CHAPTER II

Experimental Techniques

2.1. Analysis

For any good analysis of the synthesized products good characterization is required to get an insight into the nature, type and characteristics of the product. The details of the experimental set up and the tools having been used for characterization of the synthesized polymers have been elaborated in this chapter.

2.2. Electron microscopy: The Basics of SEM and TEM

Since its invention, electron microscope has been a valuable tool in the development of scientific theory and it contributed greatly to biology, medicine and material sciences. This wide spread use of electron microscopes is based on the fact that they permit the observation and characterization of materials on a nanometer (nm) to micrometer (μm) scale. This paper presents the basic theory for electron microscopy, focusing on the two basic types of electron microscopes (Ems); SEM, TEM.

2.2.1. Introduction

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield information about the topography (surface features of an object), morphology (shape and size of the particles making up the object), composition (the elements and compounds that the object is composed of and the relative amounts of them) and crystallographic information (how the atoms are arranged in the object). Electron Microscopes were developed due to the limitations of Light Microscopes which are limited by the physics of light to 500x or 1000x magnification and a resolution of 0.2 micrometers. In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria.etc.). This required 10,000x plus magnification which was just not possible using Light Microscopes. The Transmission Electron Microscope (TEM) was the first type of Electron Microscope to be developed and is patterned exactly on the Light Transmission Microscope except that a focused beam of electrons is used instead of light to "see through" the specimen. It was developed by Max Knoll and Ernst Ruska in Germany in 1931. The first Scanning

Electron Microscope (SEM) debuted in 1942 with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample.

EMs functions exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. The basic steps involved in all Ems are the following: A stream of electrons is formed in high vacuum (by electron guns). This stream is accelerated towards the specimen (with a positive electrical potential) while is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam.

The sample is irradiated by the beam and interactions occur inside the irradiated sample, affecting the electron beam. These interactions and effects are detected and transformed into an image.[1]

2.2.2. Electron-specimen interactions

When an electron beam interacts with the atoms in sample, individual incident electrons undergo two types of scattering - elastic and inelastic (Figure 2.1). In the former, only the trajectory changes and the kinetic energy and velocity remain constant. In the case of inelastic scattering, some incident electrons will actually collide with and displace electrons from their orbits (shells) around nuclei of atoms comprising the sample. This interaction places the atom in an excited (unstable) state. Specimen interaction is what makes Electron Microscopy possible. The interactions (inelastic) noted on the top side of the diagram are utilized when examining thick or bulk specimens (Scanning Electron Microscopy, SEM) while on the bottom side are those examined in thin or foil specimens (Transmission Electron Microscopy, TEM).

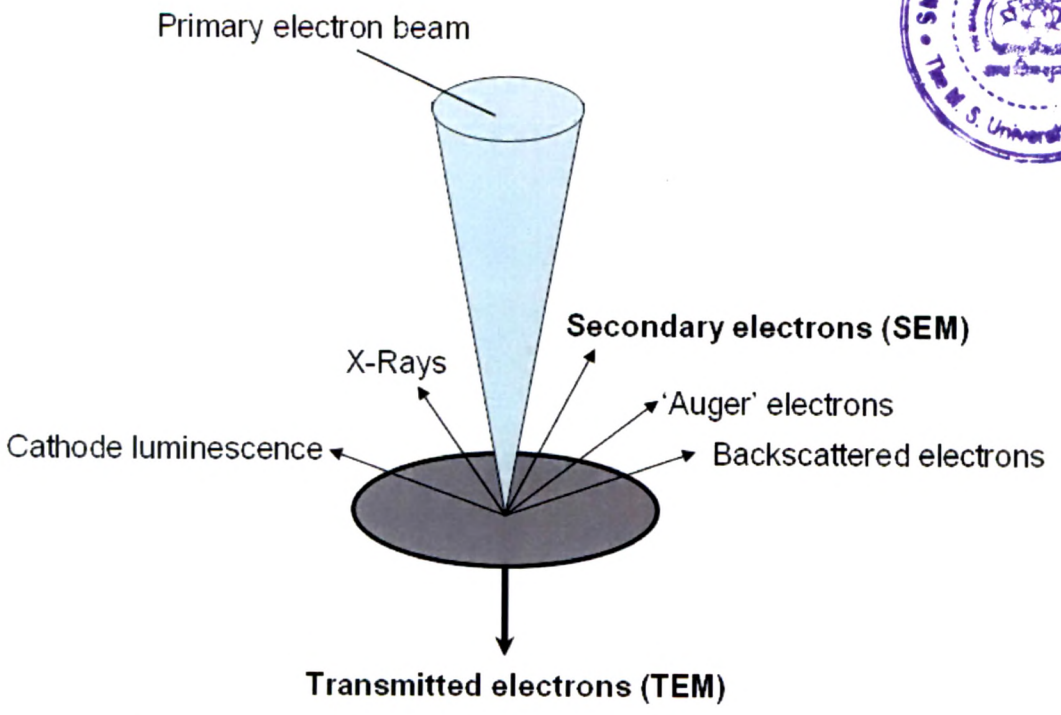

Figure 2.1. Different types of interactions can occur between an electron beam and a specimen.

2.3. Reactions Exploited In SEM

2.3.1. Secondary Electrons

When a sample is bombarded with electrons, the strongest region of the electron energy spectrum is due to secondary electrons. The secondary electron yield depends on many factors, and is generally higher for high atomic number targets, and at higher angles of incidence. Secondary electrons are produced when an incident electron excites an electron in the sample and loses most of its energy in the process. The excited electron moves towards the surface of the sample undergoing elastic and inelastic collisions until it reaches the surface, where it can escape if it still has sufficient energy. Production of secondary electrons is very topography related. Due to their low energy (5eV) only secondary electrons that are very near the surface (<10 nm) can exit the sample and be examined. Any changes in topography in the sample that are larger than this sampling depth will change the yield of secondary electrons due to collection efficiencies.

Collection of these electrons is aided by using a "collector" in conjunction with the secondary electron detector.

2.3.2. Backscattered Electrons

Backscattered electrons consist of high-energy electrons originating in the electron beam that are reflected or back-scattered out of the specimen interaction volume. The production of backscattered electrons varies directly with the specimen's atomic number. This differing production rates causes higher atomic number elements to appear brighter than lower atomic number elements. This interaction is utilized to differentiate parts of the specimen that have different average atomic number.

2.3.3. Relaxation of excited atoms

As was mentioned above, inelastic scattering, places the atom in an excited (unstable) state. The atom "wants" to return to a ground or unexcited state. Therefore, at a later time the atoms will relax giving off the excess energy. XRays, cathodoluminescence and Auger electrons are three ways of relaxation. The relaxation energy is the fingerprint of each element. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms on the specimen's surface. A resulting electron vacancy is filled by an electron from a higher shell, and an X-ray is emitted to balance the energy difference between the two electrons.

The EDS X-ray detector (also called EDS or EDX) measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. In practice, EDS (or EDX) is most often used for qualitative elemental analysis, simply to determine which elements are present and their relative abundance. In some instances, however, the area of interest is simply too small and must be analyzed by TEM (where EDS is the only option) or high resolution SEM (where the low beam currents used preclude WDS-Wavelength X-ray Dispersive Spectroscopy-, making EDS the only option).[2]

2.4. SEM-TEM

For the purpose of detailed materials characterization, two potent instruments are used: the Scanning Electron Microscope (SEM) and the Transmission Electron Microscope (TEM). Their operation is described below.

2.4.1. SEM

2.4.2. Operation

In SEM, a source of electrons is focused in vacuum into a fine probe that is rastered over the surface of the specimen. The electron beam passes through scan coils and objective lens that deflect horizontally and vertically so that the beam scans the surface of the sample (Figure 2.2). As the electrons penetrate the surface, a number of interactions occur that can result in the emission of electrons or photons from or through the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose x- and y- inputs are driven in synchronism with the x-y voltages rastering the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen.[3] As a result, the magnification system is simple and linear magnification is calculated by the equation:

$$M = L/l \qquad (1)$$

where L is the raster's length of the CRT monitor and l the raster's length on the surface of the sample.

SEM works on a voltage between 2 to 50kV and its beam diameter that scans the specimen is 5nm-2μm. The principle images produced in SEM are of three types: secondary electron images, backscattered electron images and elemental X-ray maps. Secondary and backscattered electrons are conventionally separated according to their energies. When the energy of the emitted electron is less than about 50eV, it is referred as a secondary electron and backscattered electrons are considered to be the electrons that

exit the specimen with energy greater than 50eV.[4] Detectors of each type of electrons are placed in the microscope in proper positions to collect them.

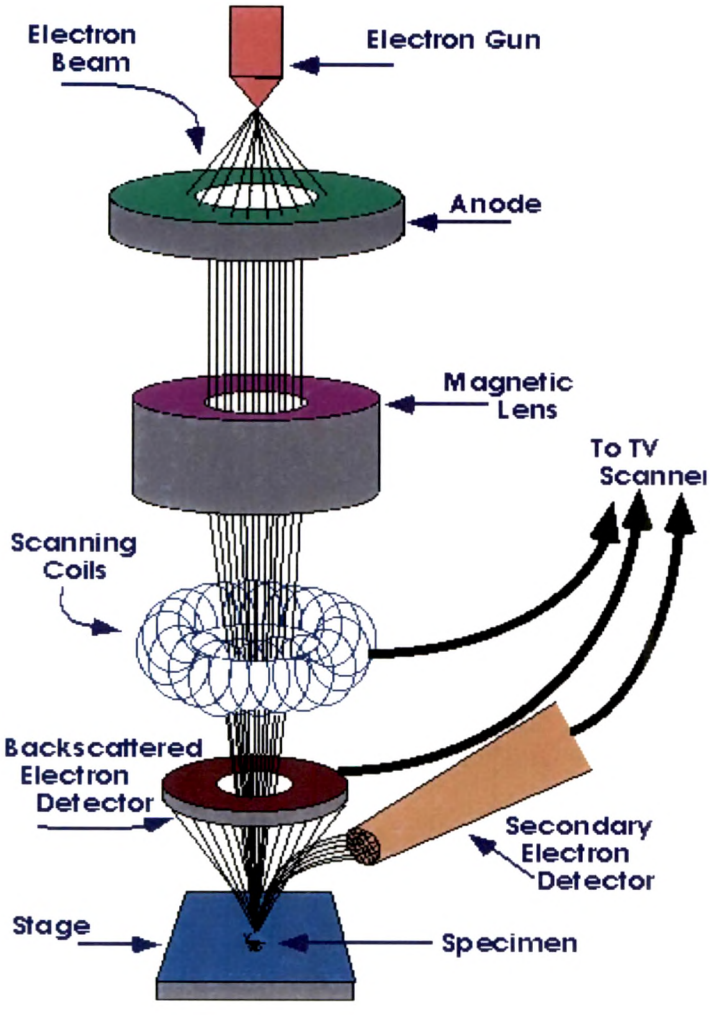

Figure 2.2. Geometry of SEM

2.4.3. Advantages and Disadvantages

Electrons in scanning electron microscopy penetrate into the sample within a small depth, so that it is suitable for surface topology, for every kind of samples (metals, ceramics, glass, dust, hair, teeth, bones, minerals, wood, paper, plastics, polymers, etc). It can also be used for chemical composition of the sample's surface since the brightness of the image formed by backscattered electrons is increasing with the atomic number of the

elements. This means that regions of the sample consisting of light elements (low atomic numbers) appear dark on the screen and heavy elements appear bright. Backscattered are used to form diffraction images, called EBSD, that describe the crystallographic structure of the sample. In SEM, X-rays are collected to contribute in Energy Dispersive XRay Analysis (EDX or EDS), which is used to the topography of the chemical composition of the sample. Consequently, SEM is only used for surface images and both resolution and crystallographic information are limited (because they're only referred to the surface). Other constraints are firstly that the samples must be conductive, so non-conductive materials are carbon-coated and secondly, that materials with atomic number smaller than the carbon are not detected with SEM.

2.4.4. SEM Today

As time goes on, the ultimate resolution of the SEM levels out near 0.6nm at 5kV. In Scanning Trasmission Electron Microscopy in which internal microstructure images of thin specimens are obtained, achieved resolution is up to 1.5nm at 30kV.

2.5. TEM

2.5.1. Operation

Transimission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen. The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses. The geometry of TEM is shown in Figure 2.3. The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and "hits" the sample surface. The electrons that are elastically scattered consist of the transmitted beams, which pass through the objective lens. The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose of the elastically scattered electrons that will form the image of the microscope. Finally, the beam goes to the magnifying system that is consisted of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens.

The formed image is shown either on a fluorescent screen or in monitor or both and is printed on a photographic film.

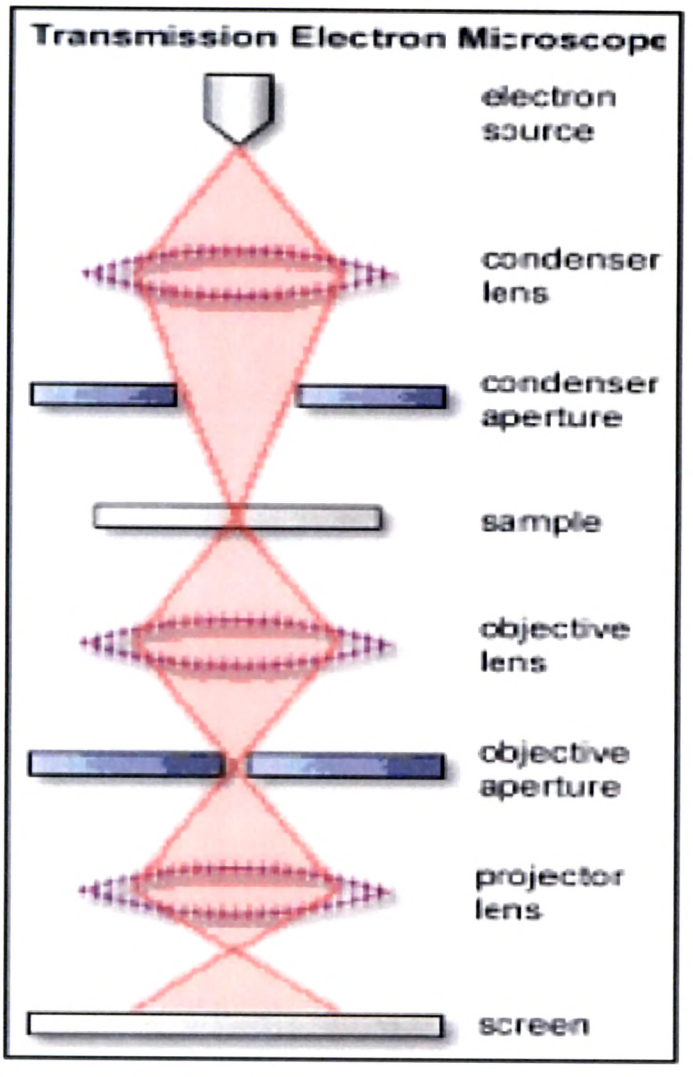

Figure 2.3. Transmission electron microscope with all of its components.

Different types of images are obtained in TEM, using the apertures properly and the different types of electrons. As a result, diffraction patterns are shown because of the scattered electrons. If the unscattered beam is selected, we obtain the Bright Field Image.

Dark Field Images are attained if diffracted beams are selected by the objective aperture. Also in TEM, analysis is done with EDX (Energy Dispersive X-ray), EELS (Electron Energy Loss Spectrum), EF-TEM (Energy Filtered Transmission Electron Microscopy), etc. data. In transmission microscopy, we can actually see the specimen's structure and its atomic columns, thus compositional and crystallographic information is attained.

2.5.2. Main difficulties in the exploitation of TEM

Transmission Microscopy provides several types of images, as reported above. The diffraction patterns show dots, regions or circles originating from the sample area illuminated by the electron beam that depend on the material's structure. Monocrystals show distinguished dots in diffraction patterns, polycrystalline materials common centred circles and amorphous materials diffused circles. Distortions and defects are visible in bright and dark field images, but expertise is needed in order to interpret whether they are defects or artifacts. Electron or ion beam damages must be considered in TEM analysis, because of the sensibility of the sample and its really low thickness. Additionally, there's always the problem of calibration and alignment of the instrument. Both of them require experience and skills so the resulting images and data that emerge are reliable and free of objective astigmatism.

2.6. Methods

2.6.1. Reverse Phased-Temperature Gradient Interaction Chromatography (RP-TGIC)[5]

Synthetic polymers have distributions in various molecular characteristics such as molecular weight, chemical composition, chain architecture, stereoregularity, and functionality. A full and precise characterization of such multivariate distributions in synthetic polymers is difficult indeed. Accordingly, the molecular characteristics are often represented by average quantities. However, it is certainly more desirable to know the full distributions of the molecular characteristics. Also, for many cases, it is sufficient to obtain a small number of molecular characteristics to gain access to the information required for a given purpose. A common approach would be to find an appropriate chromatography method sensitive to one molecular characteristic only. In favorable cases, the effect of all but one molecular characteristic can be suppressed to a negligible level. Among various liquid chromatography (LC) techniques employed for the characterization of polymers, size exclusion chromatography (SEC) has been the most widely used technique.[6,7]

The SEC method fractionates polymer molecules utilizing the partition equilibrium of polymer chains between common solvent phases located at the interstitial space and the pores of the column packing materials, typically in the form of uniform size porous beads. The stationary and mobile phases are chosen to minimize the enthalpic interaction of the polymeric solutes such that the partition equilibrium is mainly governed by the conformational entropy difference of the polymer chains in the two phases. Accordingly, SEC separates the polymer molecules in terms of the size of a polymer chain in the elution solvent. If a simple relationship exists between the chain size and the molecular weight of polymers such as for linear and chemically homogeneous polymers, SEC retention is well correlated with the molecular weight. However, SEC is not efficient in separating the polymer molecules according to the molecular characteristics that do not have a simple correlation with chain size such as chemical composition, chain architecture, and functionality. Another method, called Interaction Chromatography (IC),

is found to be more efficient for the purposes, for it uses the enthalpic interaction to control adsorption or partition of solute molecules to the stationary phase. Thus, its separation mechanism is sensitive to the chemical nature of the molecules.[8–10] In this article, we would like to summarize the recent developments in the analysis of various heterogeneities in synthetic polymers with a specific emphasis on the temperature gradient interaction chromatography (TGIC) method.

2.7. HPLC Seperation Principles of Polymers

2.7.1. SEC, IC, and LCCC

IC is a variation of the HPLC method widely used for the separation of small molecules (relative to polymers). The term of IC is yet to be accepted generally. Nonetheless, the name has a merit to represent the characteristic separation mechanism of IC in contrast with SEC. Various stationary and mobile phases have been employed in the IC analysis of many synthetic polymers. In general, IC exhibits higher resolution than SEC, but is less universal than SEC in a sense that the enthalpic interaction strength in IC has to be properly controlled with precision to achieve a reproducible and high-resolution separation. In other words, the mobile and stationary phases in IC have to be chosen for individual polymer system of interest and the gradient elution (in either solvent or temperature) is often required, whereas most of SEC separations can be done under

$$k' \equiv \frac{V_r - V_m}{V_m} = K\frac{V_s}{V_m} = \exp\left(-\frac{\Delta G^o}{RT}\right)\cdot\frac{V_s}{V_m} \quad (1)$$

isothermal and isocratic condition with many thermodynamically good solvents. The retention factor, k' in the HPLC separation is expressed as follows, where V_r is the retention volume, and the subscripts m and s stand for the mobile and stationary phases in the separation column, respectively. The distribution constant K is the ratio of the solute concentration in the stationary phase (c_s) to that in the mobile phase (c_m).

In SEC, the interstitial and pore spaces play the roles of the mobile and stationary phases, respectively. Like other equilibrium constants, K is related to the standard Gibbs

free energy change (ΔG^o) of the process and ΔG^o can be further divided into the enthalpic and entropic contribution of the process.

$$\ln k' = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} + \ln \phi, \quad \phi \equiv \frac{V_s}{V_m} \qquad (2)$$

where ΔH^o and ΔS^o are the standard enthalpy and entropy changes associated with the solute transfer from the mobile phase to the stationary phase. The transfer may be driven by adsorption, partition, or others, depending on the nature of a chromatographic method. In the SEC separation process, the separation condition is usually chosen to minimize the enthalpic interactions of the polymer solutes with the packing materials. Therefore, in the ideal SEC condition ($\Delta H^o = 0$) K_{SEC} is a function of the conformational entropy loss ($\Delta S^o < 0$) of polymer chains when transferred into the restricted pore space.

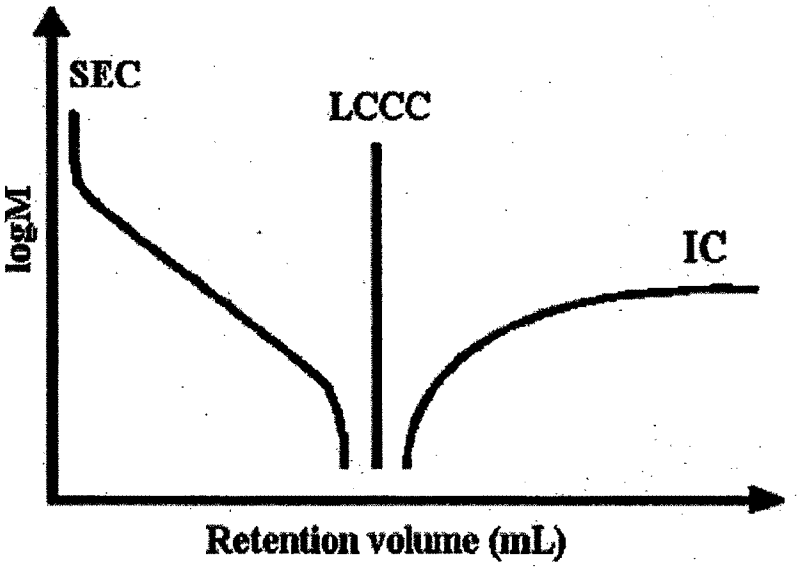

Figure 2.4. Polymer molecular weight versus retention volume in three chromatographic separation modes: size exclusion chromatography (SEC), liquid chromatography at critical condition (LCCC), and interaction chromatography (IC).

If this condition is fulfilled, SEC separates the polymers entirely in terms of the size of polymer chain in the eluent relative to the size of the pores. This condition constitutes the background of the Cassasa theory of K_{SEC}[11] and the universal calibration method.[12] On the other hand, in the IC separation process both ΔS° and ΔH° contributes to the solute retention. The sorption of polymer chains from the mobile phase to the stationary phase involves the conformational change of polymer chains, redistribution of solvent molecules associated with polymer chains as well as with stationary phase, and so on. Because porous packing materials are commonly used to increase the surface area of the stationary phase for efficient interaction, the conformational entropy change due to the size exclusion process also contributes to ΔS°. (In this case, ΔH° also becomes complicated because it should be dependent on the accessibility of polymer chains to the inner surface of the pores.) Therefore, both the SEC and IC separation mechanisms operate in the chromatographic separation of polymers when porous packing materials are used.

The separation condition determines which mechanism plays a dominant role. If the solvent strength is high (usually the case of thermodynamically good solvent in the absence of specific interaction between the polymer and the stationary phase), the polymer molecules are separated by the SEC mechanism eluting in the order of decreasing molecular weight before the injection solvent peak. If the solvent strength is not high enough, the IC mechanism plays a dominant role, and the polymers elute after the injection solvent peak and often in the order of increasing molecular weight. The schematic diagram shown in Figure 2.4 summarizes the chromatographic retention behavior of polymer solutes. The polymer solutes are separated by the SEC mechanism when the changes in the conformational entropy govern the distribution of the solutes between the stationary (pore space) and the mobile phase (interstitial space), and they elute before the injection solvent peak. If the interactions (either enthalpy or entropy driven) of the polymeric solutes with the stationary phase dominate the distribution equilibrium, the polymer solutes are separated by the IC mechanism and they elute after the injection solvent peak. Between the two limits, there exists a unique separation condition in which the molecular weight dependence of the solute retention disappears.

This is the point of enthalpy–entropy compensation that is known as the chromatographic critical condition.[13]

At this point, the polymer molecules of different molecular weights elute together. If such a coelution characteristic is maintained for a portion of a polymer chain, it would provide a unique opportunity to separate polymers according to the rest portion of the polymer chain, for instance, a specific block in a block copolymer or functional groups in a polymer chain while keeping the portion of the polymer chain at the critical condition from contributing to the retention. The term of "chromatographic invisibility" was proposed for this feature and the chromatographic separation utilizing this feature has gained wide popularity for the characterization of complex polymers.[14–16] This technique is variously termed as LC at the critical condition (LCCC), LC at the point of exclusion-adsorption transition (LC-PEAT), or LC at the critical adsorption point (LC-CAP).

2.7.2. Temperature Dependence of IC Retention and Martin's Rule

In the SEC analyses, ΔH° is usually made negligible by choosing strong solvent and inert packing materials. Therefore, the SEC retention does not show significant temperature dependence. On the other hand, the IC analysis relies on ΔH° of the solute distribution process, and the IC retention exhibits strong temperature dependence. In general, the solute retention in IC decreases with temperature increase, indicating that the solute sorption process to the stationary phase is enthalpy-wise favorable ($\Delta H^\circ < 0$). Also, in many cases, the sorption process appears entropically unfavorable ($\Delta S^\circ < 0$). This behavior is easy to comprehend because the adsorbed polymer chains should lose conformational degree of freedom (similar to the SEC process) while the sorption process should be energetically favorable to retain the solute in the column ($\Delta G^\circ < 0$). This is the enthalpy driven retention process often found in the IC separation. Less frequently, however, the contrary temperature dependence is found whereby the retention increases with temperature increase, indicating $\Delta H^\circ > 0$. In this case, the entropy change has to be positive to retain the solute in the column ($\Delta G^\circ < 0$). To put it another way, the sorption of polymer solutes to the stationary phase is driven by entropy increase.[17–19]

In the LCCC analysis of synthetic polymers, it is generally assumed that the unfavorable entropic effect due to the size exclusion mechanism ($\Delta S^{o} < 0$) is balanced by the favorable enthalpic effect due to the solute-stationary phase interactions ($\Delta H^{o} < 0$).[20,21] Consequently, it is expected that a homopolymer at the LCCC condition elutes independent of its molecular weight at the same retention volume that roughly corresponds to the total void volume of the column(s). However, the enthalpy and entropy compensation point can also be found for a process when both ΔS^{o} and ΔH^{o} are positive. For example, in the reversed-phase (RP) LC separation of poly(ethylene oxide) (PEO), enthalpy and entropy compensation was observed with the opposite entropic and enthalpic effects ($\Delta S^{o} > 0$ and $\Delta H^{o} > 0$), and the coelution retention volume was far apart from the total mobile phase volume.[17,19] In this case, the enthalpic and entropic effect of PEO sorption to the stationary phase is different from the usual LCCC separation. Such a compensation phenomenon is often found in the hydrophobic IC, a very useful LC technique in the separation of biopolymers, such as protein or nucleic acids.[22] The Martin's rule says that the interaction strength of polymer solutes (ΔG^{o}) is proportional to the degree of polymerization.[23] Accordingly, K (also k') increases exponentially with the degree of polymerization of polymer molecules, arising from the exponential relationship between k' and ΔG^{o} in eq 1.

Therefore, the IC retention of polymers changes very sensitively with molecular weight and synthetic polymers often exhibit extremely broad elution peaks due to their molecular weight distribution (MWD). To elute such a polymer sample in a reasonable experimental time period, it is necessary to change K during the elution. One method to control the retention is the solvent gradient elution, which changes ΔG^{o}, thus k', by increasing the solvent strength during the elution.[24] The solvent gradient HPLC fractionation of synthetic polymers works well, but it has a few drawbacks. It can cause significant background signal drift that makes it difficult to use many useful detection methods for polymer analysis such as differential refractometry, light scattering, and viscometry. An alternative method to control the retention is to change the temperature as easily inferred from eq 1. It is well known that temperature affects the IC retention and the temperature dependence of k' has been widely used to study the thermodynamics involved in the LC separation process.

In practice, however, temperature has not been widely employed as an experimental parameter because temperature is not a variable to control the retention as effectively as the solvent composition. It is mainly because the possible range of temperature variation is limited by the freezing and boiling of the mobile phase and the precipitation of polymeric solutes. However, temperature was found very efficient in controlling the retention in the MWD analysis of homopolymers, in particular, for polymers with narrow MWD.[25] We have utilized the method extensively for precise characterization of complex polymers and named the technique temperature gradient IC (TGIC).[25,26]

2.8. Vacuum Techniques and Glass Apparatus for the Anionic Polymerization

2.8.1 General Methods for Vacuum System

2.8.1.1 Vacuum System

The type of initiating system and the resulting anionic propagation reaction in the experiment were highly sensitive to traces of air or water. Therefore, very rigorous experimental conditions must be maintained in order to obtain quantitative data. A high-vacuum apparatus permits such rigorous experimental conditions. The type employed in this research is shown in Figure 1.4. It is primarily composed of a rotary pump and a diffusion pump. That rotary pump is capable of producing a vacuum of the order of magnitude of 10^{-2} torr and the diffusion pump can reduce the pressure in the system to 10^{-6} torr. The order of operation of vacuum system is as below,

* Set the trap and open the valve B to circulate the cooling water.
* Close the valve A and turn on the rotary pump and the diffusion pump.
* Open the valve C and valve F for 30 min.
* Close the valve C and open the valve D and E to reach the complete vacuum.
* Connect the glass apparatus for the experiment.

2.8.1.2. Treatment of Glassware

All kinds of glasswares were handmade in place on a metal supporting frame. A made apparatus was connected to the vacuum line and evacuated by rotary pump. Pinholes were checked with Tesla-coil to keep the complete vacuum conditions. After checking pinholes, this apparatus was evacuated by diffusion pump and baked with a hand torch adjusted to give a blue flame. This baking was accomplished 2 times, and the apparatus during this period was continuously being evacuated. After baking, the apparatus was allowed to cool to room temperature still under evacuation. The purpose of this treatment was to remove the adsorbed gas and water film on the surface of the glassware. Finally, the apparatus was heat-sealed at the constriction of under continuous pumping down.

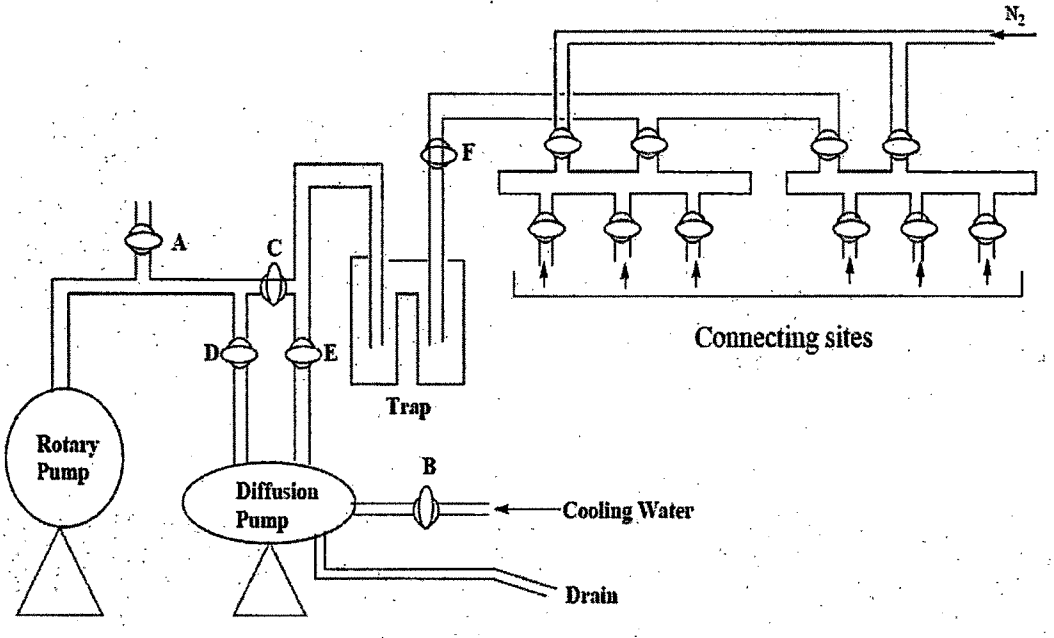

Figure 2.5. Vacuum line.

2.8.1.3. Removal of Air from Liquids

All materials employed in this work were degassed prior to any subsequent operation, such as distillation. The degassing procedure for liquids was carried out as follows. The flask containing the liquid to be degassed was connected to the vacuum line and then freezed by liquid nitrogen in Dewer flask, until it was frozen. Once the liquid contained in the flask was in a frozen state, it was evacuated by opening the stopcock between it and the vacuum line. After approximately 5 minutes, the stopcock was closed and the frozen material in reactor was thawed to a liquid state by warming to room temperature by means of an acetone bath. The freezing and thawing procedure was repeated 3-4 times. The material was then considered as degassed, and was ready for subsequent use.

2.8.1.4. Distillation of Liquids in a Vacuum System

The technique of handling volatile materials in a high vacuum system depends upon the fact that gases diffuse rapidly throughout a vacuum. This makes it possible to transfer volatile materials to any desired part of the system merely by cooling. In the absence of appreciable amounts of non-condensable gases, this transfer of volatile materials to a cooled zone takes place rapidly. However, in the presence of even small concentrations of non-condensable gases, the diffusion of the condensable molecules is hindered. It is necessary to keep the partial pressure of non-condensables below 10^{-3} torr, in order to affect quantitative transfer of condensable materials at a practical rate. Therefore, it is quite important to degas the liquids properly prior to distillation. A second factor influencing the rate of distillation of condensable vapors is the temperature of the cooling bath. Generally, liquid nitrogen bath is used for effective distillation.

2.8.2. Experimental Methods for the Polymerization in the Vacuum System

2.8.2.1. Distillation of the Monomers

Generally, anionic initiator and the propagating chain ends are highly sensitive to protonic impurities such as moisture and active hydrogen compounds. Thus, the purification of monomer was very carefully executed as the following procedure.

Monomer was dried overnight over calcium hydride and distilled under reduced pressure. The resulting monomer was distilled once more under vacuum with the apparatus shown in Figure 1.5. This joined apparatus was connected to the vacuum line and evacuated. After checking pinholes and 2 times of baking, it was sealed at the constriction J, and washing solution in the part of L was introduced into the reactor. After rinsing the glass-wall by back-distillation, the washing solution was collected to the part N and it was sealed off at the constriction M. The joint E was connected to the vacuum line and the upper side of the break-seal F was pumped down. Then, the break-seal F was broken, and the monomer was distilled again. After the distillation, the constriction denoted by I was sealed. The distilled monomer was sufficiently degassed, and the constriction G was sealed. The amount of the distilled monomer was estimated by the following equation.

$Wt_{distilled} = Wt_{fed} - Wt_{remaining}$

$Wt_{distilled}$ = Weight of distilled monomer.

Wt_{fed} = Weight of fed monomer.

$Wt_{remaining}$ = Weight of monomer remaining in the flask.

2.8.2.2. Dilution

The highly concentrated monomer or initiator in THF was divided to suitable amount for use in the anionic polymerization under vacuum. Figure 1.6 shows the apparatus for dilution. The glass apparatus was connected to the vacuum line and pinholes were checked. Being kept at 10^{-6} torr, the goblet apparatus was baked 2 times by a blue flame of a hand torch for 30 minutes. Desired amount of dry THF was vacuum-distilled into the part B from sodium-naphthalenide/THF solution in the round flask connected with the vacuum line.

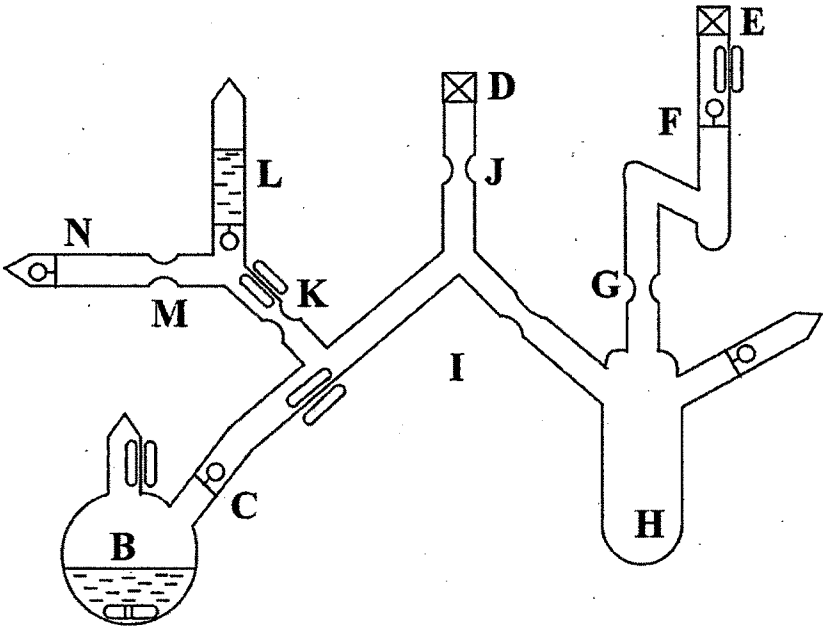

Figure 2.6. Apparatus for monomer distillation.

After several times of the freezing and thawing procedures, the apparatus was sealed off from the line at the constriction A. Distilled THF in the part B was mixed with washing solution by breaking the break-seal in the part C. A magnet enclosed with glass was used in order to break a break-seal. The inside of the apparatus was washed using this mixed solution in order to remove the remaining impurities. Then, the solution was gathered into the section F, and the inside-walls of the glass were rinsed by back-distillation using cool acetone. Finally, the part B was cooled with liquid nitrogen bath, and desired amount of THF was distilled into the part B from the section F *in vacuo*. The section F was sealed off at the constriction G. The residue of washing solution in the section F was gathered into the part D, which was heat-sealed at the constriction E. This ampoule containing the residue was used again as washing solution. The initiator or monomer in the part H was transferred into the part B by breaking the break-seal, and

uniformly mixed with finally distilled THF. This diluted solution was distributed to the each ampoule of the part I and sealed at the constrictions J.

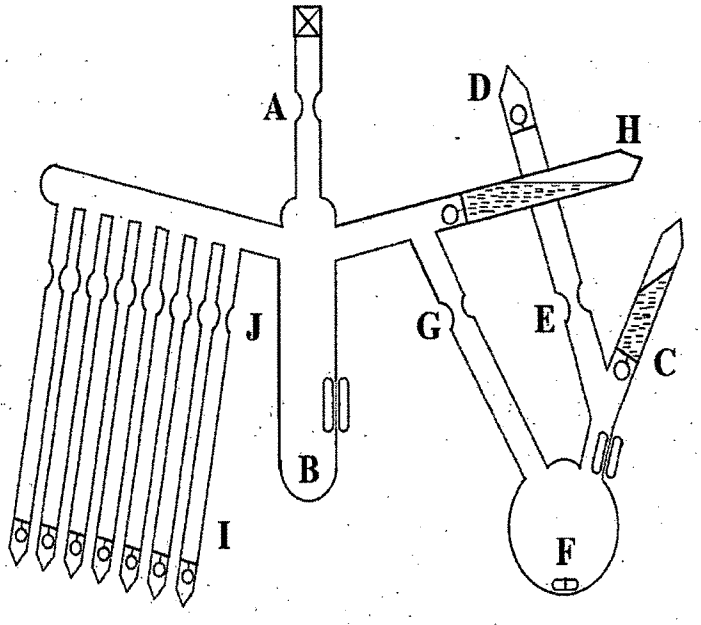

Figure 2.7. Apparatus for monomer dilution.

2.8.2.3. Titration of Initiator

The concentration of initiator was determined by titration with standard *n*-octyl alcohol in the ampoule with a break-seal under vacuum as shown in Figure 1.7. The apparatus was connected to the vacuum line, and pinholes were checked. Then, the apparatus was baked two times, being evacuated to 10^{-6} torr for 30 minutes, and sealed at the constriction A. Inside of glass-wall was purged using metal naphthalenide in THF (E). After washing, the washing solution was collected in the receiver ampoule G, which was sealed at the constriction B, and kept for the next use. Next, the initiator was introduced to the reactor C and titrated by standard THF solution of n-$C_8H_{17}OH$. Titration was carried out until the characteristic deep green color of the initiator became colorless. At that time, 1 mole of initiator reacts with 1 mole of *n*-octyl alcohol quantitatively to lose

its activity. The volume of the consumed THF solution of *n*-octyl alcohol was measured by marking the meniscus before and after titration.

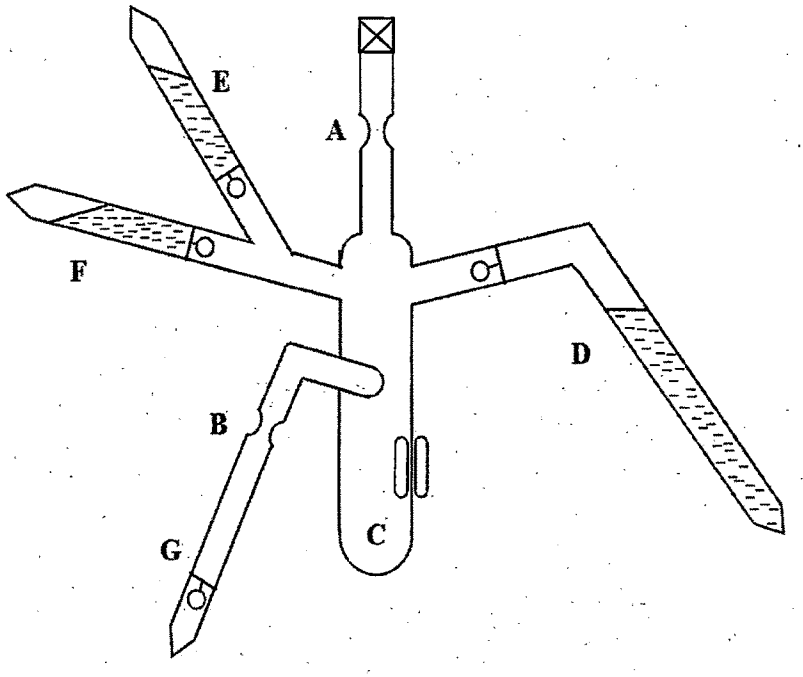

Figure 2.8. Titration apparatus (A, B: cutting point, C: main reactor, D: n-octyl alcohol. E: initiator, F: washing solution, G: receiver for washing solution).

2.8.2.4. Anionic Polymerization

2.8.2.4.1. Preparation of Constant-temperature baths

Since low temperature is suitable for anionic polymerization, constant-temperature baths were prepared according to the reaction conditions. Dewer flask was used in order to minimize heat transfer for maximum efficiency of the cooling bath. To obtain temperatures below room temperature down to 0 °C, an ice-water bath was used. For temperature down to –98 °C, using methanol with liquid nitrogen was prepared in Dewar flask. Dry ice (solid carbon dioxide) provides an easy way to obtain very low temperatures. For temperature down to –78 °C, a bath consisting of dry ice in acetone was used. Before polymerization, temperature of bath was measured using a thermometer (temperature ranges: –100 to 20 °C).

2.8.2.4.2. Polymerization

All the operations were carried out at various temperatures under high vacuum conditions (10^{-6} torr) in an all-glass apparatus equipped with break-seals as previously reported by Morton and co-workers.[27] The homopolymerization was carried out in a sealed glass tube equipped with breakable seals as shown in Figure 2.9. The apparatus was connected to the vacuum line followed by checking pinholes and baking, and sealed at the constriction A. The purging was carried out with washing solution. The washing solution was collected into the receiver D and removed from the apparatus by sealing at the constriction B. Initiator was introduced to the reactor C. Then, this reactor was cooled into the intended temperature using a cooling bath. The ampoule containing monomer was also cooled prior to introducing monomer. The break-seal F was broken and monomer was introduced into the reactor C, and then this reactor was shaken to mix the initiator introduced with monomer homogeneously.

The color of this solution changed from dark green to light yellow or transparent according to the initiator. The viscosity of this solution increased with elapse of the reaction time and the increasing rate of viscosity depended on which initiator was used. For example, in case of Li-Naph, the viscosity increased slowly, but in case of K-Naph, this solution became viscous fast. However, this increase of viscosity stopped at a certain time and the viscosity of this solution decreased as the time elapsed, which is due to degradation of growing polymer chains.

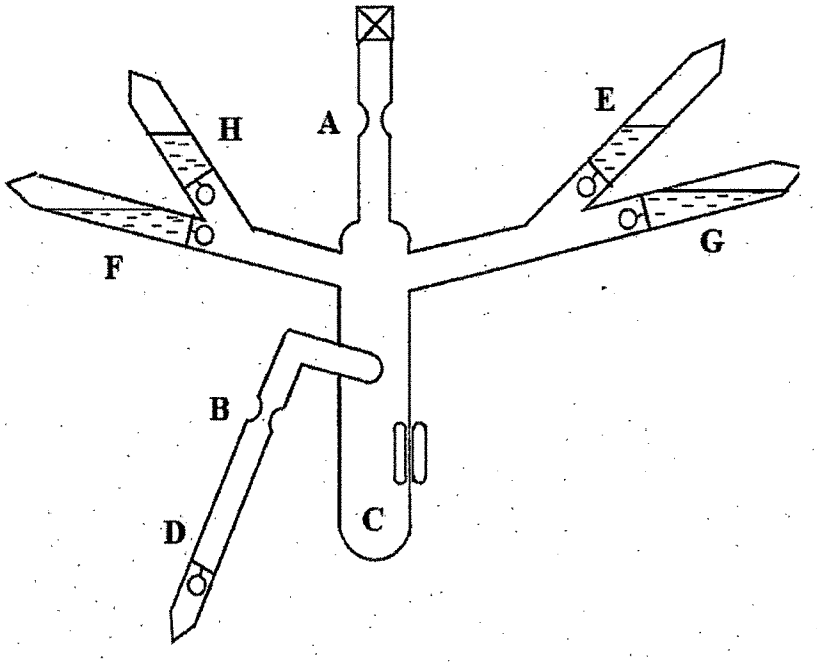

Figure 2.9. Apparatus for polymerization (A, B: cutting point, C: main reactor, D: receiver for washing solution, E: initiator, F: washing solution G: monomer, H: ligand (if used).

After polymerization for the required time, the reaction was terminated with acidified methanol. The reaction mixture was poured into a large amount of methanol, and the resulting polymer was precipitated, filtered, and dried. Precipitation was repeated to obtain highly pure polymer sample. This polymer sample was dissolved again in benzene and freeze-dried for characterization. After filtration, methanol soluble parts were analyzed quantitatively by weighing the residue after evaporation of methanol and using ^{1}H-NMR to check whether there were any unreacted monomer and/or trimers.

2.9. References

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