Chapter 2

Experimental Section

2.1 High Vacuum Line Techniques

The observation and studies of living anionic polymerization require rigorous purification of reagents[1,2] to exclude inadvertent termination of propagating polymer chain ends by impurities. In addition, particular care should be taken to prevent chemically very active polymer carbanions to react with terminating impurities in the surrounding environment. The best solution to this problem is to carry out polymerization under high vacuum in properly constructed, annealed and flamed glassware. Various techniques have been proposed for work under vacuum.[3,4] The general techniques used in this work have been developed in our group and previously described.[5] Here the detailed methods and manipulations relevant to the anionic polymerization of vinylaromatic monomers, including 2-vinylnaphthalene (2VN), are presented.

The vacuum line is constructed from Pyrex glass tubing with high vacuum Teflon plugs and grounded glass joints. A two-stage Welch Duo-Seal® mechanical vacuum pump produces vacuum in the range 10^{-2}-10^{-3} Torr, which goes to 10^{-5}-10^{-6} Torr when an oil diffusion pump and liquid nitrogen trap are used in addition to a mechanical pump. This vacuum is sufficient for most of the experiments involving carbanions. The vacuum is monitored by the Varian Model 801 on-line gauge and additionally checked by a Tesla coil.

The experimental apparatus are custom made from Pyrex glass using glass blowing techniques. Prior to experimental manipulations, an apparatus is attached to the vacuum line, evacuated and flamed several times with yellow-tipped non-sooting flame to remove any contaminants from the surface. Break-seal ampoule technique is used to introduce, mix, divide and seal reagents. Constrictions are used to hold breaking hammers and/or seal off ampoules containing reagents.

2.2 Purification and Treatment of Reagents

Tetrahydrofuran (THF)

THF (EM Science, Mallinckrodt, GR grade, 2 L) is refluxed with liquid potassium (3-4 g) and benzophenone (Fisher Scientific, m.p. 48 °C, 0.5 g) under N_2 atmosphere until the characteristic dark violet color of benzophenone dianion is observed. Then THF is distilled into a 2 L round bottom flask equipped with a Teflon plug and containing inside 2 g of potassium, 1 g of sodium (Na, Aldrich, 99%) chunks and 0.5 g of benzophenone. The flask is attached to a vacuum line with a liquid nitrogen trap on and degassed several times. THF is stirred with periodic degassing until color changes to yellow, green, green-blue and finally to dark violet and the metals form K/Na liquid alloy. The THF used for anionic polymerizations is further purified by distillation through the vacuum line onto a stable carbanion, such as 1,4-dipotassio-1,1,4,4-tetraphenylbutane (DD-K_2) or 1,4-dilithio-1,1,4,4-tetraphenylbutane (DD-Li_2). The dark red color of DD-K_2 or DD-Li_2 is an indicator of the solvent purity sufficient for anionic polymerization. THF is stirred over the stable carbanion for 1-2 hours, distilled and divided into ampoules.

Hexane

Hexane is refluxed over K/Na alloy, distilled into a 2 L round bottom flask containing K and Na cleaned chunks, attached to a vacuum line and degassed several times. K/Na alloy forms very slowly in hexane, but once formed its shiny surface is a good indicator of the solvent purity.

Toluene

Toluene is purified by distillation twice from CaH_2 and once from a potassium mirror. A detailed methodic is described below. The required volume of toluene is stirred over CaH_2 (Aldrich) under argon overnight. The flask **A** containing toluene is attached to the glass apparatus at the joint **B** (Figure 2.1). Some more CaH_2 is added into **E** and closed with septum **C**. After 2-3 freeze-and-thaw cycles, the apparatus is evacuated through **F**. The septum **C** is sealed off at the constriction **D**. It is possible to distill toluene form **A** into **E** through a vacuum line due to its quite high volatility. In this case, there is no need to have **A** and **B** on the apparatus, but it is necessary to load CaH_2 into **E** beforehand, evacuate the apparatus and seal off the septum **C**. Toluene in **E** is stirred for 5 h and then distilled into **G**. This twice purified over CaH_2 toluene is poured into **H** and sealed from the apparatus at the constriction **I**.

Toluene is further purified by distillation from a potassium mirror. Potassium mirror is formed in **E** (Figure 2.2) according to usual procedure (p. 28). Once the mirror has been formed, toluene from the ampoule **H** is poured into **E** and stirred for 5 h at room temperature and then distilled into **F** kept in a dry ice coat. It is convenient at this time to slightly warm toluene in **E** to 40-45 ºC, but there is a danger of toluene bumping. It is helpful to have a coarse frit or baffles on toluene pathway between **E** and **F**. The ampoule **F** is sealed off at the constriction **I**. Needed amounts of toluene are then distributed into ampoules, sealed off and kept in a freezer at –20 ºC. Potassium is recycled by pouring molten metal from **E** to **G** and sealing it off.

Cyclohexane

Cyclohexane (EM Science, spectrophotometric grade) is used as a solvent in photoluminescence (fluorescence) and UV-Vis measurements. It is fractionally distilled to remove trace amounts of benzene, which can introduce an appreciable error into baseline in photochemical experiments.

Chloroform

Deuterated chloroform ($CDCl_3$, Cambridge Isotope Laboratories, Inc., 99.8%) is stored over molecular sieves (Mallinkrodt, 514GT, 4 Å) and used as a solvent in NMR experiments.

Dichloromethane

Deuterated dichloromethane (CD_2Cl_2, Cambridge Isotope Laboratories, Inc., 99.9%) as a solvent for NMR experiments is used as received.

1,1-Diphenylethylene

1,1-Diphenylethylene (DPE, Aldrich, 97%) for preparation of DD-K_2 or DD-Li_2 is used as received. However, it contains benzophenone from which it is commercially prepared, so rigorous purification is necessary for DPE used as end capping reagent. In such cases, DPE is stirred overnight with freshly crushed CaH_2 under vacuum, then filtered through a medium frit. This DPE is then mixed with small amounts of t-BuLi (10% molar with respect to DPI) until persistent red color forms. It is then vacuum distilled and sealed into an ampoule. Particular care should be taken to the construction of the distillation apparatus as DPE has very high boiling point (270 °C). Accordingly, a pathway for DPE distillation should be short and distillation is best performed under dynamic vacuum. DPE is then diluted with purified THF to needed concentrations and distributed into ampoules.

tert-Butyllithium

t-Butyllithium (t-BuLi, 1.7 M solution in pentane, Aldrich) is either sublimed under dynamic vacuum or used as received. Commercial t-BuLi contains impurities, such as hydroxides, alkoxides, chlorides, etc., formed upon reaction of t-BuLi with moisture or carried over from the preparation. These impurities contribute to the yellow color of t-BuLi solutions. Sublimed t-BuLi is a white solid and its solutions are colorless. The best way to remove the impurities is to sublime t-BuLi under dynamic vacuum. The sublimation is quite straightforward, however care should be taken to prevent solvent bumping and to have short pathways between the chambers for initial and sublimed t-BuLi. The temperature of sublimation is kept below 60 °C to prevent t-BuLi decomposition. Pentane is usually distilled into a liquid nitrogen trap and, after t-BuLi has been sublimed, purified hexane is added. t-BuLi solutions are then distributed into ampoules, sealed and stored at –20 °C.

The exact concentration of sublimed t-BuLi is determined by acid-base back titration. t-BuLi is first reacted with methanol, and then a known amount of nonvolatile acid is added. Good results are obtained with sulfuric or p-toluenesulfonic acids. Further titration is performed in a classical way.[6]

The exact concentration of t-BuLi used as received is determined by the method of double titration.[7] The modification of this method for determination of active t-BuLi is described below. t-BuLi is reacted with a known excess of recrystallized fluorene (Aldrich, 98%) in THF at –78 °C. A yellow color appears instantly indicating rapid deprotonation of fluorene. After stirring for 15 minutes, 10 molar percent excess of CH_3I is added. The ratios of 9-methylfluorene and unreacted fluorene determined by GC analysis allow calculation of the t-BuLi concentration.[8]

Alkali Metals

Lithium (Aldrich, wire, 98+%) is cut into small pieces in a glove box under ultra-pure argon and placed into an initiator preparation apparatus. The apparatus is evacuated, and Li pieces are washed with THF prior to initiator preparation. Potassium (Aldrich, sticks, m.p. 64 ºC) is first washed with hexane under ultra-pure argon flow to remove mineral oil, then it is cut into small pieces in pure hexane, washed in hexane/10% v/v isopropanol to remove impurities from the surface, then again in hexane and placed into an apparatus. The apparatus is evacuated, potassium melted and poured into several ampoules, 1.5-2 g of the metal into each ampoule. Cesium (Aldrich, ingot, 99.5%) was received in an ampoule and used directly to form a cesium mirror similar to a potassium mirror (see below).

Naphthalene

Naphthalene (Naph, mp 81 °C, Aldrich, 99+%) is recrystallized two times from methanol as white flakes, vacuum dried, dissolved in THF and used for electron transfer initiator preparations.

1,1,4,4,7,7,10,10-Octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene

1,1,4,4,7,7,10,10-Octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene[9] (OMOHN) is recrystallized from methanol, dried under vacuum and dissolved in purified THF.

2-Vinylnaphthalene

Commercial 2-Vinylnaphthalene (2VN, Aldrich, Alfa Aesar, 95%) is brownish solid and as it comes it contains ~5% MeOH as stated in MSDS for the monomer and 15-20% polymer as determined by Size Exclusion Chromatography (SEC). Thus, it requires careful purification. 2VN has been purified by two methods.

Method A. 2VN (5 g) is dissolved in small amount of THF (HPLC grade, 7 mL) and placed with freshly crushed CaH_2 into **D** (Figure 2.3). Freezing **D** with liquid nitrogen, the apparatus is evacuated, and the constriction **C** is sealed off. Several freeze-and-thaw cycles follow. Keeping **D** in warm water bath (60-70 ºC) and cooling **E** with liquid nitrogen, THF is distilled into a liquid nitrogen trap, and 2VN is sublimed into **E** under dynamic vacuum. It is not recommended to raise the temperature in **D** above 70 ºC as 2VN may thermally polymerize at higher temperatures. 2VN is sublimed as clear white solid. Some polymer stays behind. The constriction **F** is sealed off and 2VN is diluted with purified THF (an ampoule with

THF attached to **E** is not shown). The solution is poured into **G** and sealed off at the constriction **H**.

An ampoule with thus purified 2VN is attached to another apparatus (ampoule **D**, Figure 2.4). Some CaH_2 is placed into **A**, the apparatus is evacuated, flamed, and the constriction **C** is sealed off. 2VN solution is poured into **A** and frozen with liquid nitrogen. The constriction **E** is sealed off under dynamic vacuum. 2VN is stirred with CaH_2 overnight and sublimed into **H** as described above. It is necessary to seal off all constrictions on **A** due to otherwise difficult control of 2VN flow into **H**. After sublimation, **F** is sealed off, 2VN is diluted to needed concentration with a solvent from **I**, poured into **J** and sealed off at **K**. This procedure may be repeated once.

Method B. 2VN (5 g) is dissolved in toluene (7 mL), stirred under vacuum with CaH_2 overnight and sublimed as described above. Then it is stirred over solid $LiAlH_4$ (Aldrich, 1.0 M solution in diethyl ether) for 5 hours at room temperature and filtered or vacuum sublimed from $LiAlH_4$ at 60 °C. The final stirring for 2-3 hours over CaH_2 and sublimation from CaH_2 is necessary to remove residual $LiAlH_4$ as it can initiate 2VN polymerization in polar solvents. Toluene is distilled into a trap, and purified THF is added. The monomer solution is distributed into ampoules equipped with break-seals.

Styrene and α-Methylstyrene

Styrene (S, Aldrich, 99%) or α-methylstyrene (AMS, Aldrich, 99%) are distilled from CaH_2 followed by distillation from dibutylmagnesium. The monomers are then diluted to needed concentrations with purified THF and distributed into ampoules equipped with break-seals.

9,9-Dimethyl-2-vinylfluorene

9,9-Dimethyl-2-vinylfluorene (DMVF) was synthesized and purified by Dr. Xi Zhang as reported.[10]

1,4-Bis(bromomethyl)benzene

1,4-Bis(bromomethyl)benzene (dibromoxylene, DBX, TCI America, Inc., 98+%) is recrystallized twice from chloroform, pumped on a vacuum line and dissolved in purified THF or toluene to needed concentrations.

Diiodomethane

Diiodomethane (DIM, Aldrich, 99%, 1 mL) is diluted with toluene (10 ml), stirred with CaH_2 overnight in the dark and distilled from CaH_2 onto Cu(0) in the dark. This procedure is repeated two times, each time diluting DIM with 10 mL of toluene. As DIM is light sensitive, particular care should be taken to prevent its exposure to the light. Cu(0) is used to prevent decomposition of DIM and free radical formation.

Dichlorodimethylsilane

Dichlorodimethylsilane (DCDMS, Acros, 99+%) is stirred with CaH_2 overnight and distilled from CaH_2. This procedure is repeated once.

9,10-Bis(chloromethyl)anthracene

9,10-Bis(chloromethyl)anthracene (BCMA, TCI America, Inc., 98%) is recrystallized once from toluene and once from chloroform, dissolved in purified toluene or THF as necessary, stirred over CaH_2 and filtered.

Chlorotrimethylsilane

Chlorotrimethylsilane (TMSCl, 1.0 M solution in THF, Aldrich) is stirred with CaH_2 overnight and distilled from CaH_2 under vacuum. This procedure is repeated once. TMSCl is distributed into ampoules and stored in a freezer.

Methanol

Methanol (MeOH, Mallinkrodt, 100%) and deuterated methanol (MeOD, Cambridge Isotope Laboratories, Inc., 99.8%) used as terminating reagents are distilled under high vacuum. Needed amounts are distributed into ampoules and stored at –20 °C.

2.3 Preparation of Initiators

Commercial t-BuLi purified as described above is used. However, electron transfer initiators, such as lithium naphthalide (Li-Naph), potassium naphthalide (K-Naph), etc., are prepared and used immediately after preparation. The time of storing these initiators at room temperature is minimized, and possible side reactions[11] are avoided by wrapping a dry ice coat around ampoules whenever possible.

Formation of a Potassium Mirror

Potassium (K, 1-2 g) is cleaned from the mineral oil in hexane, depleted of the surface impurities by reaction with 30% i-PrOH/hexane mixture under argon and then washed with hexane again. The potassium is melted under dynamic vacuum and distributed into several ampoules equipped with break seals.

An ampoule (**B**) with shiny K metal (Figure 2.2) is attached and the apparatus is evacuated. The break seal at **B** is broken and potassium is allowed to flow down into the thick walled chamber **D** by heating **B** and **D** with a yellow tipped non-sooting flame. The constriction **C** is sealed off and potassium is distilled under dynamic vacuum into **E** kept in ice bath (0 °C). The mirror covering 40-50% of lower part of **B** is formed in 20-30 min and is extremely reactive as indicated, for instance, by an immediate blue color formation upon introduction of THF. Needed manipulations are performed, and potassium cleaned with THF is transferred into **G** and recycled.

Preparation of Potassium and Lithium Naphthalides

Naphthalene solution in THF (10 mL) is added from **H** onto freshly formed potassium mirror in **E** (Figure 2.2). Instant green color appears and intensifies as the reaction proceeds. The reaction mixture is stirred for 15 min at 0 °C and then dark green K-Naph/THF solution is poured into **F** and sealed off at the constriction **I**. It is convenient to have a coarse frit on the pathway to **F**, so no metal particles may make their way into the initiator solution.

Lithium naphthalide (Li-Naph) is prepared similarly using lithium pieces (Li, Aldrich, 98+%). Additional care is taken to not overreact Naph with Li excess, as the formation of violet dianion is favorable under these conditions. Usually 15 minutes at 0 °C and Naph concentration of 10^{-2} M is sufficient to form Li-Naph in ~80% yield without presence of any noticeable dianion.

Preparation of Potassium and Lithium OMOHN Radical Anions

The radical anions K-OMOHN and Li-OMOHN are prepared similarly to the corresponding naphthalene radical anions (K-Naph and Li-Naph) by reaction of K mirror or Li pieces with OMOHN (1,1,4,4,7,7,10,10-Octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene) in THF at 0 °C. Although more reactive as electron transfer reagent and suitable for preparation of narrower molecular weight distribution polymers (as discussed below), OMOHN radical anions are preferred for synthesis of high molecular weight polymers. OMOHN is experimentally more difficult to remove from the prepared polymer compared to naphthalene which is easily sublimed and well soluble in THF/MeOH mixtures used for polymer precipitation. The high OMOHN content in precipitated polymers may complicate analysis and interpretation of results.

Preparation of AMS Oligomer Dianions

The usual procedure to prepare α-methylstyrene oligomer dianions (AMS-K_2 and AMS-Li_2) involves the reaction of AMS with potassium mirror or lithium pieces in THF at room temperature.[12] However, in some cases it was found convenient to prepare these initiators by electron transfer to AMS. For instance, to a stirred 4-fold excess of AMS/THF solution is added drop-wise K-OMOHN/THF solution. Instant appearance of red color indicates fast electron transfer reaction. The solution is warmed to 30 °C and stirred for 20 min, then brought to –78 °C and stirred for additional 10-20 min. Thus prepared initiator is used immediately.

2.4 Polymerization, Block-Copolymerization, End Capping and Coupling Reactions under High Vacuum

Typical experimental set-up is custom-made form Pyrex glass and shown in Figure 2.5. All of the ampoules with known concentrations of needed reagents are attached to the apparatus, and the apparatus is evacuated and flamed 2-3 times to remove impurities from the inner surface. The quality of vacuum is checked by a vacuum gauge and Tesla coil. When satisfactory vacuum is achieved, needed amount of THF (~10 mL) is distilled into **A** through the vacuum line. The plug **B** is closed, and the apparatus is taken off the vacuum line. A THF solution of a stable carbanion, such as DD-K_2 or DD-Li_2, is introduced from **C** to **A**, and the entire apparatus is washed. This solution is then transferred into a side bulb (not shown) and THF is distilled several times to remove traces of a stable carbanion. Initiator solution is poured from **D** into **A**, and **A** is brought to –78 °C applying iso-propanol/dry ice bath. A monomer solution pre-cooled with dry ice is introduced from **E** into vigorously stirred initiator solution in **A** as a one-time addition or drop-wise if equipped with a Teflon plug on the pathway from **E** into **A** (not shown). After the polymerization has been completed, 1/2 to 2/3 of the living polymer solution is transferred into **F** for further manipulations and closed with plug **G**. To the polymer in **A** any desired end capping reagent (such as DPE) is added from **H** and/or polymer anions are either terminated with methanol or end capped as necessary with a proper reagent from **I**. To the polymer in **F** a coupling reagent is added from **J** drop-wise through the plug **K**, or if the preparation of a block-copolymer is desired, a second monomer is introduced from **J** into **F**, and after appropriate time the polymer anion is terminated or end capped with a reagent in **L**.

The polymers are removed with a syringe, analyzed by SEC and precipitated in most cases by addition of large amounts (100-150 mL) of methanol. Precipitated polymers are dried under vacuum at 50 °C for 2 days and additionally analyzed by SEC if necessary as the precipitation may cause fractionation of polymers affecting their molecular weight (MW), especially for low MW polymers.

2.5 Polymerization, End Capping and Coupling Reactions under Argon

Some of the experiments (kinetic studies of 2VN polymerization in toluene/THF mixtures) were run under ultra-pure argon (Ar). Although high vacuum techniques are preferred for anionic polymerization as better control of manipulations and higher degree of reagent purification can be achieved, sometimes it is easier to perform certain tasks using an inert gas atmosphere. For instance, when a number of aliquots is to be withdrawn with a hypodermic syringe, the fastest and easiest way is to do it under a slight pressure of an inert gas.

A typical glassware assembly used in such experiments is shown in Figure 2.6. Manipulations with this apparatus combine high vacuum techniques with those under ultra-pure argon. Ampoules with known concentrations of necessary reagents prepared and sealed under vacuum are attached to the apparatus, and the apparatus is evacuated and flamed in usual manner as described above. The two compartments **A** and **B** are separated by closing the plug **C**. A solution of t-BuLi (commercial reagent, used as received, 1.5×10^{-2} moles) and triphenylmethane (TPM, Aldrich, 99%, 0.2 g) in 15 mL toluene is poured from **D** into **A** and cooled to –78 °C with i-PrOH/dry ice bath. High purity argon is slowly introduced through the vacuum line and bubbler **E** into **A** controlling the flow with **F**. When **A** has been filled with argon, in **B** anionic polymerization is started under vacuum by introducing a purified solvent (**G**) and t-

BuLi initiator (**H**) into **B**, cooling it to –78 °C and introducing an additive (**I**) and pre-cooled with dry ice monomer solution (**J**). After the polymerization in **B** has started, argon is allowed to slowly flow into **B** controlling the flow with **C**. As anionic polymerization in non polar solvents including those containing polar additives is quite slow, monomer conversions reach only 5-10% during the time of argon addition (5-10 min) into **B**, which is acceptable for consequent kinetic studies. A number of aliquots of polymer anion solution is taken with a hypodermic syringe though a septum (not shown) during the polymerization, terminated with methanol distilled under argon and analyzed by SEC.

2.6 Polymerization and Cyclization Reactions under High Vacuum

Preparation of macrocyclic polymers requires high dilution conditions (10^{-5}-10^{-6} M) to maximize the yield of macrocycles and minimize the yield of high MW polycondensation products formed by the inter-molecular coupling. Accordingly, the apparatus (Figure 2.7) is constructed using larger (500 mL, **B** and **E**, 200 mL, **C**) round bottom flasks. The experiment starts with attaching ampoules containing necessary reagents with known concentrations, and the apparatus is evacuated and flamed several times. Coupling reagent in **K** is used as a dilute solution (for instance, 10-50 mg DBX in 80-100 mL THF) for better control of addition during cyclization. After sufficient vacuum has been attained, 150 mL THF is distilled into **B** through the vacuum line, the apparatus is closed at **A** and taken off the vacuum line. A solution of a stable carbanion, such as DD-K_2 or DD-Li_2, is introduced from **D**, and the entire apparatus is washed to remove traces of impurities from the inner surface and from THF. THF is poured into **E** and distilled several times into **B** and **C** to completely wash off the traces of a stable carbanion. Finally, 25 mL THF is distilled into **C**, plug **J** is closed and the rest of THF is distilled into **B**, plug **G** is closed. Baffle **F** is used to prevent bumping of the red carbanion solution into **B**. Anionic polymerization in **C** is performed in usual manner. Electron transfer initiator is added from **M**, the mixture in **C** is brought to –78 °C and a monomer pre-cooled with dry ice is added drop-wise from **H**. After 15-20 min, 2/3 of the living polymer solution is poured from **C** into **I** kept in dry ice coat all the time. A cold polymer solution is added slowly drop-wise from **I** into vigorously stirred THF in **B** at –78 °C simultaneously with a pre-cooled with dry ice coupling reagent that is added also slowly drop-wise from **K** into **B**. The rate of addition is regulated by plugs **J** and **L** so that the solution color in B is kept barely perceptible light green. After the cyclization, the solution in **C** is terminated by methanol from an ampoule (not shown), and the contents are brought to room temperature. The polymer solution in **B** and **C** is removed by a syringe, filtered (optional), precipitated by addition of large amounts of methanol (150 mL) and filtered through a fine frit. THF in the solution containing macrocycles (from **B**) is first evaporated to 10-15 mL, then methanol is added. In some cases, especially for low MW macrocycles, addition of water is necessary to facilitate precipitation. All linear and macrocyclic polymers are analyzed by SEC both prior and after precipitation/fractionation.

2.7 Polymer Characterization and Analysis

2.7.1 Size Exclusion Chromatography

All polymers are analyzed by Size Exclusion Chromatography (SEC) prior to precipitation. In some experiments, polymers were analyzed by SEC after precipitation and/or fractionation, as well. In addition, fractionation of macrocyclic polymers is monitored by SEC until satisfactory results are obtained in terms of high MW polycondensation product removal. SEC is carried out at room temperature with THF or toluene as the carrier solvent at a flow rate of 1 mL/min. The SEC line consists of a Waters Model 510 pump, a Model 680 automated gradient controller, a Model 410 differential refractometer (RI detector), a Model 484 tunable absorbance detector (UV detector) and two "Ultrastyragel" 500 Å and 10^4 Å columns. A calibration curve is prepared using polystyrene standards (Polysciences, Inc.) with MW's of 1,000, 4,000, 30,000, 200,000 and narrow MW distributions (1.05-1.10). An analyzed polymer solution in THF or toluene (5×10^{-2} M, 1-2 mL) is filtered twice through a 0.45 μm filter (Gelman) and 30-50 μL is injected into SEC.

SEC analysis using RI detector is a fast and convenient method to determine molecular weight (MW) and MW distribution and/or to follow a polymerization progress, extent of coupling or polymer fractionation. Occasionally, it is useful to characterize a polymer by SEC using a UV detector. P2VN contains naphthalene which absorbs light in UV region (300-325 nm for S_1 transition and 250-300 nm for S_2 transition),[12] so SEC-UV analysis with a UV detector set at 290 nm may give additional information about homogeneity of a polymer MW distribution. In experiments where anthracene is incorporated into polymer chains, SEC-UV at 405 nm is run to confirm the presence and distribution of anthracene throughout a polymer sample.

2.7.2 Nuclear Magnetic Resonance

Proton and carbon-13 NMR data was acquired on Bruker AM-250 FT instrument operating at 250 and 62.9 MHz, respectively, with $CDCl_3$ or CD_2Cl_2 used as a solvent. A solvent peak at 7.26 ppm ($CDCl_3$) or 5.30 ppm (CD_2Cl_2) is used as an internal standard.[13] For proton NMR, 10 mg of a precipitated and dried under vacuum polymer dissolved in one mL of a solvent is used with typical number of scans equal to 40. For carbon-13 NMR, 50 mg of a polymer dissolved in one mL of a solvent is used with number of scans equal to 25,000 (overnight run). A water peak is usually observed at 1.56 ppm in proton NMR run in $CDCl_3$ interfering with the aliphatic polymer resonances and making MW calculations not reliable. To eliminate the water peak from spectra, NMR is run occasionally in sealed under vacuum tubes using a solvent distilled from sieves through a vacuum line.

Proton NMR is a powerful, fast and convenient method of observation of functional groups at polymer chain ends. TMSCl is used to terminate polymer anions and introduce trimethylsilyl (TMS) groups, which are easily detected in proton NMR. TMS signal (0.2 to –0.4 ppm) in conjunction with well-resolved t-Bu initiator signal (0.8 to 0.3 ppm) makes it possible to estimate the degree of end-functionalization and/or the degree of polymer chain-end deactivation. In addition, the ratio of integrals of P2VN aromatic and initiator or P2VN aliphatic and initiator signals allow calculation of number average molecular weight (M_n). This method is limited to low MW polymers (below 30,000) as for higher MW's intensities of the respective signals are on the order of base-line noise.

2.7.3 UV-Vis Absorption and Fluorescence Spectroscopy

UV-Vis experiments are run to confirm the presence and degree of incorporation of spectroscopically active groups (such as anthracenylidene) into polymer chain ends or to observe transformations in polymer chains upon reactions with coupling reagents. Typically, an exact mass (5 mg) of a precipitated and vacuum dried low MW P2VN is dissolved in a 10 mL volumetric flask in fractionally distilled cyclohexane, then 1 mL of this solution is taken and diluted with 10 mL of freshly distilled cyclohexane. P2VN of MW higher than 3,000 is dissolved in cyclohexane containing 10% v.v. of distilled THF. Polystyrene (PS) is dissolved in pure cyclohexane. As PS extinction coefficient is considerably lower (ε=250 at λ=260 nm) than that of P2VN (ε=5,600 at λ=280 nm),[12] 5 mg of PS dissolved in 10 mL of cyclohexane is used. UV-Vis is run on a Varian Cary 50 spectrometer using 1 or 10 mm quartz cells with a baseline set using a respective solvent.

Fluorescence experiments are typically run in a 10 mm fluorescence cell for the same polymers and concentrations as the UV-Vis described above. Emission spectra are recorded on a PTI QuantaMaster^{TM} Model C-60SE spectrofluorometer using a 1527 PMT detector and a slit width in the range from 1 to 3 nm. For consistency and comparison of results, fluorescence experiments are run at the same time on a set of polymer solutions with the same settings of the instrument.

2.7.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is used to determine glass transition temperature (T_g) of linear and macrocyclic polymers for additional characterization and observation of significant differences in polymer chain mobility. DSC is run using 5-10 mg of precipitated and vacuum dried polymer on a Perkin Elmer DSC-7 instrument in the temperature range from 25 to 175 °C in a thermostat with a scanning rate 10 °/min in two consecutive runs for each polymer sample. The data of the second run is reported. Due to exceedingly small intensity of the respective thermodynamic transitions, the T_g values are determined as the maxima on the respective DSC curves which deviate $\pm 2^o$ from the actual T_g values but are more straightforward to determine.

2.7.5 Thermal Gravimetric Analysis

To study thermal decomposition of linear and macrocyclic P2VN under non-oxidative conditions, thermal gravimetric analysis (TGA) is carried out. The experiments are run on a Shimadzu TGA-50 instrument under nitrogen flow of 40 ml/min with 5 mg of polymer.

2.7.6 Evidence for Macrocyclic Polymers

There are several properties reflecting differences between linear and macrocyclic polymer architectures. First, macrocycles have smaller hydrodynamic volume compared to the linear precursors (the same degree of polymerization). This is clearly observed on SEC curves by a symmetrical shift of macrocyclic polymer peak to higher elution volumes. The ratio of the respective apparent peak MW's (M_p)

for macrocyclic and linear polymer is a characteristic called <G> value.[14] Second, significant differences are observed for T_g's of macrocyclic and linear polymers of the same degree of polymerization (DP_n), especially for low MW polymers. As MW increases, the differences become less apparent and virtually disappear for DP_n>350. Third, thermal decomposition (TGA) of macrocyclic polymers differs from that of the linear precursors with macrocyclic polymers being more robust to non-oxidative decomposition. The differences become less pronounced as DP_n increases.

2.8 References

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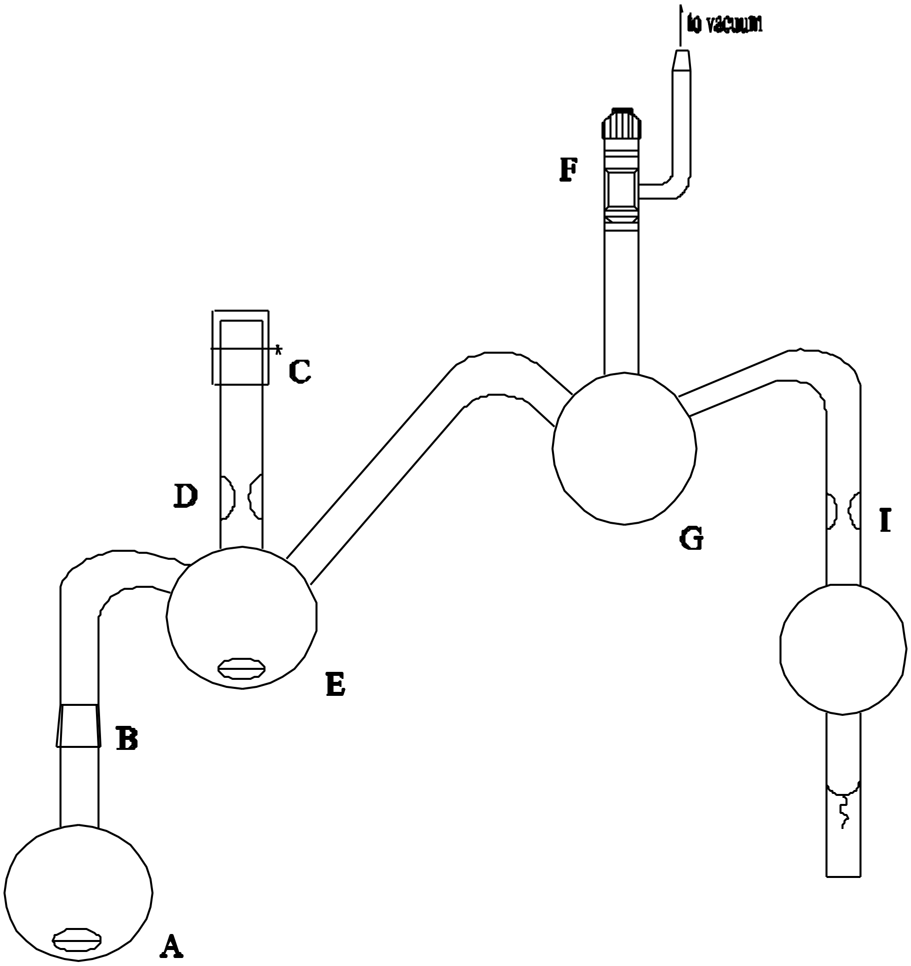

Figure 2.1. Typical set up for distillation of toluene or similar low boiling point liquids under high vacuum.

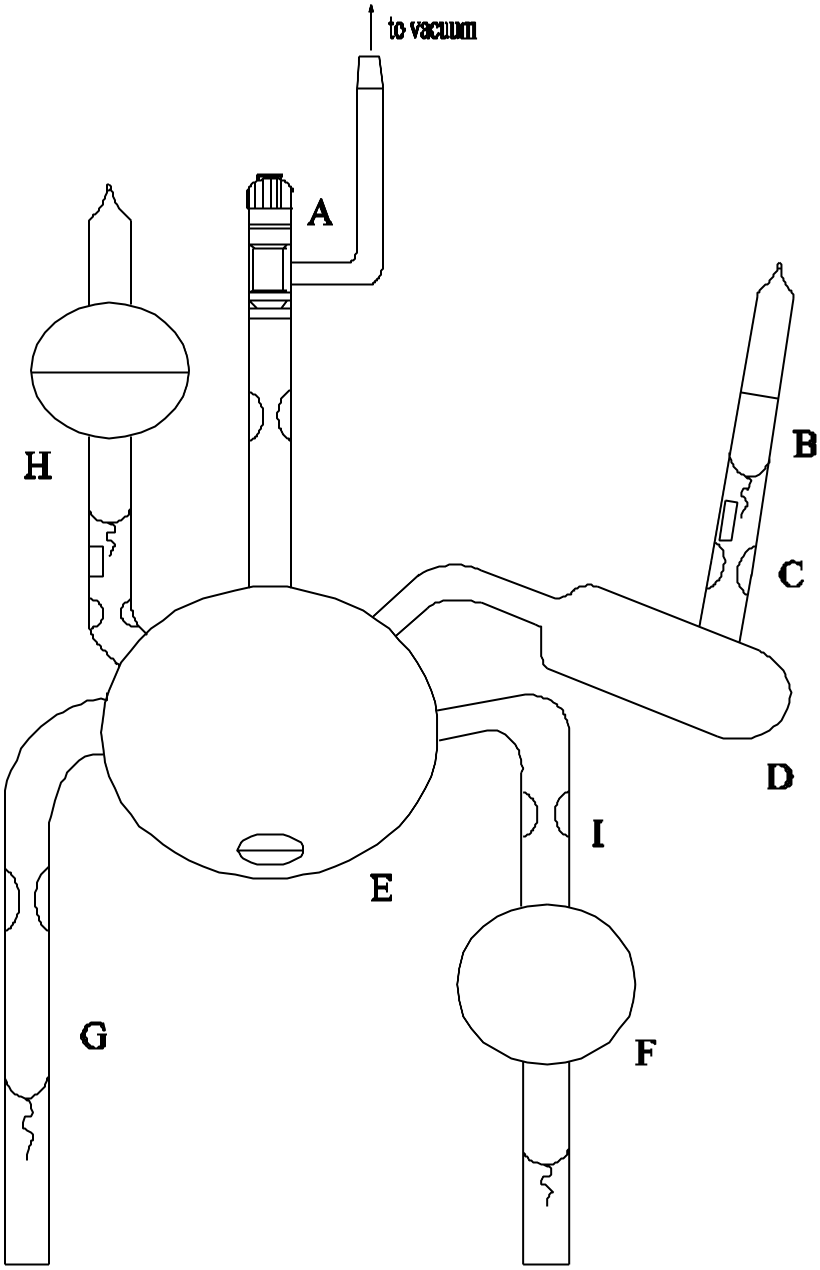

Figure 2.2. Apparatus for formation of a mirror of an alkali metal under high vacuum for initiator preparation or thorough solvent purification.

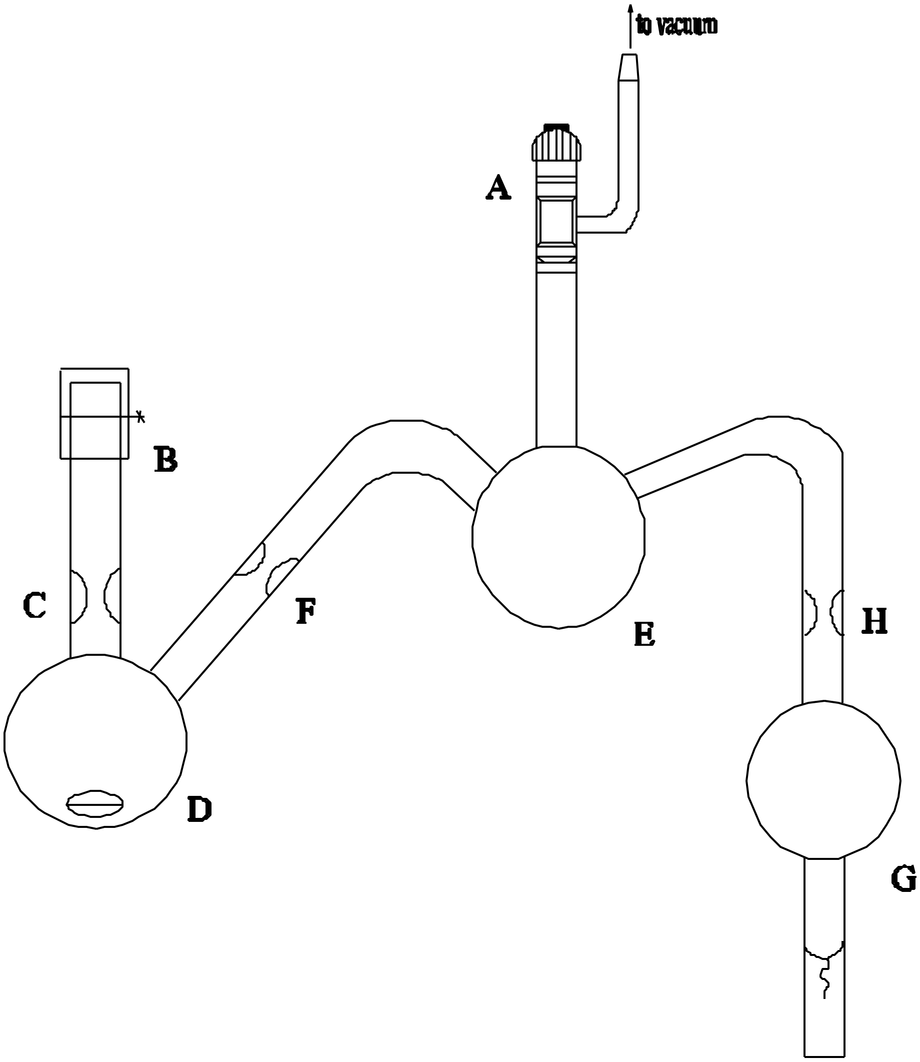

Figure 2.3. Set up for pre-purification of 2-vinylnaphthalene by sublimation from a mild scavenger (CaH_2) under high vacuum.

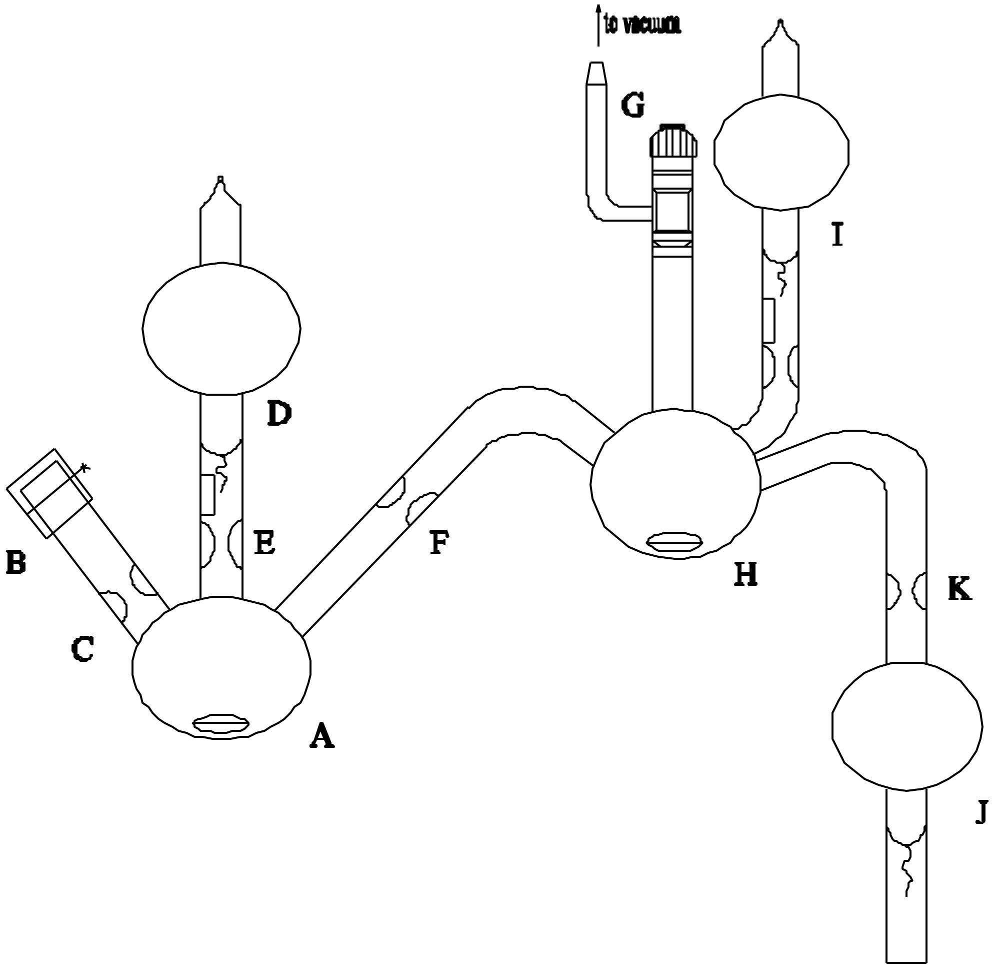

Figure 2.4. Set up for rigorous purification of 2-vinylnaphthalene by sublimation from a scavenger (CaH_2 or $LiAlH_4$) under high vacuum.

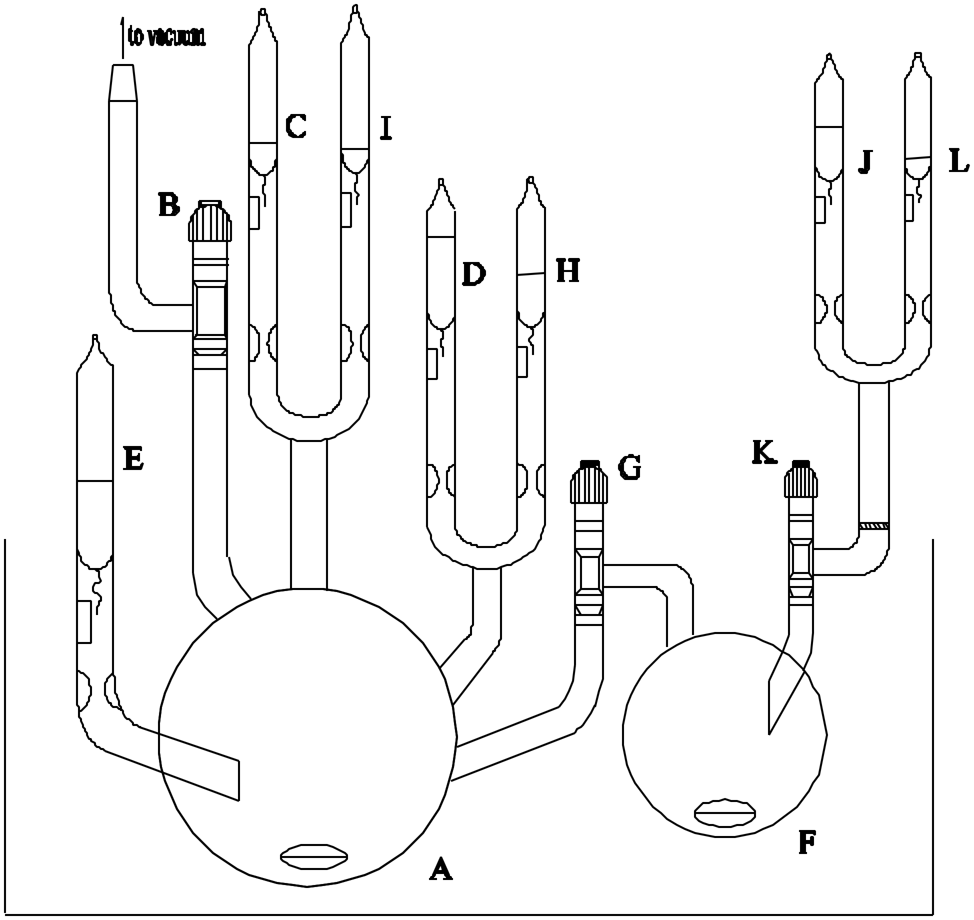

Figure 2.5. Typical apparatus for polymerization and consequent reactions involving polymer carbanion under high vacuum.

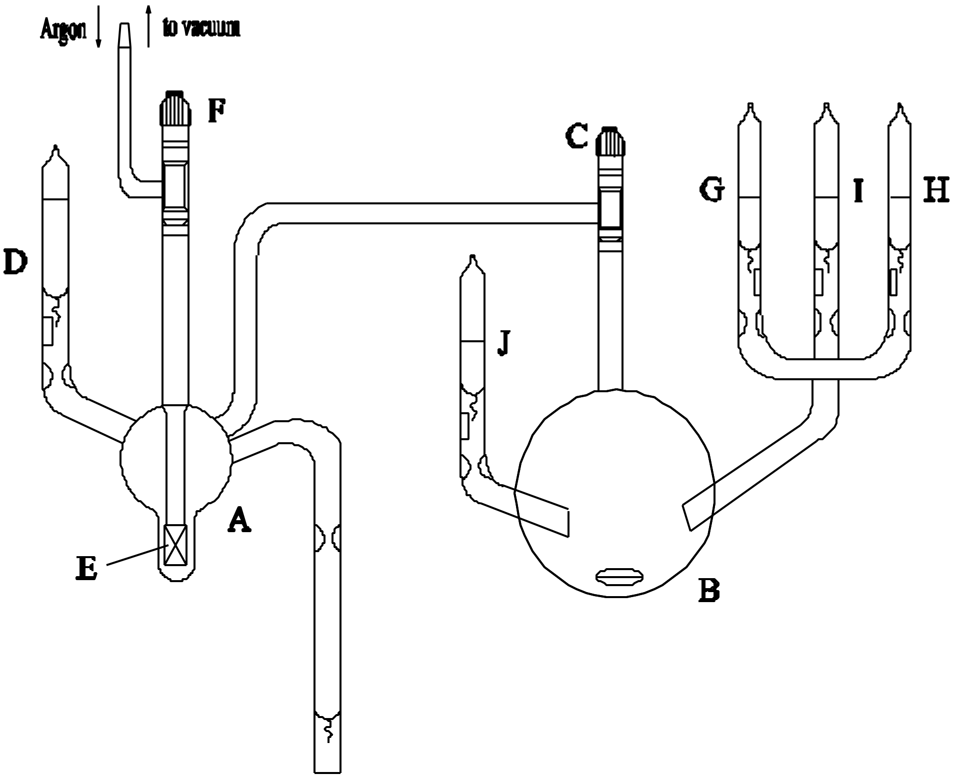

Figure 2.6. Typical apparatus for polymerizations under ultra pure inert gas.

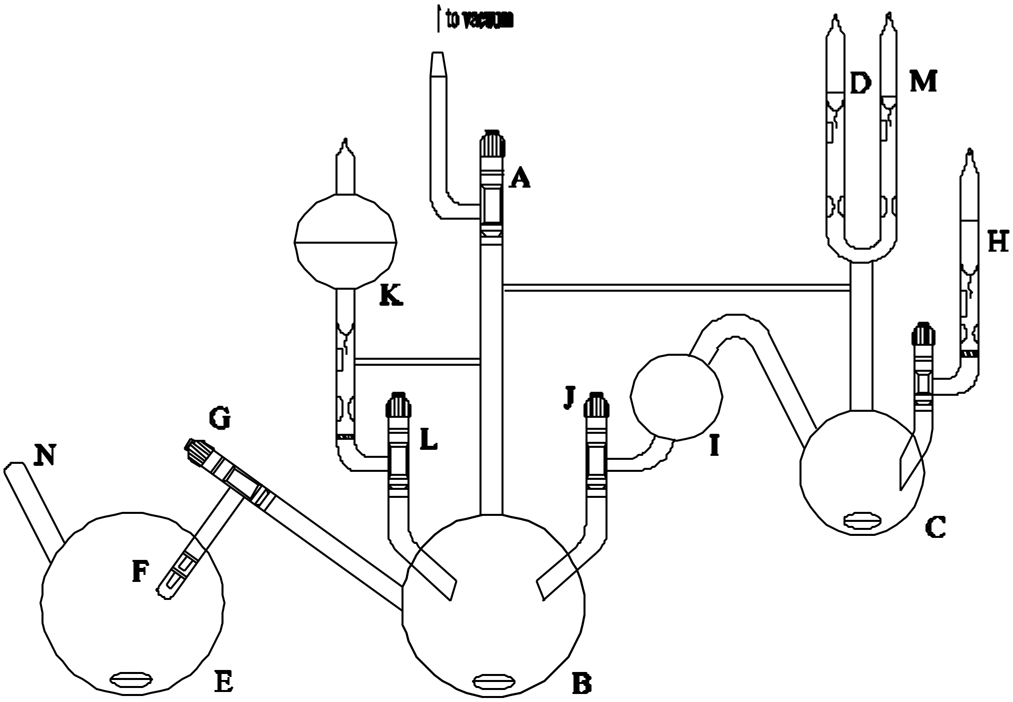

Figure 2.7. Apparatus for polymerization and consequent cyclization of polymer dianion under high vacuum.