organo-magnesium halides are capable of participating in a complex chemical equilibrium, now known as “Schlenk equilibrium” [2]. The name Wilhelm Schlenk is familiar to many chemists also because of the techniques he developed and the widespread use of the “Schlenk flask” to handle air-sensitive compounds (Fig. 1) [3]. He also designed a double manifold known as the “Schlenk line” which incorporates an inert gas line and a vacuum system joined by three-way glass taps that allows the user to switch between gas and vacuum for the manipulation of air-sensitive substances.

Although anionic polymerization-high vacuum techniques (HVTs) [4] are the most reliable experimental tools for preparing polymer samples with well-defined and complex macromolecular architectures [5–11], they require mastery of glass-blowing and highly demanding experimental techniques in order to make and utilize specially designed reactors. Due to time consuming nature of HVTs and the requirement for skilled technical personnel, most researchers in the anionic polymerization field employ the more facile “Schlenk technique”. This technique is attractive due to its convenience and acceptable performance for many applications.

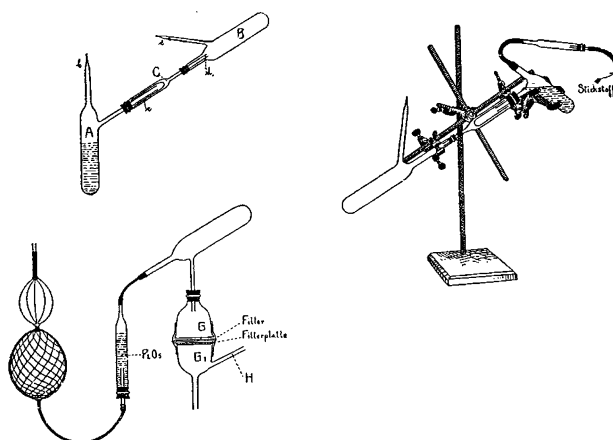


Fig. 1 Examples of Schlenk's glassware from his paper (from reference [3])

2 Different Component of Schlenk Techniques

To work with Schlenk techniques, the basic requirements are a good oil vacuum pump (secured with a liquid nitrogen trap), inert gas with an associated purification system, different types of Schlenk flasks, and a Schlenk line which is a dual manifold with several ports (Fig. 2).

2.1 Vacuum Pump

One manifold of the Schlenk line is connected to an oil vacuum pump with a capacity of 10^{-2} – 10^{-4} mbar through a liquid nitrogen or dry ice/acetone cold trap, used to condense any volatile substances such as solvent vapors or gaseous reaction products and prevent contamination of the vacuum pump oil (Fig. 2).

2.2 Inert Gases-Nitrogen (N_2) or Argon (Ar)

The inert gas line is vented through an oil bubbler and/or purification system before being connected to the Schlenk line. Depending upon the reaction sensitivity, UHP (Ultra High Purity) grade nitrogen (N_2) or argon (Ar) is used with or without further purification. There are different methods for purification of inert gases to remove moisture which is deleterious to sensitive compounds and living polymers. In some cases inert gases are purified by passing through a column containing molecular

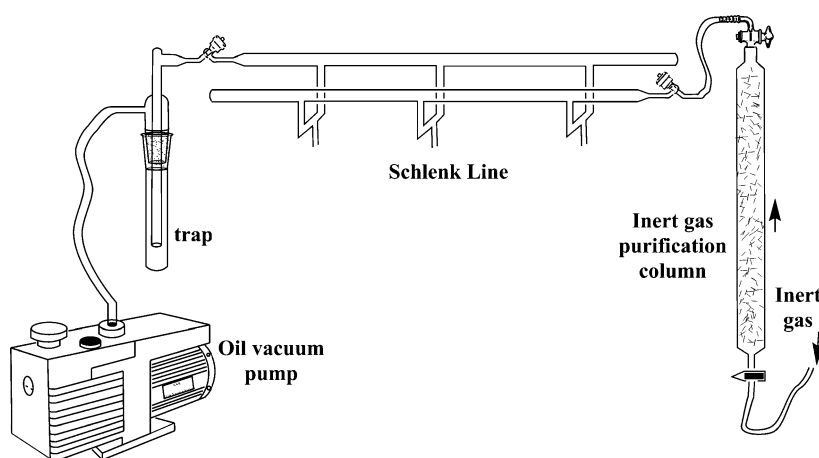


Fig. 2 General representation of a Schlenk line

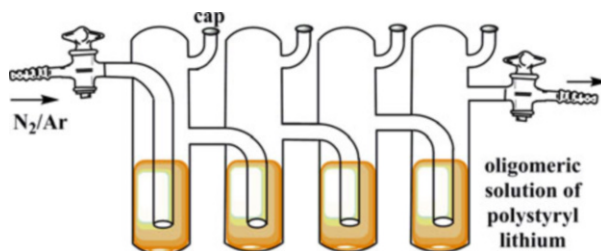


Fig. 3 Use of bubblers for purification of inert gases

sieves or silica gel with a color indicator (Fig. 2). This purified inert gas is then fed to the manifold through rubber tubing for use in reactions.

In another method, commercial nitrogen gas containing traces of moisture and oxygen is passed through columns (2 or 3) containing activated 4 Å molecular sieves and another (2 or 3) columns containing activated copper (Cu) deposited on kieselguhr kept at ~ 200 °C. This purified N₂ is then again passed through a bubbler containing a dark red solution of oligomers of poly(styryl) lithium in toluene (Fig. 3). The moisture in N₂, if present, quenches the living oligomers while passing through this bubbler, rendering the gas free of moisture. On regular basis, activation of molecular sieves and Cu columns is performed. Molecular sieves are activated by heating at ~ 200 °C under vacuum for 6 h and cooled under nitrogen, whereas Cu columns are activated by passing hydrogen (H₂) gas at 180 °C for 7–8 h and the water formed by the reaction of H₂ and Copper(II) oxide or cupric oxide (CuO) is removed under vacuum. There is a visual indication for determining the appropriate time for reactivation of Cu columns. Before activation the copper catalyst looks pale green in color, but it turns to dark brown after activation.

2.3 Schlenk Line

The Schlenk line, also called a vacuum gas manifold, is a double manifold incorporating a vacuum system and a gas line joined by double oblique taps that allow the user to switch between vacuum and gas for the manipulation of living polymerization systems or air-sensitive compounds. One manifold is connected to a source of purified inert gas, while the other is connected to an oil vacuum pump secured with liquid nitrogen trap. Special three-way glass stopcocks or Teflon taps are used for these ports on manifolds. They allow for vacuum or inert gas to be selected without the need for placing the sample on a separate line.

Different types of Schlenk lines can be designed as per user's requirements. Ports can be made of glass or high vacuum "o" ring stopcocks with only ground joints or only hoses (rubber tubing) or both (called a hybrid system), as shown in Fig. 4a–c.

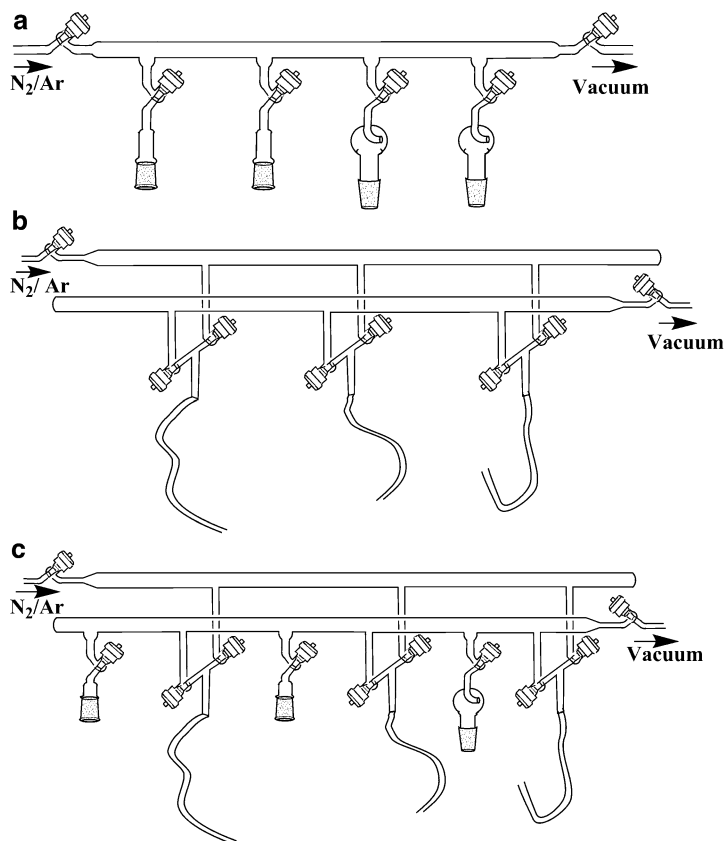


Fig. 4 (a) Schlenk line with ground joints. (b) Schlenk line with rubber tubes. (c) Schlenk line with ground joint and rubber tubes

2.4 Schlenk Flasks and Tubes

2.4.1 Specially Designed Schlenk Flasks and Storage Ampoules Using Septum Adaptors

For purification and storage of monomers, and solvents, as well as to perform polymerization, there are different types of Schlenk flasks. Initially these flasks were specially designed using three-way stopcocks with rubber septa. Addition of reagents and removal of aliquots using syringe techniques is possible through the septa. Using same three-way stopcocks, small and big storage ampoules are also made, as shown in Fig. 5. These types of Schlenk flasks can be connected to the Schlenk line through rubber tubing to have either gas or vacuum in it. Addition of

Fig. 5 Schlenk round bottom (RB) flask and ampoules

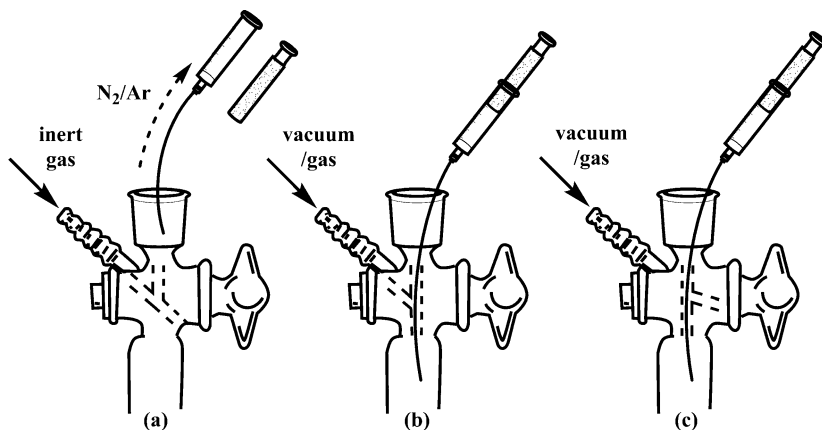
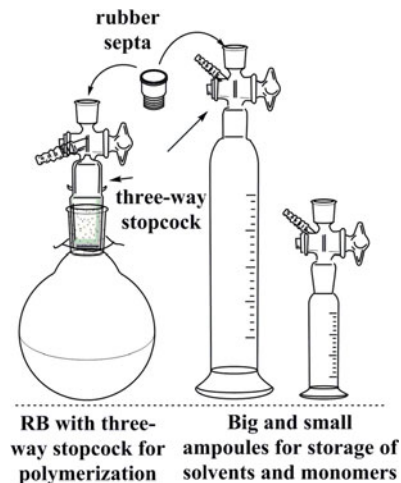


Fig. 6 Syringe flushes with inert gas (a) and addition of reagents (or removal of aliquots) in presence (b) or absence (c) of vacuum/gas

reagents by syringe through septa, in presence or absence of gas/vacuum, can be controlled by three-way stopcock positions (Fig. 6).

2.4.2 Commercially Available Different Types of Schlenk Flasks and Tubes

Later, reaction vessels with a Teflon tap/stopcock for the addition and removal of gases were made available commercially, and are known as Schlenk flasks (Fig. 7a) or Schlenk tubes (Fig. 7b) [12].

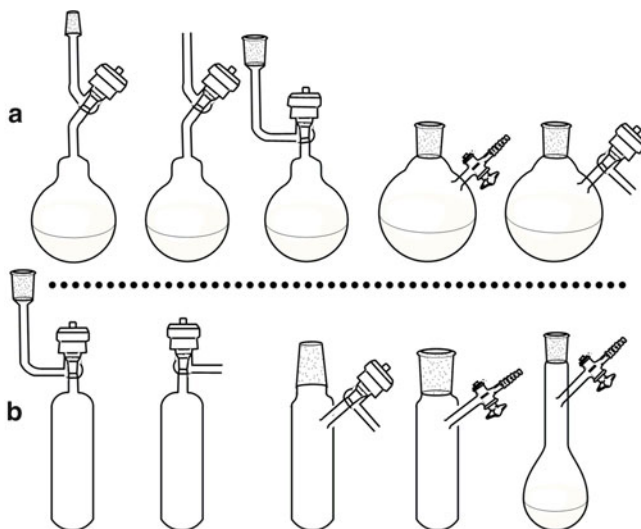


Fig. 7 Schlenk flasks (a) and tubes (b)

3 Procedures

3.1 Degassing

In anionic polymerization, in order to avoid termination of living anions from air (oxygen, carbon dioxide, moisture) every reagent needs to be purified before use. A degassing procedure is the first step of purification which helps to remove oxygen and other dissolved gasses from a liquid. The Schlenk flask containing the liquid is connected to the Schlenk line directly through a ground joint or via rubber tubing (Fig. 8). The stopcock (glass or Teflon) is opened two or three times to vacuum for a few seconds until bubbles are produced. With the stopcock closed, the liquid is frozen using a Dewar flask containing liquid nitrogen, and then the stopcock is opened to vacuum for a sufficient time so that the entire system can be pumped down. After some time the stopcock is closed and the liquid is thawed. This freeze-degas-thaw cycle is repeated two or three times to adequately remove dissolved gases.

3.2 Distillation

3.2.1 Simple Distillation of Solvents and Monomers

Under static vacuum, distillation of liquids (solvents, monomers, etc.) becomes simple by slightly heating the source flask and freezing the receiving flask (Fig. 9).

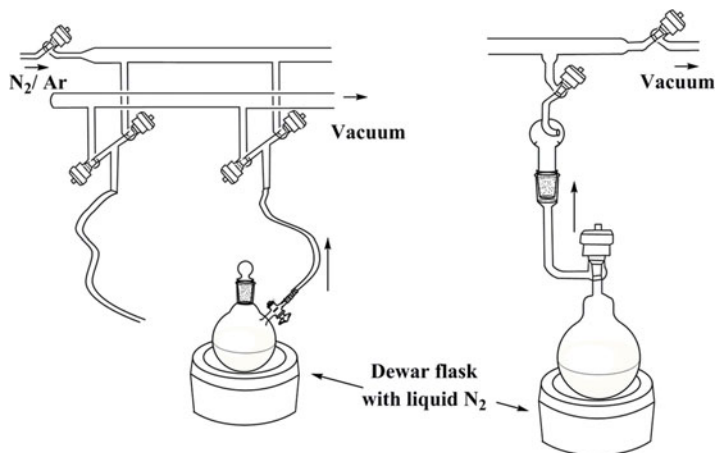
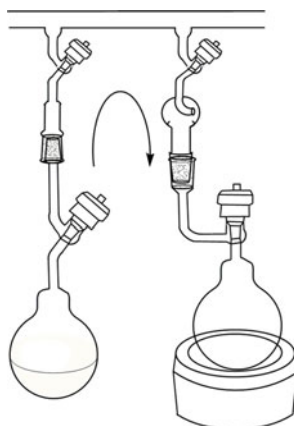


Fig. 8 Degassing of liquids

Fig. 9 Simple vacuum distillation of solvent or monomer

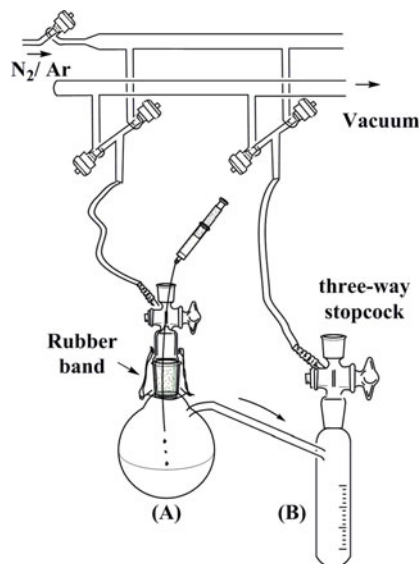


Before the beginning of the distillation the liquid is degassed two or three times. After completion of the distillation process, the receiving flask is opened to dynamic vacuum and the frozen liquid is degassed again. At the end of degassing the stopcock is closed and the liquid is thawed and stirred.

3.2.2 Short Path Distillation

On a Schlenk line having rubber tubing, high boiling liquids (usually monomers) are distilled using a specially designed glass apparatus, as shown in Fig. 10. From two sides (A and B) the apparatus is connected to the Schlenk line through rubber tubing and flame dried under vacuum. Then the liquid to be distilled is transferred

Fig. 10 Short-path distillation apparatus for high-boiling liquids



into flask (A) (with some purifying reagent, if necessary) using a dry syringe (after flushing with inert gas; Fig. 6a), degassed two times, and then distilled into a calibrated ampoule (B). Source flask (A) is round bottom flask fitted with a three-way stopcock and secured with rubber bands under inert gas pressure. After distillation, the required amount of purified liquid is taken by syringe from ampoule (B) in presence of inert gas. Under inert gas pressure, after closing both of the stopcocks, the apparatus is removed from the Schlenk line by detaching the rubber tubing. The remaining amount of purified reagent is stored until further use by keeping entire apparatus in the refrigerator.

3.3 Purification

In this section the purification of the most commonly used solvents and monomers for anionic polymerization is described.

3.3.1 Solvents

Toluene is fractionally distilled over CaH_2 (freshly ground chunks is recommended, rather than powdered CaH_2 which is rapidly deactivated on storage) and stored over hot activated molecular sieves. The fractionated solvent is refluxed over K or Na metal and then distilled. Benzophenone is added to show the distinct blue color as an indication of dryness and purity. Alternatively, toluene distilled over CaH_2 is

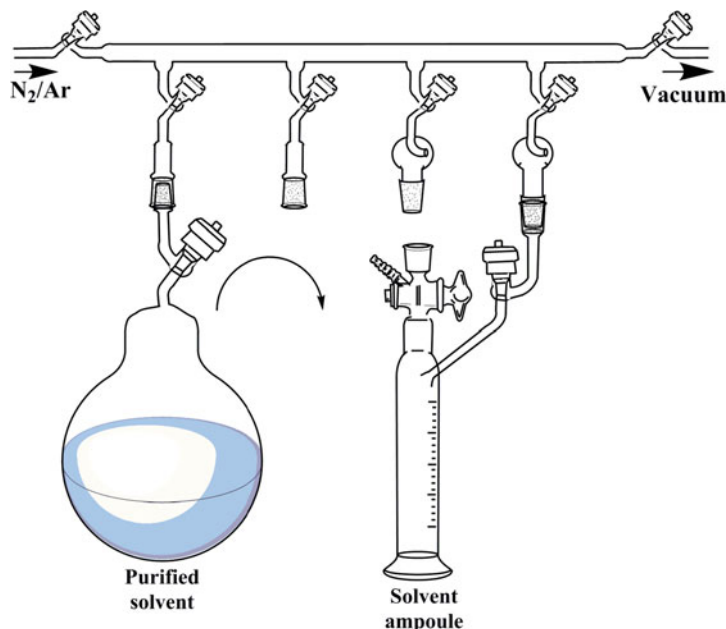


Fig. 11 Distillation of solvent to ampoule

stored (after proper degassing) in solvent storage flasks containing Na/K (1/3) alloy under high vacuum and kept continuously stirred. The required amount of solvent is distilled out into specially designed Schlenk ampoules (as shown in Fig. 11) just before the polymerization reactions. This type of solvent ampoule is used on all types of Schlenk lines.

Alternatively, toluene is stirred over CaH_2 overnight and distilled in a reservoir containing *n*-butyllithium and 1,1-diphenyl-ethylene (DPE) as an indicator of dryness (by showing a distinct red color). It is then directly distilled into a reactor before polymerization. Alkanes such as *n*-hexane, cyclohexane, heptane etc. are purified similarly with CaH_2 and then *n*-BuLi/DPE

Tetrahydrofuran (THF) is left to stir with CaH_2 overnight to react with moisture and then distilled. It is then refluxed over small pieces of sodium metal and distilled. The solvent is then degassed and distilled in a flask containing a Na/K (1/3) alloy. After stirring for some time it gives the blue color, which indicates that the solvent is free from impurities.

Benzene is also purified with CaH_2 and stored over mixture of *n*-BuLi and styrene or *n*-BuLi and DPE so as to give orange or red color, respectively, which indicates the purity of solvent.

3.3.2 Monomers

In this section the purification of the most commonly used monomers in anionic polymerization is discussed.

Styrene and other styrenic monomers [*tert*-butylstyrene, *p*-methylstyrene, α -methylstyrene, etc.] are purified using the same method. The monomer is dried overnight with freshly ground CaH_2 and distilled into a flask containing dibutylmagnesium (DBMg) [1 M solution in heptane]. DBMg, having one *n*-butyl and one *sec*-butyl group, shows higher solubility in hydrocarbon solvents. The monomer is allowed to stand overnight with continuous stirring and distilled in a Schlenk flask. The purified monomer develops a light yellow-green color indicative of high purity.

Isoprene monomer is dried over finely ground CaH_2 overnight followed by distillation into a flask containing *n*-BuLi where it remains with continuous stirring for 20–30 min at 0 °C (note that it is critical to use the less efficient initiator, *n*-BuLi not *sec*-BuLi, and keep the monomer at 0 °C for not more than 30 min in order to avoid potential exothermic polymerization of the isoprene). It is then further distilled in to a Schlenk flask and stored at low temperature.

Butadiene and ethylene oxide are gaseous monomers at room temperature. First the monomer is condensed into a round bottom flask containing CaH_2 at –78 °C (dry ice/isopropanol bath), stirred for 30 min at –10 °C (ice/salt bath). Then it is distilled into another flask with *n*-BuLi, stirred there for 20–30 min at –10 °C. With butadiene it is critical, as with isoprene (see above), to use only the *n*-BuLi isomer and keep the temperature low and duration to <30 min in order to avoid a violent exotherm. Finally the monomer is distilled into a calibrated Schlenk tube. In a few cases the monomer is diluted with purified solvent in a ratio of [monomer]/[solvent] lower than 0.2, which reduced the vapor pressure for storage.

Commercially available *acrylates and methacrylates* monomers may contain considerable amounts of residual alcoholic impurities. These monomers are first dried over CaH_2 overnight to remove traces of water, but CaH_2 does not react appreciably with alcohols. Therefore before polymerization these monomers are purified with trioctylaluminum (TOA). The treatment with TOA removes the residual alcohol present in alkyl(meth)acrylates, and the excess alkylaluminum then forms a complex with the carbonyl groups of (meth)acrylate monomer. The alkylaluminum-monomer complex has a characteristic bright yellow color indicating the end point of impurity titration. Immediate distillation under high vacuum affords extremely pure (meth)acrylate monomer.

Solid monomer such as *hexamethylcyclotrisiloxane* (*D3*) is purified by dissolution in a solvent like toluene or benzene. After 1 h stirring, the azeotropic mixture of solvent and moisture is removed on the vacuum line. This step is repeated two or three times in order to obtain pure moisture-free solid monomer.

1,1-Diphenylethylene (*DPE*) is stirred over CaH_2 for 5–6 h and then distilled using a short path distillation apparatus in vacuum. It is then stored in an ampoule under nitrogen or argon. Alternatively, *DPE* is distilled over a small amount of *n*-

BuLi (1.6 M solution in *n*-hexane). The desired amount of DPE is transferred into a flame dried distillation unit by syringe, and *n*-BuLi is added drop-wise to the DPE under stirring at room temperature. *n*-BuLi reacts with traces of impurities and residual benzophenone in DPE. After reacting with impurities, the excess of *n*-BuLi then adds to the double bond of DPE to form the 1,1-diphenylhexyllithium (DPHLi) anion. This DPHLi is red in color, which indicates the end point of impurity titration. The excess DPE is distilled over DPHLi under dynamic vacuum at 120 °C.

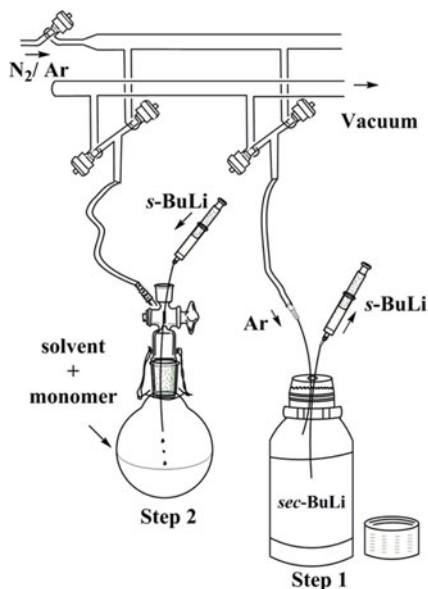
Despite the fact that DPE cannot homopolymerize (living terminator), it is included in this section due to double bond.

3.4 Initiators Synthesis

3.4.1 Commercially Available

Many initiators are used in anionic polymerization such as benzyl lithium (BzLi), potassium alkoxides, trityl potassium and *n*- or *sec*-butyl lithium (*n*- or *sec*-BuLi). *sec*-BuLi, available commercially, is the most commonly used initiator for anionic polymerization. Under inert atmosphere, a known amount of initiator solution is transferred into the polymerization apparatus by syringe (as shown in Fig. 12) and allowed to polymerize a known amount of styrene. The molecular weight of formed polystyrene is determined by size exclusion chromatography [SEC; calibrated with polystyrene (PS) standards] and the initiator concentration is back calculated using

Fig. 12 Use of commercial grade *sec*-BuLi as an initiator for polymerization



the relationship: moles of initiator = g of styrene/ M_n (PS). Once the concentration is known, it is used for other polymerizations.

3.4.2 Triphenylmethylpotassium (TPMK) or Trityl potassium (Ph_3CK) or Potassiumtriphenyl Methanide

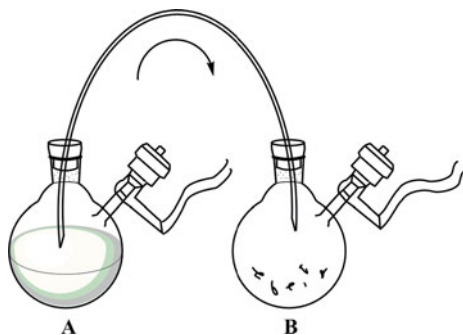
It is prepared in the laboratory from triphenylmethane and potassium metal in THF as described below.

- Triphenylmethane is dried under vacuum for 2 days at room temperature, and purified THF is added into the same flask under inert atmosphere.
- At room temperature, the above THF solution of triphenylmethane (A) is transferred through a cannula (hollow steel needle with two sharp ends) into another flask (B) containing a potassium mirror, as shown in Fig. 13. If the pressure in the flask (A) is greater than flask (B), the solution will be pushed from (A) to (B). This pressure difference is achieved by placing flask (A) under inert gas pressure and partially evacuating flask (B).
- Red color indicates the formation of triphenylpotassium.
- The reaction is kept stirring under vacuum for 6–7 h.
- The excess metal is filtered off, and the concentration of the TPMK solution is determined by double titration.

3.4.3 1,1'-Diphenylhexyllithium (DPHLi)

It is prepared from DPE and *n*-BuLi. A known amount of purified DPE in dry THF is added into the equimolar amount of *n*-BuLi at 40 °C under inert atmosphere. The solution immediately turns red, indicating the formation of DPHLi. The reaction mixture is slowly cooled to room temperature, stirred for 1 h and stored under inert gas at low temperature.

Fig. 13 Synthesis of TPMK initiator



3.5 Examples of Polymerization

3.5.1 (Meth)acrylate Esters

Anionic polymerizations of alkyl(meth)acrylate [methyl methacrylate (MMA), *n*- or *tert*-butylacrylate (*n*-BA or *tert*-BA), Methacrylate (MA)] using DPHLi or BzLi are performed by adding neat monomer, or the solution of the monomer, into the initiator solution at the desired temperature.

An experimental procedure for the anionic polymerization of MMA using DPHLi as initiator is given below:

- To a flame-dried flask with a septum adapter, the required amount of dry solvent (toluene or THF) is transferred by a cannula (double-tipped stainless steel needle) under inert atmosphere (Fig. 14).
- The DPHLi initiator solution is added drop-wise by a syringe until a red color remained. After quenching all impurities, the calculated amount of initiator for polymerization is added.
- The temperature of the flask is brought to $-78\text{ }^{\circ}\text{C}$ using a dry ice (solid CO_2)-acetone (or dry ice/isopropyl alcohol) cold bath.
- The purified monomer is added to the cold initiator solution and allowed to polymerize for 15–20 min.
- The reaction is terminated with degassed methanol, and the polymer is precipitated into *n*-hexane or methanol.

3.5.2 Synthesis of Polystyrene-*b*-Polyisoprene Block Copolymer (PS-*b*-PI)

- By following a similar experimental procedure, as discussed above, styrene monomer (liquid) is polymerized using commercial grade *sec*-BuLi in benzene.

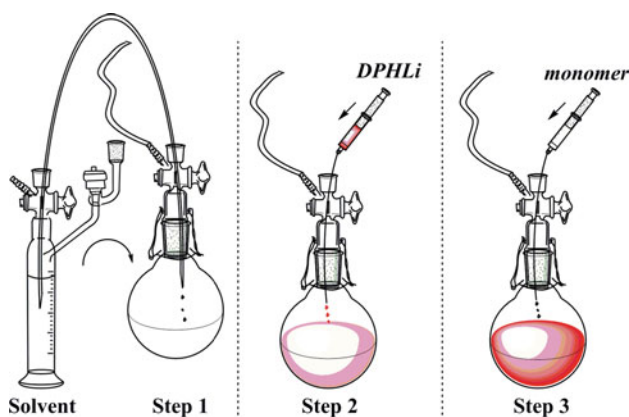


Fig. 14 Polymerization of (meth)acrylate liquid monomer

- After complete polymerization, a small aliquot is taken out by syringe for molecular weight determination.
- Pre-purified isoprene (liquid) monomer is added to the same flask containing living polystyryllithium to form PS-*b*-PI copolymer.
- The reaction is terminated by addition of degassed methanol.

3.5.3 Polymerization Solid and Gaseous Monomers

Solid monomers, such as hexamethylcyclotrisiloxane (D3) and lactides are polymerized by adding the initiators and/or catalysts to their solutions. Also in a few cases, especially when the solid monomer needs to be added as a second or third monomer, the polymerization is started by adding its solution in an inert gas flow into the solution containing the initiator or the precursor (co)polymer and the catalyst [13].

The polymerizations of gaseous monomers, such as butadiene and ethylene oxide, are conducted similarly. For example, a desired volume of purified butadiene is cryo-condensed on the Schlenk line into a reaction flask containing the solvent and the initiator (*sec*-BuLi). The solution is stirred at room temperature (in non-polar solvents such as benzene and cyclohexane) or $-78\text{ }^{\circ}\text{C}$ (in tetrahydrofuran) until the polymerization is completed. Recently developed phosphazene-catalysed metal-free ring-opening polymerization of ethylene oxide requires the premix of the protic compound (a small molecule or macromolecule containing a protic moiety) and the phosphazene catalyst for the deprotonation of the initiator and the generation of anionic initiating species [14, 15]. The purified ethylene oxide is then introduced in the reaction flask by cryo-condensation, and then allowed to polymerize at an elevated temperature.

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