Synthesis, characterization and chemical modification of a novel cationic polyelectrolyte poly(methylene amine)

Dissertation

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Nihar Ranjan Kundu
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Dedicated to my parents

Jai Mata Di

Perseverance pays and pays substantially....

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List of Symbols

M_n Number Average Molecular Weight
M_w Weight Average molecular weight
M_w/M_n Polydispersity index
$[\eta]$ Intrinsic viscosity
T_g Glass Transition Temperature
T_m Melting Temperature
T   Temperature
λ The X- ray wavelength

List of Abbreviations

FT-IR   Fourier transform infrared spectroscopy   DLS   Dynamic Light Scattering

NMR   Nuclear magnetic resonance spectroscopy   SLS   Static Light Scattering

GPC   Gel permeation chromatography   AICC 1,1(azobis cyclohexanecarbonitrile)

PL   Photoluminescence spectra   AIBN Azobis isobutyronitrile

EL   Electroluminescence spectra   PMA   Poly (methylene amine)

TGA   Thermogravimetric analysis   THF   Tetrahydrofuran

DSC   Differential scanning calorimetry   cm   Centimetre

WAXD Wide–angle X-ray diffraction $CHCl_3$ Chloroform

RT   Room temperature   g   gram

DMSO Dimethylsulfoxide   MeOH Methanol

DMF   N,N-Dimethylformamide   nm   nanometer

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DMAc Dimethylactamide

NMP N-Methylpyrrolidinone

THF Tetrahydrofuran

mp Melting point

mol Mole

min Minute

IEP Isoelectric point

DEG Diethyleneglycol

$CDCl_3$ Deuterated Chloroform

CEVE Chloroethylvinylether

LPEI Linearpolyethyleneimine

LR Lawesson´s Reagent

NCA N-Carboxyanhydride

PDIm Poly(1,3-diacetylimidazole-2-one)

DADMAC Diallydimethylammonium chloride

MR Meerwein´s Reagent

TLC Thin Layer Chromatography

b.p Boiling point

UV/VIS- Ultraviolet Visible

BPMA-S Brush Poly(methylene amine)

BPVAm-S Brush polyvinylamine

SAXS Small Angle X-Ray scattering

PCD Particle Charge Detector

DMPU 1,3-Dimethyl-3, 4, 5,6 tetrahydro 2(1*H*)-pyrimidinone

PEG-400 = Polyethyleneglycol -400

PEI Polyethyleneimine

PCD Particle charge Detector

PES-Na Sodium polyethylenesulfonate

PVAm polyvinylamine

PFIm Poly(1,3-diformylimidazol-2-one)

PDADMAC Poly(diallydimethylammoniumchloride)

The past five decades have been characterized by the rapid developments in the field of macromolecular chemistry. This has led, as is well known, to a broader application of synthetic polymeric materials. Due to the increasing requirements of environmental and health protection, processes and applications involving water treatment have become more regulated. Therefore, the development of technologies for water treatment and wastewater processing has become necessary for the protection of aqueous resources. One group of specialty polymers which has become significant, due to the development of auxiliary materials, additives and finishing components, is that of the synthetic anionic and ampholytic water soluble polymers or polyelectrolytes.[1] Polymers containing stable primary amine functionality have been playing a leading role as materials for wastewater treatment and have established themselves commercially as potential candidates. This class of polymers has attracted attention not only for their ability to demonstrate pH dependent cationic nature, but also for the high reactivity of their pendant amino groups that make these polymers suitable for a host of applications through cross linking and derivatization.[2,3] Despite the huge commercial potential, these polymers have been inadequately explored. To date, only a few amine containing linear aliphatic polymers, such as polyethyleneimine, poly(diallyldimethylammoniumchloride), poly(allylamine) and polyvinylamine, have achieved a measure of commercial success.[4] Although, all of the above polymers bear amino groups yet the way they form a part of the main chain depends on their synthetic methodology. The number of amino groups and the way they are linked to the main chain largely decide the end use applications of these polymers.

1.1 A brief introduction to commercially available aliphatic polyamines

1.1.1 Branched polyethyleneimine

Polyethyleneimine (PEI) is the most important polymer among this class of materials due to its salient properties and commercial availability. Although, the linear polymer has the empirical formula $(C_2H_5N)_n$, a more accurate and widely accepted depiction of its structure is shown below (Figure 1.1).
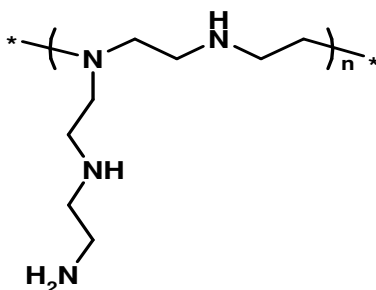
Figure 1.1 Structure of branched polyethyleneimine

Due to its versatile use, PEI is commercially available in a number of trade names like Polyaziridine, Corcat, Montrek, Polyamine and Polyamine P. Many commercial types of PEI are not linear but branched to different degrees. Consequently, the macromolecule contains three different types of amino groups; 2° and 3° amino groups in the main chain and 1° and 2° groups in the side chain. The relative ratios of 1°, 2° and 3° vary between 1:1:1 and 1:2:1 referred to primary, secondary and tertiary amine groups, but variable in principle, depending on the degree of branching.[5-7]

1.1.2 Synthetic Scheme for linear polyethyleneimine

Linear polyethyleneimine(LPEI) is obtained by cationic polymerization of cyclic iminoethers as oxazoline and oxazine derivatives producing a linear low molecular compound with a high crystallinity (Scheme 1.1).[8-10]
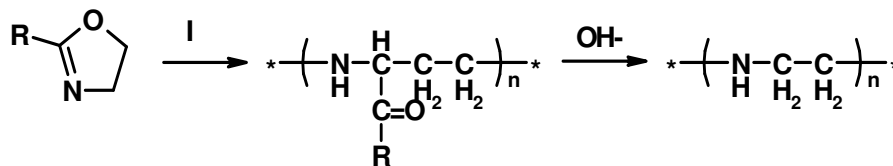
Scheme 1.1 Synthetic scheme for linear polyethyleneimine

Linear polyethylene imines contain only secondary amino groups in the main chain in contrast to commercial PEI with a branched structure.

1.2 Polyallylamine

The most important commercial monomers for polyallyamines include diallyldimethylammonium chloride(DADMAC), N-methyldiallylamine hydrochloride and allylamine.[11,12] The monomers are prepared by the reaction of allylchloride with dimethylamine, diethylamine, N-methylamine and ammonia, respectively. A typical reaction scheme for the synthesis of DADMAC is represented in Scheme 1.2.[1]
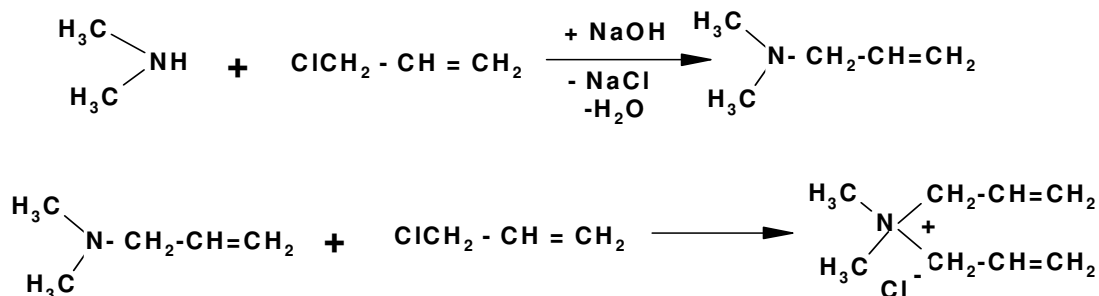
Scheme 1.2 Synthesis of DADMAC

The above synthesis is carried out by alkylation of dimethylamine with ally chloride in aqueous alkaline medium. Followed by purification, resulting in polymerizable monomer solutions.[13,14]

1.2.1 Synthetic scheme for poly(diallyldimethylammoniumchloride) (PDADMAC)

The monomer DADMAC is polymerized in both homogeneous and heterogeneous systems and the kinetics and mechanisms are investigated in aqueous solutions and inverse emulsions.[1,15] The structure of water soluble PDADMAC is established as cyclic as shown in Scheme 1.3. The mechanism of propagation is defined as an alternating intra-intermolecular chain propagation, later termed as "cyclopolymerisation".[16]
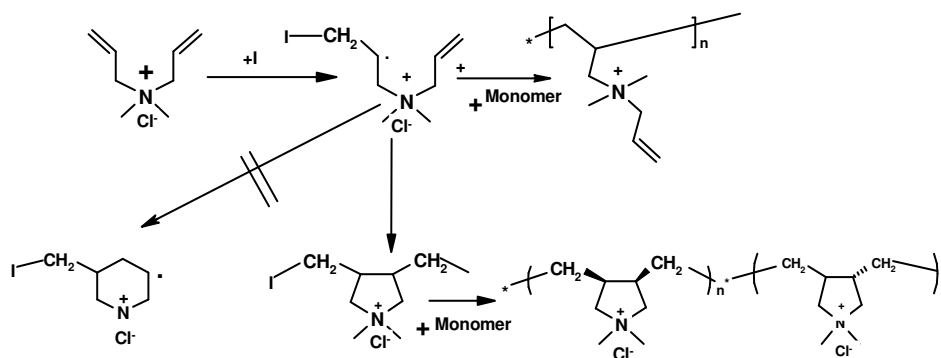
Scheme 1.3 The structure of water soluble PDADMAC

Based on the general scheme presented in scheme 1.3, the chemical structure of PDADMAC is determined by the ring size of cyclic units, portions of cyclic and linear structure units and extent of branching or cross linking resulting from the reaction of the pendant double bond.

1.3 Polyvinylamine (PVAm)

Polyvinylamine is the polymer with maximum content of amino groups available to date. This polymer, having one amino group on every alternate carbon atom, is well soluble in water and lower alcohols like methanol and ethanol. The simplest precursor to polyvinylamine, vinylamine monomer, is unavailable, because it tautomerises to acetaldehyde imine. Polyvinylamine can therefore be synthesized only via indirect routes. Attempts have been made to synthesize polyvinylamine from acrylic acid via Schmidt reaction[17] or from polyacrylamide via Hoffman reaction.[18-22] These methods suffer from incomplete conversion of the carboxylic acid and amide moieties to amines, from chain scission, and from a number of side reactions that give incomplete amine formation. Attempts have also been made to synthesize polyvinylamine via the hydrolysis of poly(N-vinylimide)s,[23-25] poly(N-vinylcarbamate)s[26] and poly(vinylacetamide).[27] The commercially available polyvinylamine is synthesized from low cost N-vinylformamide.

1.3.1 Synthetic scheme for polyvinylamine

Polyvinylamine is prepared by acidic or basic hydrolysis of amide functionalities on poly (N-vinylformamide). Poly(N-vinylformamide) is obtained through free radical polymerization of N-vinylformamide. The monomer displays high reactivity towards homo-and copolymerization. Thus, N-vinylformamide is polymerized to polyvinylformamide via a number of polymerization techniques that include bulk, solution, precipitation and inverse emulsion polymerization.[28,29] The subsequent basic or acid hydrolysis of the polyvinylformamide results in polyvinylamine and polyvinylamine hydrochloride (PVAm.HCl), respectively, as represented in Scheme 1.4.
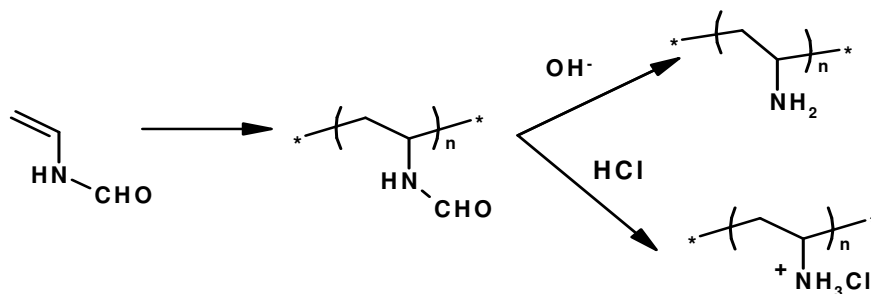
Scheme 1.4 Preparation of polyvinylamineamine and polyvinylamine hydrochloride

Commercially viable synthetic methodology coupled with high charge density has made polyvinylamine a leading retention aid in paper industries and a flocculant in waste water treatment.[2,30]

1.4 Applications of polyamines and their hydrochlorides

The applications of polyamines are quite numerous and can be broadly categorized into two major sectors. The first arising from cationic charge density and molecular weight and other stemming from highly reactive pendant amino groups. Majority of applications are governed by the cationic charge density of these polymers. Some of the most important and well- established applications are discussed below.

1.4.1 Paper manufacturing

Amine containing cationic polyelectrolytes are used in paper and textile production as retention aids, for coagulation, flocculation, wet and dry strength, dry strength improvement, dewatering, color fastness, dye fixation, antistatic agents and antimicrobial treatments.[1]

A. Retention and drainage agents

Paper machines operate through a series of continuous processes, which include forming, dewatering, pressing and finally drying a web of paper fibers.[31]Basically, a dilute solution slurry is applied onto a continuous wire screen which can have several configurations. Retention is a measure of the material that remains on the paper machine wire and is incorporated into the final sheet. Retention occurs by filtration and adsorption onto the fibers via the formation of secondary chemical bonds. Drainage implies the removal of water from the paper machine. Copolymers of acrylamide and DADMAC are widely employed as retention drainage agents.[32] PVAm.HCl with M_w >100,000 and PVAm.HCl modified with lower aldehydes are used as filler retention agents especially for use with recycled fiber.[2]

B. Wet strength additives

Wet strength is a desirable attribute in many paper products including napkins, paper towels, house hold tissues and disposable hospital wear, all of which come in contact with water during their use. Typically they lose 95% of their strength when saturated with water. Wet strength additives function by forming covalent bonds between fibers and generating their own cross-linked network. This enhances the dry strength of the paper as well. Permanent wet strength additives retain strength of the paper to a tune of 50% of its original strength on 5 minuets exposure to moisture in comparison with temporary wet strength additives after the same exposure period. Some of the temporary wet strength agents

are based on glyoxylated acrylamide–DADMAC copolymers, as in case of some commercial products (Parez 631 NC, manufactured by Cytec and described by Cosica *et.al*).[33,34 3,35,36]

1.4.2 Mining industry

Amine containing polymers are widely used for solid-liquid separation of different slurries in mining industry. Specific examples of the minerals treated with these polymers include coal, taconite, trona, sand gravel and titania slurries. By far, DADAMAC and its copolymers are reported in the patent literature. The claims in these patents include;

1. Recovery of clean coal and the reduction ash content through the use of (PDADMAC).[37]
2. Separation of gangue from coal in a coal refuse slurry in a multi stage separation process.[38]
3. A method for dewatering coal tailings and clean coal products by the use of copolymers of DADMAC and vinyltrialkoxysilane.[39]

It has been indicated that branched DADMAC displayed improved dewatering performance over its linear counterparts and other cationic and anionic acrylic polymers. Improved dewatering of waste solids generated in common mining processing operations is claimed by the use of hydrophobically modified copolymer of DADMAC and acrylic monomers. DADMAC–vinyl trialkoxysilane copolymers and copolymers of DADAMAC and acrylamide cross-linked with triallyamine.[40,41] Besides, DADMAC-PVAm.HCl is reported to be quite useful for enhanced oil recovery. High molecular weight PVAm.HCl maintains high viscosity under stimulated drilling conditions, as is required for acidified fracturing fluids and sea water drilling muds.[42] PVAm derivatives are also useful in metal complexation.[2]

1.4.3 Water treatment industry

Polyamines are widely used as flocculants for waste water treatment. Ever since, PDADMAC was employed for this application successfully,[43] there has been a constant

urge for improvement on the commercial viability, process viability and discovery of novel cationic polyelectrolytes. As amine-containing polymers are widely used as flocculants in wastewater treatment, it would be interesting to describe in brief, the role of a cationic polyelectrolyte as a flocculant.

Role of a cationic polyelectrolyte in coagulation and flocculation

Impurities present in raw water are in suspended, colloidal, and dissolved forms. These impurities are dissolved organic and inorganic substances, microscopic organisms, and various suspended inorganic materials. In order to coagulate into particles (agglomerate) the suspended materials are destabilized followed by their removal through filtration. Colloidal material is the most difficult to remove from raw water. Processes that remove colloids from water also remove suspensions.

Colloids have an extremely small size (approximately 0.0001 to 1.0 microns) and a large surface area in relationship to their weight. Because of these factors, they do not readily settle out of solution.

Electrical charge

Most colloids found in water show a negative charge. Because like charged particles repel, colloidal material will not join to form suspended particles unless the particles' electrical charge is reduced or neutralized.

I. Coagulation principles

In coagulation, a chemical (polymer) is fed to the raw water to neutralize and destabilize particle charges on the colloids as shown in Figure 1.2. Destabilized colloidal particles adhere to each other.
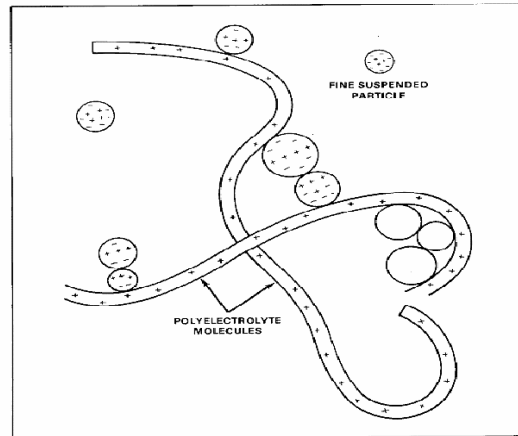
Figure 1.2 Formation of a floc particle.

Because many colloidal particles are present in the water, charge neutralization among all particles requires immediate and even dispersion of the coagulant. The destabilization reactions occur very rapidly. Therefore, incomplete or slow mixing results in wasted chemical and uneven flocculation.

II.Principles of flocculation

Once colloidal destabilization has occurred, random motion of particles causes their collision, resulting in formation of a larger particle or floc. These neutralized particles stick together forming floc masses (Figure 1.3). Bacteria particles are also neutralized (but not physically deactivated) and become entangled in the floc. As this process continues, particle size and weight increase to a point where the larger floc can be removed by filtration.
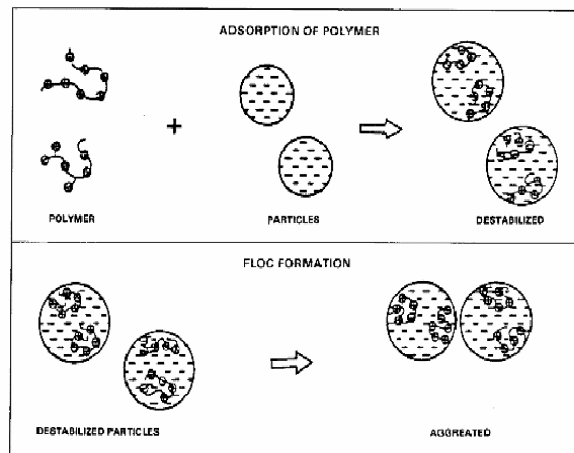
Figure 1.3. Floc formation process

Although, the mechanism of flocculation is very simple yet there are several factors that influence coagulation and flocculation such as turbidity, pH and color of raw water and physical factors like temperature, presence of nuclei and flash mixing. The coagulant dosage and nature of coagulant is optimized through a series of trial runs of the equipments. Furthermore, in order to enhance the effect and expedite the process of flocculation, chemical aids are used. These chemical aids are polyelectrolytes of high molecular weight. These synthetic polyelectrolytes are available in anionic, cationic and neutral forms. The anionic and non-ionic forms are generally used as flocullant aids, while cationic ones are used as primary coagulants or coagulant aids. The strength of the polymer solution is usually 1% or less since more concentrated solutions can start to solidify causing clogging or feeding devices or valves. The advantage of using cationic polyelectrolyte lies in their ability to produce very large and dense floc that can dramatically increase the rate of particle removal. In addition, the polymers are easily influenced by pH of water, alkalinity, hardness and turbidity in comparison to other chemical aids.

1.5 Derivatization of amines

Apart from well-established applications of amino containing polymers by virtue of their cationic nature, the nucleophillicity of the pendant amino group leads to an array of novel materials through polymer analogous reactions with electrophiles.[44,45]These modifications are carried out to achieve desired properties in the modified polymer through introduction of moieties that impart specific properies. For instances, introduction of ester linkage on the polymer through Michael addition of acrylic acid derivatives such as ethyl acrylate and acrylonitrile results in new structures.[46] The hydrolysis of the ester linkage generates acid groups making the polymer a polyampholyte. Incorporation of photoactive units like cinnammoyl chloride on to the polymer makes it photo crosslinkable. Some of the major areas of application are discussed in detail.

1.5.1 Photosensitive polymers

Here, the modification of macromolecular structures and materials have been attained photochemically using cinnamic acid derivatives.[47-50] Interestingly, for some of these applications the expected dominant effect is not conventional cross-linking. Stepwise photo coupling of low or medium molecular weight compounds to polymeric surfaces or into polymer matrices was achieved and studied for improving the biocompatibility of synthetic implants and for improving the durability and performance of nonlinear optically active materials. Self–organizing materials based on di- or tri-block polymers were crossed-linked in the presence of a block selective solvent by means of cinnamate dimerization for obtaining permanent stabilization of the lyotropic mesophase or for producing nanospheres from vesicles. Thermotropic liquid crystalline systems have also been designed with inclusion of dimerizable chromophore of the cinnamic type as comonomer unit. In liquid crystal display technology, cinnamoylated polymer photochemistry conducted under polarized light recently proved to be very efficient to obtain alignment layers. The modified polymers with cinnammoyl moiety undergo facile cross-linking via [2+2] photocycloaddition of cinnamide side groups.[51] The cross linked

polymer chains are bridged by cyclobutane formation(Figure1.4).[52] The amino functionality of the polymer is well suited to achieve partial functionalization by coupling with electrophilic reagents to yield reactive polymers while presenting hydrophillicity together with good aptitude for giving specific interactions through covalent coupling, ionic association or chelate formation.[53]
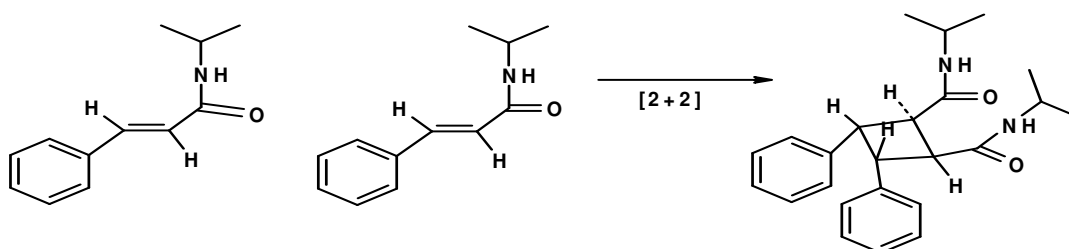
Figure 1.4. Simplified sketch of the photocrosslinking process via β-truxinic diamide.

1.5.2 Brush polymers

Polymer brushes are systems in which chains of polymer molecules are attached through an anchor group to a surface, to an interface or to the backbone of another polymer in such a way so that the graft density of the polymer is high enough to stretch the attached chains away from the main backbone resembling a brush like conformation as shown in Figure 1.5.[54] Stretching of the chains is triggered by their overlapping with chains in the vicinity and the effect becomes pronounced with the increase in graft density.[55]

a   **b**
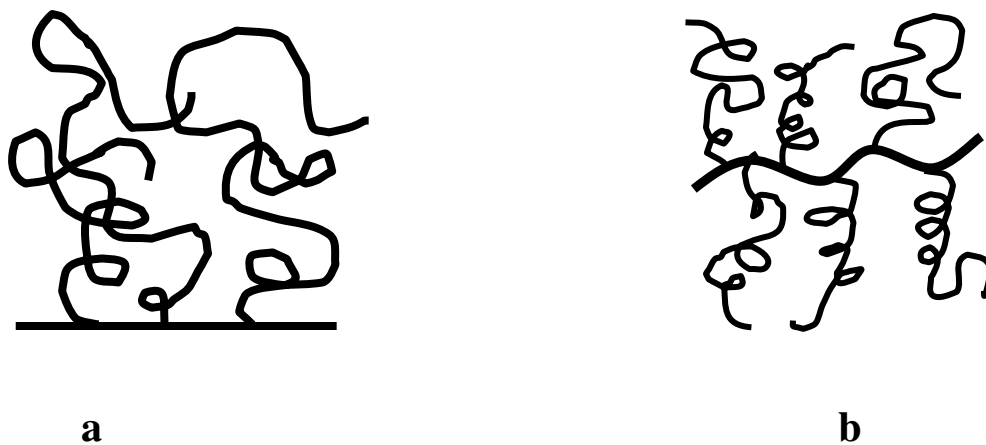
Figure 1.5 Schematic representation of brush regimes (a) at a solid surface (b) chains attached to the back bone of another polymer.

These brushes at solid surfaces are formed either by adsorption of charged block copolymers from solution or by anchoring amphiphillic, charged block copolymers at the air-water interface, compression and subsequent transfer of the layer to a solid substrate. Another widely used method these days is, the attachment of polymer chains to the surface of a substrate via chemical linkage. Generally, attachment of polymer chains chemically onto a surface is carried out in one of two ways (1) linking of reactive end groups of the attachable polymer to the appropriate reactive site on the surface of anchor, the so called "grafting to" procedure; (2) the formation of a surface monolayer with an initiator attached onto the surface of the anchor as shown in Figure 1.6.This initiator layer is subsequently used for polymerization of the monomers. The formed polymers are projected out like bristles. The process is termed as "grafting from" or surface initiated polymerization. In normal practice the anchoring surface is mica, glass or gold substrates. These surfaces are coated with a layer of immobilized-initiator that subsequently initiates the process of polymerization emanating from the surface. The surface initiated polymerization method is preferred over "grafting to" method in eliminating diffusion barrier which strongly limits film growth.[56-58]

1. Grafting to procedure

2. Grafting from procedure
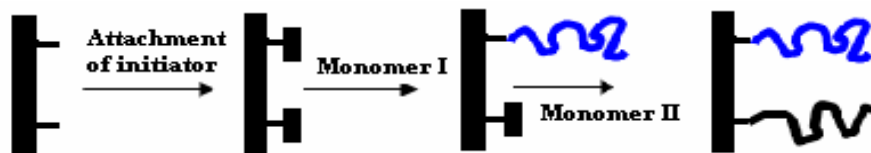
Figure 1.6 Schematic representation of "grafting to" and "grafting from" approaches for synthesis of binary polymer brushes.

Following a similar path, the synthesis of a mixed brush polymer is realized.[59,60]Usually, neutral homopolymer brushes are synthesized by "grafting to" or "grafting from" method

and the second homopolymer is then grafted in the next step. Finally, the mixed polymer brush is prepared from the mixed neutral brush with an appropriate polymer.[61-63] Efforts are also ongoing to use poly(methylene amine) as well as polyvinylamine as anchors to brush polymers via "grafting from" approach.

1.5.3 Polyampholytes

Polyampholytes are charged macromolecules carrying both acidic and basic groups.[64,65] Under appropriate conditions, such as in aqueous solutions, these groups dissociate into ions. The ionization results in positively and negatively charged groups on the polymer chain.

If these groups are weak acids or bases, the net charge of the polymer chain can be tuned by varying the pH. At a particular pH, called the isoelectricpoint (IEP), the negative charge balances the net positive charge. At this pH there is equal number of positively and negatively charged species on the polyion. In the vicinity of isoelectric point(IEP), the polymers exhibit the unusual properties of polyampholytes. At higher charge asymmetry, i.e. far above and far below the IEP, these polymers demonstrate typical polyelectrolyte behavior.[66-73]

Polyampholytes have attracted wide spread interest because of their complex solution properties. Ampholytic polymers in dilute solutions typically exhibit unique globule to coil transition with increasing electrolyte concentration. Such transitions are accompanied by increases in the hydrodynamic volume and solution viscosity, this phenomenon is often called anti-polyelectrolyte effect.[74-80] Polyampholyte solubility and solution properties are governed by a complex interplay of polymer-solvent and polymer-polymer interactions. Polyampholyte or polyelectrolyte solution behavior can be elicited by changes in the solution pH, and thus systems with pH triggerable solution properties are possible. Such pH responsive polyampholytes are well suited for applications requiring triggerable changes in the solution viscosity, including enhanced oil recovery and the formulation of coating, cosmetics, and personal care products.[81-83]

These polymers are usually prepared by free radical polymerization. The free radical polymerization can proceed by several routes, such as copolymerization of acidic and basic vinyl monomers like acrylic acid and dimethylaminoethylmethacrylate resulting in random copolymers, polymerization of ampholytic ion-pair co-monomers in solution or emulsion polymerization of sulfobetaine or carbobetaine monomers. The structure of these polymers is shown in Figure 1.7.[68,84,85]
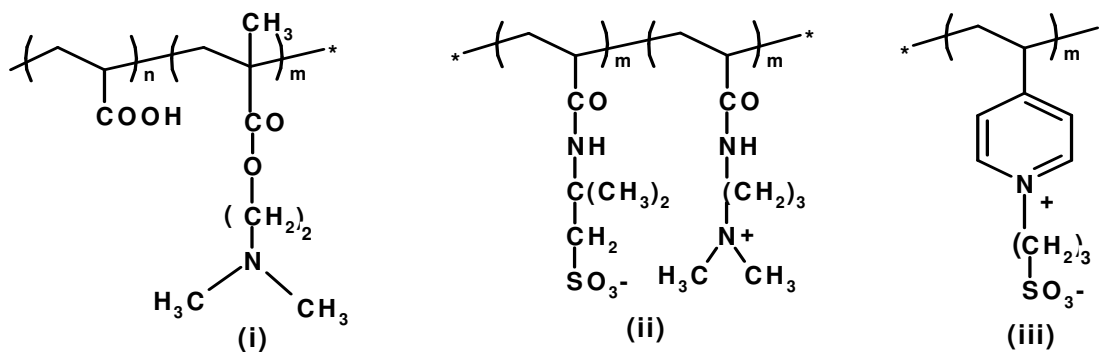
Figure1.7 Polyampholytes (i)Random copolymer from acrylic acid and dimethylaminoethylmethacrylate.(ii)Copolymer from an ion pair (iii)polymeric sulfobetine from a betaine monomer.

Polyampholytes have also been synthesized through polymer modification reactions. Some typical examples include aminolysis of alternating copolymers of maleic anhydride with excess diamines leading to regular polyampholytes containing amine and carboxylic groups. Hydrolysis of cyclic polymers containing amide bonds in the ring (Figure1.8), which can readily be prepared by cyclopolymerization, results in regular polyampholytes. Hofmann degradation of polyacrylonitrile provides a simple route to a random copolymer of acrylic acid and vinylamine. The reaction of polyacrylonitrile with dicyandiamide as well as with hydroxylamine leads to polyampholytes, which are soluble only in acidic or basic media.
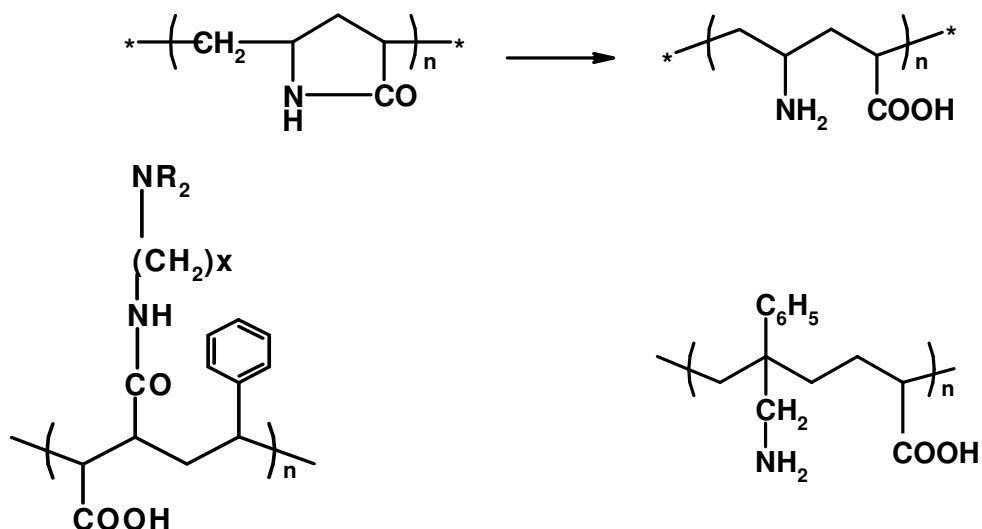
Figure 1.8 Polyampholytes obtained by polymer modification

Between pH 3-9 these polymers are insoluble in water, forming rapid sedimenting flocks that can be used as organic primary flocculants and for the immobilization of heavy metals. [68,86]

1.6 Recently developed synthetic methodologies towards amine-containing polymers

Versatility of application coupled with industry needs has been driving researchers every where towards the development of novel synthetic routes to polyamino polymers. As a result, a number of synthetic routes have been proposed and realized. One of the striking methods is modification of poly(chloroethylvinylether). The monomer chloroethylvinylether (CEVE) can be polymerized in a cationic living way,[87] subsequently the chloro groups can be substituted to obtain tailor made functional polymers.[88,89] Several substitution reactions were performed with the anions of pyrrolidone,[88] succinimide, imidazole and pyrazole.[90] Hashimato *etal*. followed by Velde *etal*. developed an efficient route to linear amino containing polymers through

substitution of potassiumpthalimide onto backbone of poly(chloroethylvinylether). Upon hydrolysis gave polyamino(ethylvinylether) (Scheme 1.5).
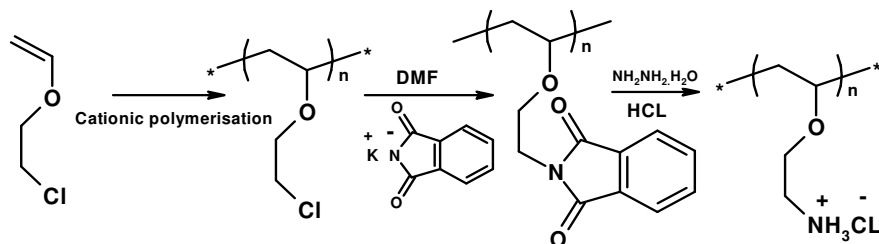
Scheme 1.5 Synthesis of polyamino(ethylvinylether) hydrochloride

Toste *et.al.* recently discovered a novel route to polyethyleneimine through controlled radical polymerization of aziridines via anionic ring-opening polymerization of N-mesylaziridine (Scheme 1.6).[91] The route leads to polyethyleneimine with narrow dispersity (Polydispersity index = 1.06).
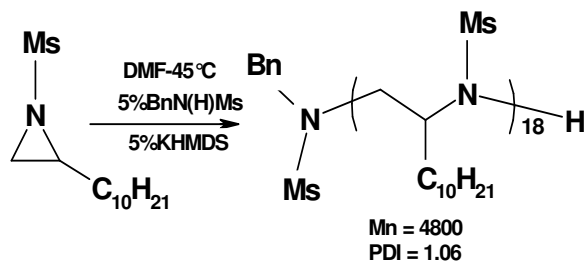
Scheme 1.6 Synthesis of polyethyleneimine from 2-n-decyl-N-mesylaziridines.

OBJECTIVES AND MOTIVATION

The synthesis of polymers containing stable primary amine functionalities has long been a dream of polymer chemists primarily for following reasons.[92] The amino groups on the polymer backbone are highly reactive; as a result these polymers are well suited for derivatization as well as cross linking agents. In addition, linear aliphatic polyamines demonstrate high cationic charge density at low pH values.[92] The existing polymer with maximum number of amino groups on polymer backbone, poly (vinylamine), has one amino group on every alternate carbon atom. The versatility of application of this polymer such as flocculation of particulate matter from turbid natural wastes, sludge dewatering besides functionalization, grossly depends on the cationic charge density and molecular weight.[93] This prompts us to synthesize the lowest homologue in the aliphatic polyamine series, poly(methylene amine) that outweighs all the existing amines in maximizing the number of amino groups on the polymer backbone. The maximum cationic charge density on the polymer backbone would make it a potential candidate for wastewater treatment, paper retention aid and numerous polymer analogous reactions leading to novel materials.

Objectives:

The objectives of the current work are as follows:

1. To synthesize precursors leading to poly(methylene amine) and improve the molecular weights by adopting different polymerization techniques.

2. To investigate the prospects of poly(methylene amine) as a novel polyelectrolyte through evaluation of its properties such as charge density, hydrodynamic radius, diffusion behavior, shape of the polymer etc. by using advanced characterization techniques like laser light scattering, GPC-MALLS, Particle charge detector (PCD) etc..

3. To functionalize poly(methylene amine) in order to achieve novel materials and explore their applications and evaluate the properties against its upper homologue polyvinylamine.

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SYNTHESIS OF PRECURSORS

OF POLY(METHYLENE AMINE)

2.1 Introduction

Synthesis of poly(methylene amine) via direct polymerization of 1,2-diaminoethene was not possible due to tautomerization of the monomer leading to non-polymerisable azomethine structure. Thus, like in the case of the synthesis of its upper homologue, polyvinylamine, the amino groups directly linked to the polymerizable double bond needed protection with hydrolysable groups. An easy yet seemingly feasible route to target polymer was to polymerize protected 1,2-diaminoethene monomers and subsequently, to remove the protecting groups by acid or basic hydrolysis so as to liberate free amine groups. Thus, a series of protected diaminoethene was synthesized via Bamberger cleavage of imidazole.[1,2] A typical experiment involved the treatment of an aqueous solution of imidazole with ethylchloroformate[2] while maintaining the pH of the system between 7-8 [1,3] (Scheme 2.1). The resulting white precipitate was filtered, washed extensively with water and recrystallized from aqueous alcohol into white needle like crystals (yield=60%). The structure of the monomer **1** was established by IR, ^{1}H-NMR, ^{13}C-NMR, UV spectroscopy and melting point determination. All the attempts made by BASF[4] to polymerize these monomers via radical polymerization yielded oligomers. The use of different initiators like dicumyl peroxides, di-tertiary butyl peroxides, azo initiators or changes in reaction conditions did not improve the molecular weight. The lack of reactivity was ascribed to shielding of the polymerizable double bond by protecting groups.
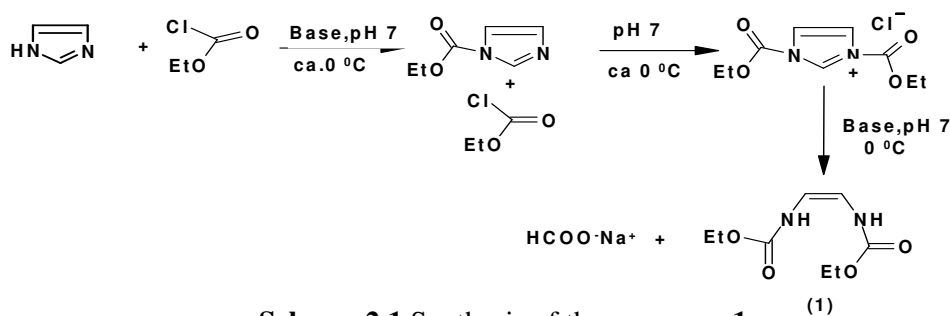
Scheme 2.1 Synthesis of the monomer **1**

2.2 Work Plan

As already investigated by BASF and described above, the monomers based on diaminoethene did not lead to polymers with high molecular weights. The reason for obtaining olegomers was attributed to the shielding of double bonds by protecting groups as well as ene-amine tautomerism resulting in delocalized double bond. Thus, to achieve high molecular weight precursors of poly(methylene amine), the above mentioned drawbacks must be overcome. To circumvent these problems, cyclization of the molecules based on 1,2-diaminoethene to form rings and synthesis of novel cyclic monomers were considerd worth investigating. Therefore, the underlying work narrates the synthesis of cyclic monomers based on 1,2-diaminoethene backbone. In addition, attempts have been made to polymerize these monomers under different experimental conditions to achieve maximum possible molecular weight precursor polymers of poly(methylene amine).

2.3 Synthesis of cyclic monomers

1,3-*2H*-4-imidazoline-2-one(2), 1,3–diacetyl-1,3-dihydroimidazol-2-one(3), 1,3-Diformyl-1,3-dihydroimidazole-2-one(4), 1,3-dicarbethoxyimidazoline-2-one(5)

1,3-Diacetyl-1,3-dihydro-imidazole-2-one(**3**) was synthesized from commercially available α-aminoactealdehyde acetal, in three steps (Scheme 2.2). In the first step α-aminoacetaldehyde acetal was reacted with potassium cyanate in the presence of hydrochloric acid to obtain ureidoacetaldehyde acetal. Ureidoacetaldehyde acetal was cyclizized to 1,3-2H-4-imidazoline-2-one(**2**) in presence of sulfuric acid.[5-7] The compound **2** was refluxed with acetic anhydride to obtain 1,3-diacetyl-1,3-dihydro-imidazol-2-one(**3**). The structure of **2** was confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The IR spectrum of the compound **2** displayed characteristic bands at 3145 cm^{-1} (N-H stretching vibrations), 1250 cm^{-1} (N-C bending amide) and 1713 cm^{-1} (carbonyl stretching vibration). The ^{1}H-NMR spectrum, in DMSO-d$_6$, displayed signals at 6.2 ppm and 9.75 ppm arising from –CH and – NH groups, respectively. ^{13}C-NMR showed two signals, one at 155 ppm for C=O group and the other at 108 ppm for C-H groups.
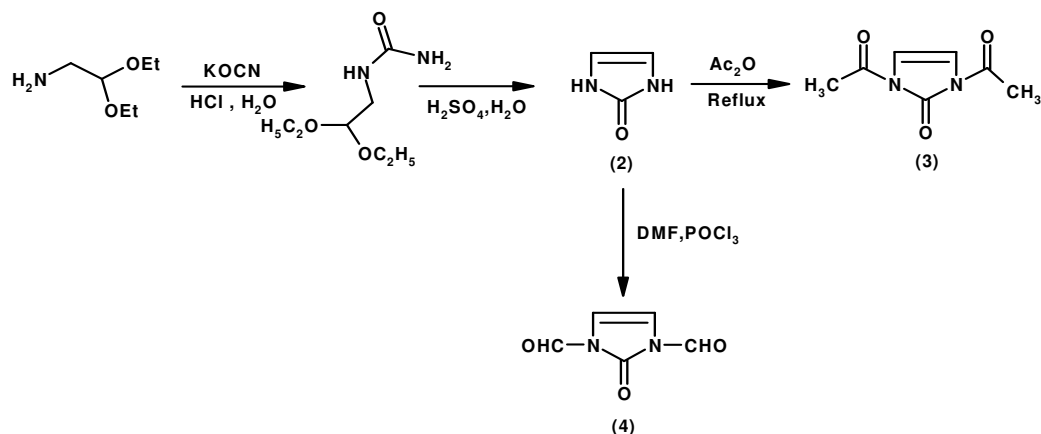
Scheme 2.2 Synthesis of monomers **3** and **4**

The structure of **3** was similarly confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. Characteristic bands appeared in IR spectrum of this compound at 3130 cm^{-1} (stretching vibrations of CH=CH groups), 1760 cm^{-1} (C=O stretching vibration of acetyl group) and 1713 cm^{-1} (C=O stretching vibrations of the ring). ^{1}H-NMR spectrum of **3** showed two signals, one at 7.0 ppm that characterized the protons of CH=CH group and the other at 2.61 ppm that characterized protons of CH$_3$ groups of the compound (Figure 2.1).^{13}C-NMR spectrum showed peaks at 168 ppm for C=O of acetyl groups, at 149 ppm for C=O groups of the rings, at 109 ppm due to CH=CH groups and at 24 ppm due to CH$_3$ groups.

Monomer **4** was synthesized from **2** by using a mixture of dimethylformamide (DMF) and phosphorus oxychloride (POCl$_3$). DMF in excess was used as solvent. In another procedure 1,2-dichloromethane was used as solvent, according to a method described in the literature.[8] The resulting monomer was further purified by sublimation. The structure of the compound **4** was identified by IR, ^{1}H NMR and ^{13}C-NMR spectroscopy. In the IR spectrum characteristic bands appeared at 1770 cm^{-1} arising from lateral C=O groups and at 1740 cm^{-1} due to presence of the carbonyl of the rings. ^{1}H-NMR spectrum showed two signals; one at 7.2 ppm due to presence of –CH groups and the other at 9.05 due to presence of lateral formyl groups.
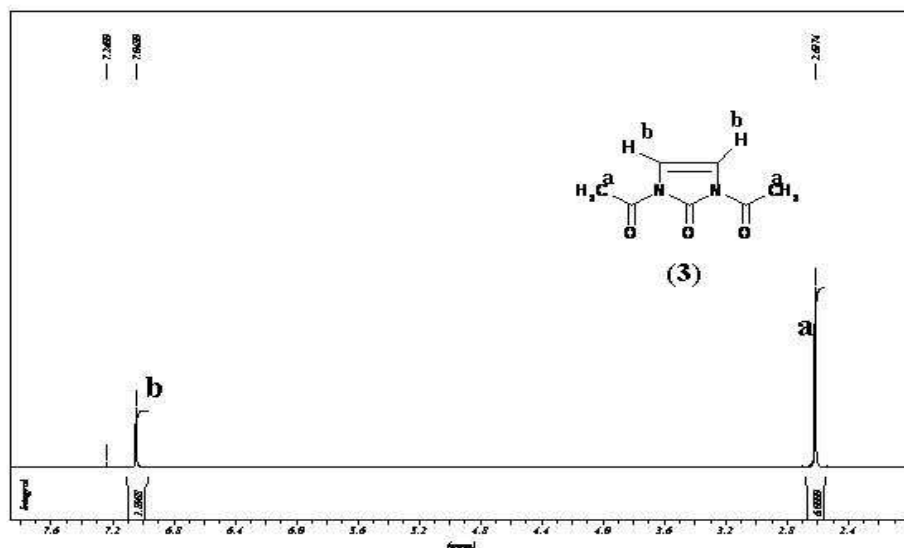
Figure 2.1 [1] H-NMR (250 MHz) of 1,3 –Diacetyl-1,3-dihydroimidazole-2-one**(3)** in CDCl$_3$.

Monomer **5** was synthesized from **1** by cyclization with phosgene as represented in scheme 2.3. Solution of **1** in dry THF was treated with PhLi (phenyl lithium) followed by dropwise addition of a solution of phosgene in toluene. The product was eluted through a column of silica gel with 20% acetone in high boiling petroleum ether. Pure product was isolated in 22% yield.
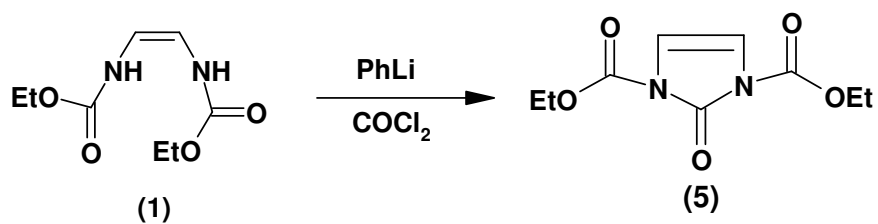
Scheme 2.3 Synthesis of the monomer **5**

2.4 Radical polymerization of the cyclic monomers 2, 3 & 4

Radical polymerization of **2** was carried out in bulk as well as in solution. The polymerization of **2** in solvent such as DMF or NMP yielded oligomers. Polymerization reactions in bulk were also unsuccessful owing to partial decomposition of the monomer at elevated temperature, required to obtain a melt.

(mp.of **2** 242 °C). A possible explanation for low reactivity of **2** towards radical polymerization is the generation of a stable radical 2-hydroxyimidazol that shows no tendency to polymerize due to its aromatic character (scheme 2.4).
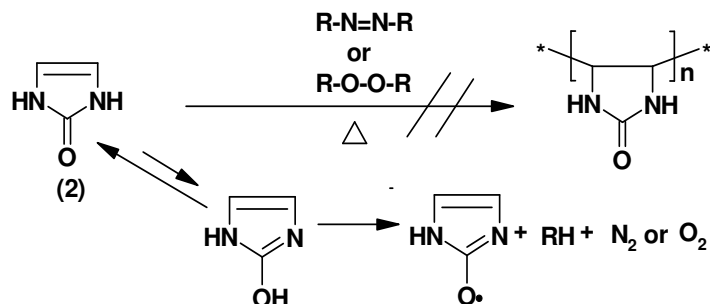
Scheme 2.4 The formation of radical 2-hydroxyimidazole

2.4.1 Radical polymerization of 1,3-diacetyl-1,3-dihydro-imidazol-2-one(3).

Monomers 1,3-diacetyl-1,3-dihydro-imidazole-2-one**(3)** and 1,3-diformylimidazole-2-one**(4)** were polymerized in bulk as well as in solution. The lateral acetyl groups of symmetrical monomer **3** not only protected the amino groups but also lowered the melting point of the compound (mp.102^{0}C) allowing bulk polymerization at reasonable temperature. In addition, the ring structure of the monomer limits the rotation of the acetyl groups in comparison to open structures based on 1,2-diaminoethene derivatives.
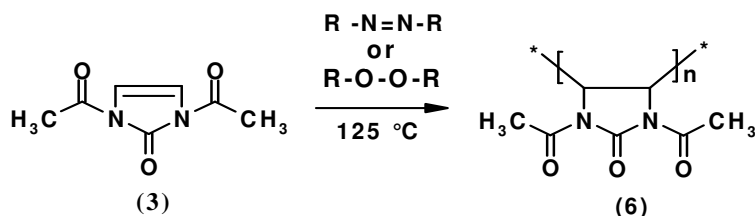
R-N=N-R = 1,1`Azobis(cyclohexanecarbonitrile)

R-O-O-R = t-Butylhydroperoxide

Scheme 2.5. Radical polymerization of 1,3-diacetyl-1,3-dihydroimidazol-2-one**(3)**

The monomer **3** was homopolymerised by radical polymerization using azo and peroxides initiators (scheme 2.5). The polymerization was performed in bulk by heating the monomer up to 140 °C. The solution of the initiator in suitable solvent

was introduced at this temperature. The investigations with tertiary butyl-hydroperoxide as initiator showed that radical polymerization of **3** in bulk was not linearly dependent on quantity of initiator. It was assumed that at 120 – 130 °C this initiator generated high concentration of radicals. The reaction was exothermic and took place instantaneously, in a minute or so. The reaction was difficult to control. The other disadvantage of the reaction was the loss of appreciable amount of monomer arising from its sublimation during heating up to 120-130 °C. This led to a decrease of yield as well as to inconsistent molecular weights of the resulting polymers under similar experimental conditions. The molecular weights of the polymers obtained in different experiments under similar experimental conditions are listed in Table 2.1.

The study was extended to investigate the influence of initiator to monomer ratio on the molecular weight of the resulting polymer. A set of experiments was carried out by varying stoichiometry of initiator to monomer. The results are listed in Table 2.2. It is evident from the table that the decrease of the initiator weight percentage to that of monomer resulted in increase of molecular weight. However, the trend was not linear. This anomaly was attributed to sublimation of monomer as well as shorter half-life of the initiator. Consequently, during the process of polymerization the stoichiometry of initiator to monomer is varied giving rise to unexpected molecular weight.

Table 2.1. The results of different experiments using similar experimental conditions (5g, 0.029 mol) of monomer **3**; 0.1 ml t-Butylhydroperoxide solution 70%, ($7x10^{-2}$ g; 7.7×10^{-4} mol; 1.4% of the quantity of monomer **3**); time of the reaction 1 h.

Experiment No	$M_n{}^a$ (g/mol)	$M_w{}^b$ (g/mol)	Polydispersity index (PDI) = M_w/M_n
PDIm-1	2.16×10^4	4.7×10^4	2.20
PDIm-2	2.35×10^4	5.24×10^4	2.22
PDIm-3	2.41×10^4	5.6×10^4	2.32
PDIm-4	2.98×10^4	9.41×10^4	3.15

[a] Number average molecular weight, from GPC measurement; [b]Weight average molecular weight, from GPC measurement.

Table 2.2 The molecular weight of the polymers obtained using different quantities of the initiator (t-Butylhydroperoxide solution 70% in water) for the same quantity of monomer (5g, 0.029 mol).

Experi-ment	Initiator					M_n[a]	M_w[b]	PDI[c]
	% concentrat-ion	(ml)	(mmol)	Wt.% of mono-mer	(mg)	(g/mol)	(g/mol)	
PDIm-5	70	0.1	0.77	1.4	77	2.1×10^4	4.67×10^4	2.2
PDIm-6	70	0.05	0.38	0.7	35	1.44×10^4	3.5×10^4	2.43
PDIm-7	50	0.1	0.55	1	50	4.14×10^4	11.5×10^4	2.77
PDIm-8	35	0.1	0.38	0.7	35	1.89×10^4	5.4×10^4	2.87
PDIm-9	35	0.05	0.19	0.35	17	2.20×10^4	6.46×10^4	2.93
PDIm-10	17.5	0.05	0.097	0.175	8.7	4.4×10^4	9.47×10^4	2.12
PDIm-11	7	0.1	0.077	0.14	7	3.47×10^4	11.3×10^4	3.22

[a] Number average molecular weight, from GPC measurement; [b] Weight average molecular weight, from GPC measurement; [c] Polydispersity index.

In order to overcome the problems of sublimation and higher rate of reaction, *tert*-butylhydroperoxide was replaced with an azoinitiator, 1,1'-Azobis (cyclohexanecarbonitrile); with longer half-life time. The initiator was employed to polymerize **3,** under experimental conditions similar to those with *tert*-butylhydroperoxide. This initiator has longer half-life time than *tert*-butylhydroperoxide even at high temperature (120°C). The initiator is a solid and was introduced in the reaction together with the monomer. The reaction mixture was heated up to 130°C under inert atmosphere. The reaction took place very fast and was exothermic. Although the polymerization was instantaneous and looked complete yet a holding time of 1 hour was allowed for completion of diffusion controlled chain propagation if any, involving Trommsdorf [9,10] or "gel" effect. The polymer was dissolved in DMF and precipitated from methanol. This reaction was also performed using a small quantity (0.2 ml) of solvent (DMF), the same initiator (1,1`-Azobis (cyclohexanecarbonitrile)), and at the same temperature. The results of different experiments with varying ratios of monomer/initiator are presented in Table 2.3.

Table 2.3 Radical polymerisation of 1,3-diacetyl-1,3-dihydro-imidazol-2-one**(3)** using 1,1'-Azobis(cyclohexanecarbonitrile) as initiator.

Exp. No.	Mono-mer (g)	1,1'-Azobis(cyclohexane-carbonitrile)		Tempe-rature (°C)	Solvent (ml)	$M_n{}^a$ (g/mol)	$M_w{}^b$ (g/mol)	Time (h)
		(mg)	Ratio to monomer (mol/mol)					
PDIm-12	1	1.46	1/1000	130	in bulk	8.0×10^4	21.4×10^4	1
PDIm-13	1	0.73	1/2000	130	in bulk	10.4×10^4	26.3×10^4	1
PDIm-14	5	10.5	1/800	125	in bulk	4.0×10^4	12.4×10^4	1
PDIm-15	5	10.5	1/800	125	in bulk	5.5×10^4	16.4×10^4	1
PDIm-16	5	10.5	1/800	125	in bulk	4.2×10^4	10.7×10^4	1
PDIm-17	1	1.46	1/1000	125	0.2 ml DMF	6.6×10^4	17.2×10^4	1
PDIm-18	1	1.46	1/1000	125	0.7 ml DMF	1.3×10^4	3.45×10^4	1

[a] Number average molecular weight, from GPC measurement; [b] Weight average molecular weight, from GPC measurement.

The number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by GPC using THF as solvent and polystyrene as standard. It was observed that the addition of solvent (DMF) reduced the reaction exotherm; however it decreased the molecular weight to an appreciable extent. In order to gain preliminary understanding of the polymerisation in solution and to optimize the reaction conditions, few experiments were made in different solvents. The results are listed in Table 2.4.

Table 2.4 Radical polymerization of 1,3-diacetyl-1,3-dihydro-imidazol-2-one**(3)** using different solvents and 1,1'-Azobis(cyclohexanecarbonitrile) as initiator.

No Exp.	Mono- mer (g)	Initiator (mg)	Tempe- rature (°C)	Yield (%)	Solvent (ml)	M_n^a (g/mol)	M_w^b (g/mol)	Time (h)
PDIm-19	1	1.46	125	50	DMF (4)	3250	4000	10
PDIm-20	1	1.46	125	12	NMP (6)	1200	1370	10
PDIm-21	2	2.92	125	61	T (8)	9340	17900	10
PDIm-22	2	2.92	125	26	EG (10)	4290	9260	10
PDIm-23	1	1.46	125	5	*o*-DC (6)	-	-	10
PDIm-24	1	1.46	65	7	THF (6)	1250	2250	10

[a] Number average molecular weight, from GPC measurement; [b] Weight average molecular weight, from GPC measurement. DMF = dimethylformamide; NMP = N-methylpyrrolidone; Tol = toluene; EG = ethylene glycol; *o*-DC = *o*-dichlorobenzene; THF = Tetrahydrofuran.

As it is evident from Table 2.4, polymerization of **3** in solution yields low molecular weight polymers in all the cases. Increase of polymerization time did not improve the molecular weight. Further, to gain deeper insight into polymerization in solution, the monomer **3** was polymerized in polar aprotic solvents like DMF and NMP, at varying reaction conditions. In all the cases high boiling polar aprotic solvents were chosen due to elevated temperature conditions at which polymerization was performed. Table 2.5 compiles the results from radical polymerization of **3** in DMF at varying molar ratio of initiator to monomer. It was apparent from the findings that increase in the amount of solvent lowered the molecular weight dramatically (input 1, **PDIm-25,** seite 40). With this run (**PDIm-25**), at a solvent weight percentage of 132% with respect to the weight of monomer **3,** the weight average molecular weight (M_w) was lowered to 12,000 g/mol. At similar reaction conditions but with lesser amount of solvent weight percentage (76% with respect to the weight of monomer), the weight average molecular weight was nearly double (25,800 g/mol). Further, the yield of the polymers decreased with increase in the solvent weight percentage. This variation in molecular weight was attributed to chain transfer to solvent. The maximum molecular

weight (M_w) of 52,300 g/mol was achieved by polymerizing this monomer **3** in DMF (18% by weight of monomer) at 125 ℃. Further extension of investigation in this direction was done with another polar aprotic high boiling solvent DMPU. The results of polymerization are tabulated in Table 2.6. The results obtained by polymerizing the monomer in DMPU(1,3-Dimethyl-3,4,5,6-tetrahydro-2-(1H)-pyrimidone) were not very different to those obtained in case of DMF as solvent. At very high weight percentage of solvent DMPU (148% with respect to the weight of monomer), no polymer was isolated, indicating the formation of oligomers. As expected, lowering the amount of solvent led to increase in the molecular weight. The yield of the isolated polymers exhibited similar trend that is, with increase in the amount of solvent the polymer yield dropped gradually. Maximum molecular weight M_w of 11,900 g/mol was achieved at a solvent weight percentage of 14.13 % to that of monomer. Thus, it was evident from the above series of experiments that although polymerization in solution reduced reaction exotherm yet it affected the molecular weights of resulting polymers and their yields adversely. Consequently, polymerization in solution did not prove fruitful toward increase in molecular weight while circumventing the problem of high reaction isotherm. Therefore, at this stage, polymerization in bulk remained an indispensable method toward achieving high molecular weight precursor to poly(methylene amine), poly (1,3-diacetyl-1,3-dihydro-imidazole-2-one)**(6).**

The other aspect under consideration for improved molecular weight was steric hindrance imposed by bulky lateral methyl groups on the monomer**,** 1,3-diacetylimidazole-2-one**(3).** Thus, it was anticipated that replacement of methyl groups with smaller groups would help in yielding high molecular weight polymers. Thus, a monomer with less bulky side groups, 1, 3-Diformylimidazole-2-one**(4),** was synthesized and polymerized in bulk as well as in solution.

Figure 2.2 shows the models of 1,3-Diacetyl-1,3-dihydro-imidazole-2-one**(3)** and 1,3-Diformylimidazole-2-one**(4)** respectively**.** The lateral bulky methyl groups of 1,3-diacetyl-1,3-dihydro-imidazole-2-one**(3)** was believed to cause steric hindrance and were replaced with less bulky hydrogen atoms in 1,3-diformylimidazole-2-one**(4)**.

(I)   **(II)**

● = **Nitrogen** ● = **Carbon**   ● = **Oxygen** ■ = **Hydrogen**
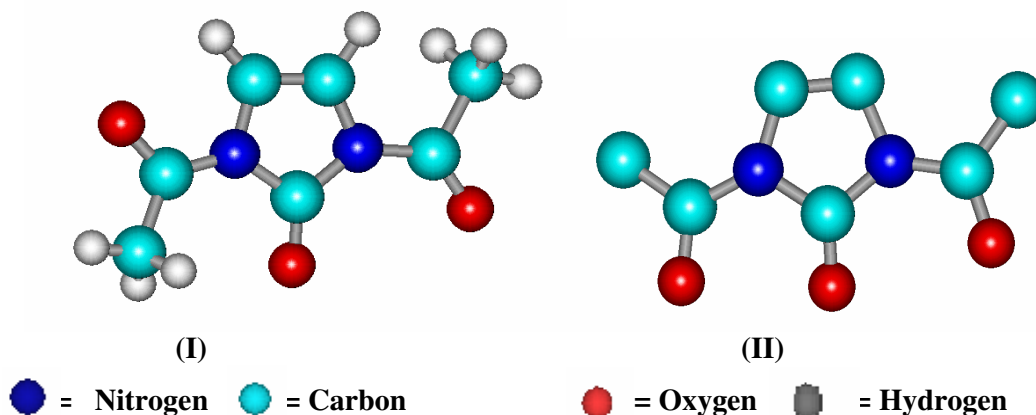
Figure 2.2 1,3-diacetylimidazole-2-one (I) and 1,3-Diformylimidazole-2-one (II).

2.4.2 Radical polymerization of 1,3-Diformylimidazole-2-one (4)

The polymerization of monomer **4** was performed in bulk as well as in solution. The schematic representation of the polymerization process is presented in Scheme 2.6.

(4)   **(7)**

R-N=N-R = 1,1`-Azobis(cyclohexanecarbonitrile)
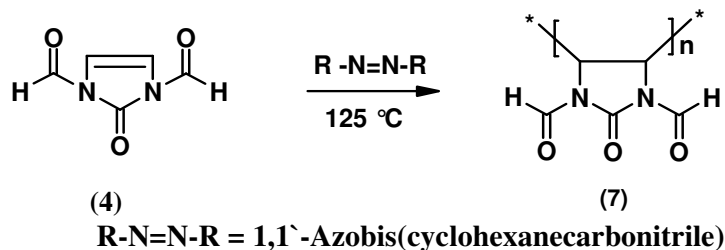
Scheme 2.6 Radical polymerization of the monomer **4**

The polymerisation of this monomer, **4** was carried out in solution as well in bulk at different molar ratio of monomer to initiator (1,1`-Azobis(cyclohexanecarbonitrile)). Some of the results are listed in Table 2.7. The initiator to monomer molar ratio of 1/500 yielded the polymer **7** with M_w = 45,200 g/mol. With decrease in the ratio to 1/1000 a M_w of 70,000 g/mol was achieved. However, further decrease in the molar ratio to 1/1245 yielded a partially soluble polymer. The M_w of soluble fraction was determined to be 48,900 g/mol. The limited solubility of this polymer against its methyl counterpart was ascribed to better macromolecular packing due to presence of less bulky hydrogen atoms.

Table 2.7 Radical polymerisation of 1,3-diformyl-1,3-dihydro-imidazol-2-one in presence of 1,1`-Azobis(cyclohexanecarbonitrile).

SL.No.	Initiator		Temp.(°C)	Solvent	T	M_n	M_w	PDI
	(mg)	Mol/mol			(h)		(g/mol)	
PFIm-1	1.69	1/500	130	bulk	1	2.12×10^4	4.52×10^4	2.13
PFIm-2	0.845	1/1000	130	bulk	1	5.0×10^4	7.0×10^4	2.34
PFIm-3	0.42	1/1245	130	bulk	1	1.94×10^4	4.89×10^4	2.51
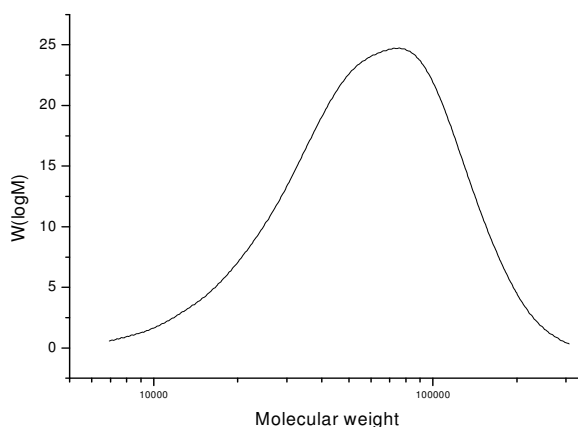
Figure 2.3 GPC curve of poly(1,3-diformyl-1,3-dihydro-2H-imidazol-2-one)**(7)**

2.5 Characterization of the polymers 6 & 7

2.5.1 Solubility

Polymer **6** was soluble in CHCl$_3$, THF, DMF and DMSO. The solubility of this polymer can be explained by the presence of the lateral acetyl groups connected to the nitrogen atoms of the rings. These groups are relatively bulky, flexible and hinder macromolecular packing thereby reducing the interaction between the macromolecules.

(A)   **(B)**

H_f = -212.3 kcal /mol H_f = - 225.19 kcal/mol
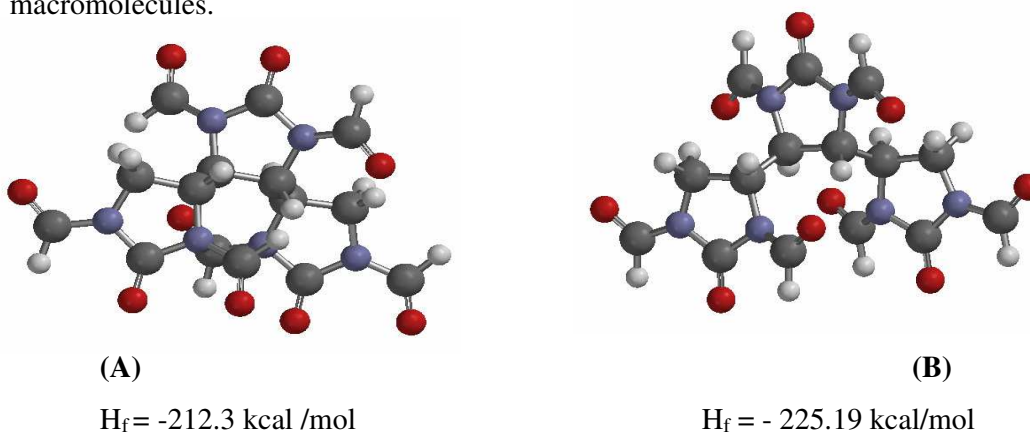
Figure 2.4 Minimum energy conformations of poly(1,3-diformylimidazole-2-one)**(7).**

The influence of lateral groups on the packing and hence solubility of the polymers are discussed in terms of their ability to pack into low energy conformations. The minimum energy conformations of these polymers (comprising of three repeating units each) were obtained by molecular mechanics calculations. In addition, dihydro derivative**(6A)**, obtained through controlled hydrolysis of these polymers, is also presented to support the underlying arguments responsible for improved solubility.

(A)   **(B)**

H_f = -252.7 kcal /mol H_f = - 238.66 kcal/mol
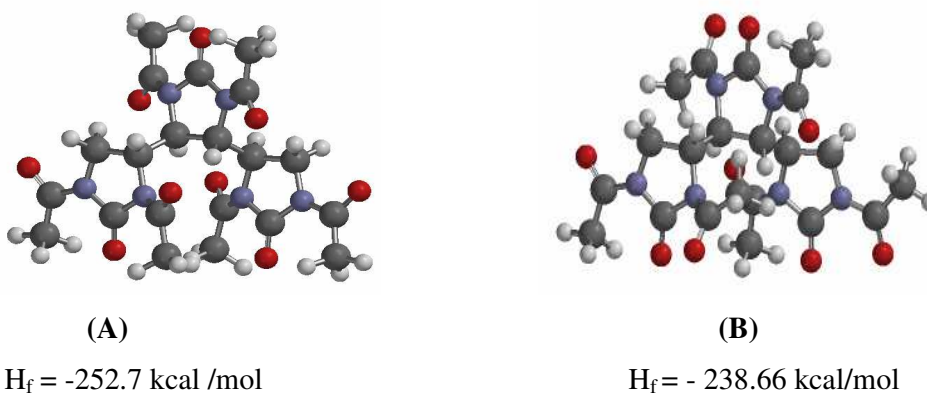
Figure 2.5 Minimum energy conformations of poly(1,3-diacetyl-1,3-dihydro-imidazole-2-one)**(6)**

Figure 2.4 shows minimum energy conformations of poly(1,3-diformylimidazole-2-one)**(7)** consisting of three repeating units. The conformation with both the carbonyl groups on the same side (Figure 2.4 A) had higher energy (H_f = 212.3 kcal/mol) in comparison to its counterpart with both the carbonyls opposite to each other (Figure 2.4 B).
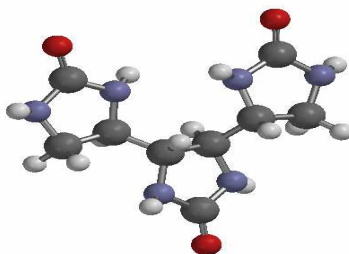
H_f = -58.4 kcal/mol

Figure 2.6 Minimum energy conformations of poly(1,3-dihydroimidazole-2-one)**(6A)**

On comparison with poly (1,3-diacetyimidazole-2-one) (Figure2.5), the most stable conformation with carbonyls facing opposite to each other has H_f = -238.66 kcal/mol, (Figure 2.5 B) which is nearly 14 kcal/mol higher than the most stable conformation of poly(1,3-diformylimidazole-2-one). This variation in energy could be argued on the basis of bulkier methyl groups imposing

Scheme 2.7 The preparation of polymer **6A**

steric hindrance resulting in higher energy conformation. The fact that bulky groups contribute toward steric hindrance and restricted packing is further supported by unexpectedly low energy (H_f = -58.4 kcal/mol) conformation occupied by poly(1,3-dihydroimidazol-2-one)**(6A).** This polymer was obtained from selective hydrolysis of diacetyl groups of poly(1,3-diacetylimidazole-2-one)(Scheme 2.7). It was insoluble in organic solvents. The insolubility of this polymer was explained in terms of hydrogen bonding and superior packing. The strong hydrogen bonding between the hydrogen attached to the nitrogen of imidazolone ring and the carbonyl group make this polymer insoluble. In addition, absence of any lateral group helps the polymer pack better acquiring the lowest energy conformation.

2.5.2 Structure elucidation

Structures of the polymers **6** and **7** were established by IR, ^{1}H-NMR and ^{13}C-NMR. IR spectrum of poly(1,3-diacetylimidazol-2-one)**(6)** is shown in Figure 2.7. The characteristic bands appeared at 3019 cm^{-1} due to the CH vibration, 2940 cm^{-1} due to the presence of CH$_3$ groups, 1774 cm^{-1} due to the presence of the carbonyl of acetyl groups and 1700 cm^{-1} due to the presence of C=O of the rings. The ^{1}H-NMR spectrum of **6** showed two broad signals at 4.3 ppm due to the presence of CH groups and at 2.32 ppm due to the presence of methyl groups (Figure 2.8). In ^{13}C-NMR spectrum a broad signal appeared at 52 ppm due to the presence of CH groups and other peaks at 168 ppm (carbonyl of acetyl groups), 147 ppm (carbonyl of the ring) and 20.6 ppm (methyl groups) (Figure 2.9).

Figure 2.7 IR spectrum of poly(1,3-diacetyl-1,3-dihydro-imidazol-2-one)(**6**).

Molecular weights of the polymers were determined by GPC in THF and polystyrene as standard. In all cases, unimodal distribution of the curve was obtained. ^{1}HNMR spectrum of poly(1,3-Diformylimidazole-2-one)(**7**) showed a broad peak centred around 4.5 ppm (CH groups) and a signal from aldehyde protons at 8.9 ppm (Figure 2.10). IR spectrum showed carbonyl absorbtions at 1770 cm^{-1} and 1743 cm^{-1}. GPC curves showed monomodal distribution for most of the polymers. The polymer with relatively low molecular weight was soluble in DMF and the molecular weight was determined by GPC.
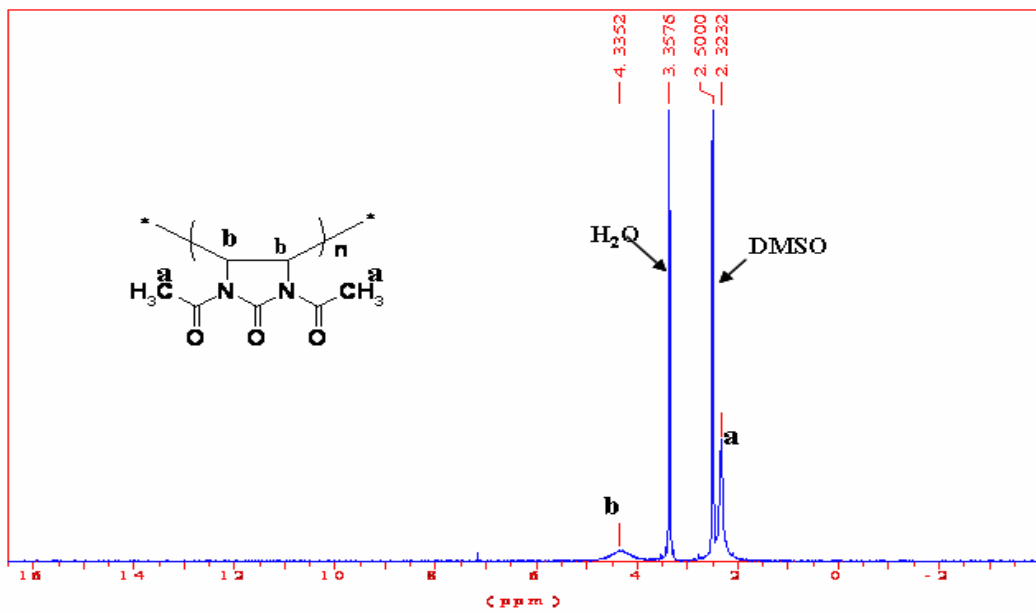
Figure 2.8 ^{1}H-NMRspectrum of poly(1,3-Diacetyl-1,3-dihydroimidazol-2-one)**(6)**

Table 2.5 Radical polymerisation of 1,3- Diacetyl –1,3-dihydro-2H-imidazoline -2-one**(3)** with 1,1`- Azobis(cyclohexanecarbonitrile) at varying concentration of solvent DMF.

| Expt.No | Monomer | | Initiator | | | | Solvent | | | Reaction time | Reaction temperature | Molecular weight | | PDI | Yield | Polymerization technique |
	Wt (g)	Mol X 10^{-3}	Wt (mg)	Mol X 10^{-6}	Mol % of monomer	Initiator/ monomer ratio	Wt (g)	ml	Wt % of monomer	(h)	(°C)	$\overline{M_n}$ (g/mol)	$\overline{M_w}$ (g/mol)		(%)	
PDIm-25	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.66	0.7	132	1	125	7.3×10^4	1.2×10^4	1.6426	52.8	Solution
PDIm-26	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.38	0.4	76	1	125	1.3×10^4	2.58×10^4	1.9300		Solution
PDIm-27	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.18	0.2	36	1	125	1.09×10^4	2.08×10^4	1.9049	57.14	Solution
PDIm-28	1.0	5.947	0.7	2.864	0.0482	0.4816/1000	0.18	0.2	18	1	125	2.6×10^4	5.23×10^4	1.9998	59.05	Solution
PDIm-29	0.5	2.97	0.350	1.432	0.0482	0.4821/1000	0.18	0.2	36	1	125	1.49×10^4	2.7×10^4	1.81	74.00	Solution

M_n Number average molecular weight (g/mol); M_w Weight average molecular weight (g/mol);   PDI Polydispersity index.

Table 2.6 Radical Polymerisation of 1,3-diacetyl –1,3-dihydro-2H-imidazolin-2-one with 1,1`- Azobis(cyclohexanecarbonitrile) at varying concentration of solvent DMPH (1,3 – dimethyltetrahydropyrimidin-2-one).

Expt.No	Monomer		Initiator				Solvent			Reac-tion time	Reaction tempera-ture	Molecular Weight		PDI	Yield %	Polymeri-zation Technique
	Wt (g)	Mol X 10^{-3}	Wt (mg)	Mol X 10^{-6}	Mol % of monomer	Initiator/ monomer ratio	Wt		Wt % of monomer	(h)	(°C)	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)			
							(g)	(ml)								
PDIm-30	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.742	0.7	148.4	1	125	–	–			Solution
PDIm-31	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.742	0.7	148.4	1	125	–	–			solution
PDIm-32	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.424	0.4	84.8	1	125	3800	4800	1.2564	7.62	Solution
PDIm-33	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.212	0.2	42.4	1	125	5100	6900	1.3643	32.2	Solution
PDIm-34	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.742	0.7	148.4	1	125	65,60 0	2,13.000	3.250	85.6	Bulk
PDIm-35	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.424	0.4	84.8	1	115	3900	4800	1.2194	6.14	Solution
PDIm-36	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.212	0.2	42.4	1	115	4800	6400	1.3464	53.66	Solution
PDIm-37	0.5	2.97	0.7	2.864	0.0964	0.9643/1000	0.212	0.2	42.4	1	135	4500	5900	1.3210	28.44	Solution
PDIm-38	1.0	5.947	0.7	2.864	0.0482	0.4816/1000	0.212	0.2	21.2	1	125	5700	9000	1.5588	42.75	Solution
PDIm-39	1.5	8.920	0.7	2.864	0.0321	0.3211/1000	0.212	0.2	14.13	1	125	7000	11,900	1.7030	43.04	Solution

M_n Number average molecular weight (g/mol); M_w Weight average molecular weight (g/mol); PDI Polydispersity index.
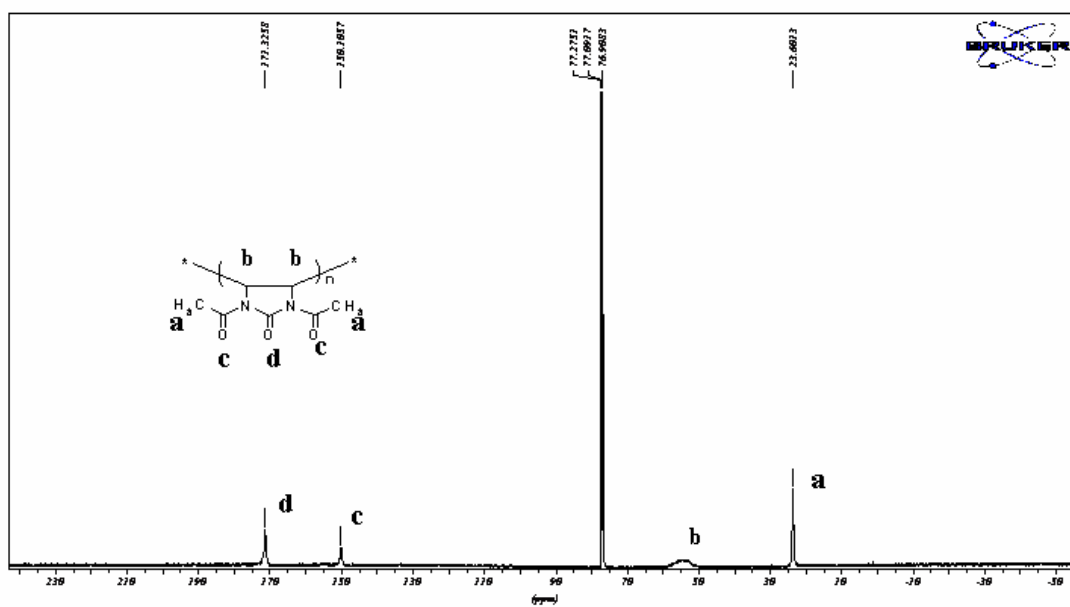
Figure 2.9 ^{13}C-NMR spectrum (175MHz) of poly(1,3-Diacetyl-1,3-dihydro-imidazole-2-one)**(6).**
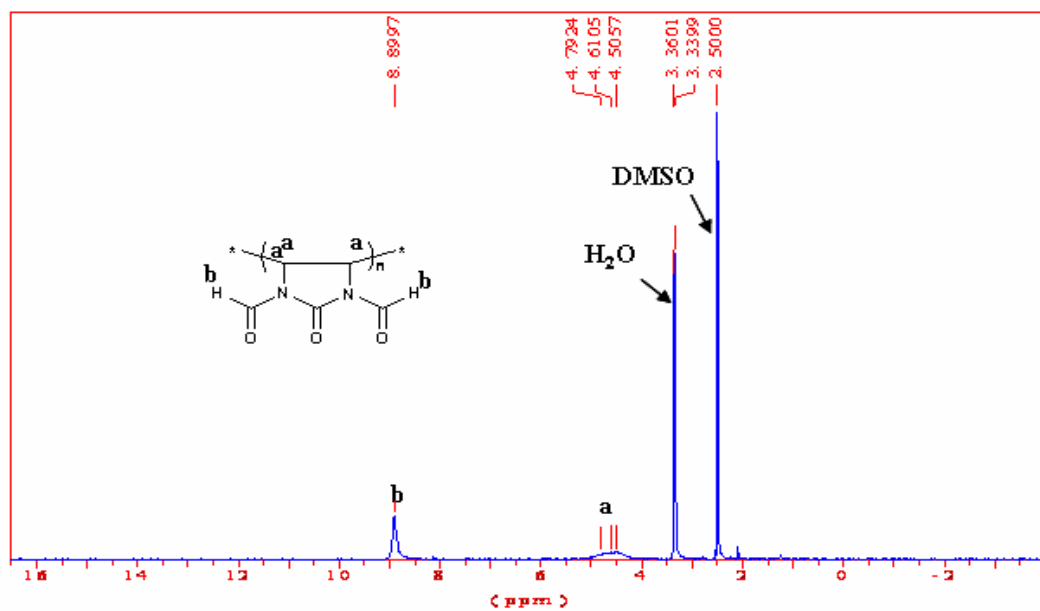
Figure 2.10 ^{1}H-NMR spectrum of poly(1,3-Diformylimidazol-2-one)**(7)** (DMSO, 250 MHz)

2.6 Thermal properties of poly(1,3-diacetylimidazole-2-one)(6) and poly(1,3-diformylimidazole-2-one)(7)

Both the polymers demonstrated good thermal stability. Poly(1,3-diformylimidazole-2-one)(**7**) was stable up to 250 °C. Thermogravimetric curve exhibited two steps of degradation, the first one, in the interval of 300-350°C, could be mainly due to degradation of the formyl groups and the second step, in the range of 370-450 °C, was attributed to degradation of the polymer backbone. TGA curve of poly(1,3-diformylimidazole-2-one)(**7**) is shown in Figure 2.11 (a). On the other hand, poly (1,3-Diacteyl-1,3-dihydro-imidazol-2-one) exhibited a single-step degradation at 400 °C which was attributed to the degradation of the polymer backbone.(Figure 2.11(b))

(a)   (b)
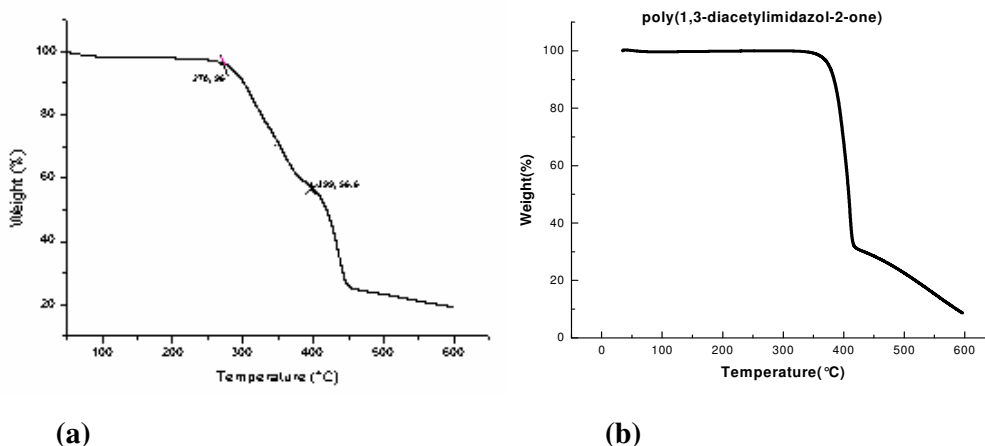
Figure 2.11.   **(a)** TG curve of poly(1,3-diformylimidazol-2-one)
(b) TG curve of poly(1,3-diacetylimidazol-2-one)

Table 2.8 Degradation of poly(1,3-diacetylimidazol-2-one) and poly(1,3 - diformylimidazol-2-one) at different temperature intervals.

Polymer	T^d_5	T^d_{10}	T^d_{20}	T^d_{50}
Poly(1,3-diacetyl-1,3-dihydro-imidazol-2-one)	372	382	393	408
Poly(1,3-diformylimidazol-2-one)	96	241	314	418

As seen in the Table 2.8, poly(1,3-Diacetyl-1,3-dihydroimidazole-2-one) is more stable in comparison with poly(1,3-diformylimidazol-2-one). Poly(1,3-diformylimidazol-2-one) experienced a weight loss of 5% at 96°C which was attributed to loss of water. The polymer being highly hygroscopic tends to absorb moisture on exposure to atmosphere. Further, 20% of weight loss was observed at 314°C. This was attributed to cleavage of less stable lateral formyl groups. On the other hand, its diacetyl analogue was relatively more stable. Its thermogram exhibited one major slump at around 400°C which was attributed to degradation of polymer backbone. Nevertheless, both the polymers demonstrated 50 % weight loss at around 400°C due to degradation of polymer backbone.

The DSC curve of poly(1,3-diacetylimidazol-2-one)(**6**) showed a glass transition temperature at 115°C. The curve also exhibited a crystallization dip centered at 220°C. The partial crystalline domain was also detected by X ray scattering (**Fig.2.12**) where diffractogram demonstrated predominant amorphous domain. However, poly (1,3-diformylimidazol-2-one) showed a crystallization crest T_c around 105 – 154 °C and melting trough T_m around 154-235°C in the first heating run on DSC curve. Further, the second heating run demonstrated only an endothermic dip at T_m 247-298 °C.
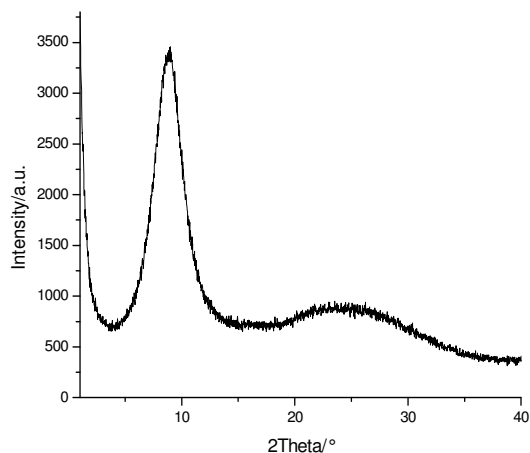
Figure 2.12 2D-WAXS diffractogram of poly(1,3-diacetyl-1,3-dihydroimidazol-2-one)(**6**)

2.7 Conclusions

The monomer **1** was synthesized by Bamberger Cleavage of imidazole. However; polymerization of these monomers led to olegomers. The lack of reactivity was attributed to shielding of the polymerizable double bonds. In order to circumvent these problems a set of cyclic monomers **2**, **3** and **4** were synthesized and polymerised. Polymerisation of **2** always led to oligomers due to low reactivity. Monomers **3** and **4** were polymerised by radical polymerisation under varying reaction conditions. Although decrease in initiator concentration at a constant monomer concentration led to an increase in molecular weight, the trend was not linear. In addition, the polymerisation reaction was highly exothermic and instantaneous. In order to facilitate better heat dissipation, the monomers were polymerized in solution. Besides, an initiator (1,1'-Azobis(cyclohexanecarbonitrile) with longer half-life was employed to facilitate further heat dissipation. Nevertheless, it resulted in lowering of M_w due to chain transfer to solvent. The maximum molecular weight of. (Mn = 26,000 g/mol and Mw = 52,000 g/mol) was achieved by polymerizing the monomer **3** in solution (DMF). However, the maximum possible molecular weight of **6** (M_n = 65,600 g/mol and M_w = 2,13,000 g/mol) of **6** was achieved by carrying out polymerisation in bulk with 1,1'-Azobis(cyclohexanecarbonitrile) as initiator.

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Chapter 3   SYNTHESIS OF   POLY(METHYLENE AMINE)

3.1 Introduction

The most challenging step in the synthesis of poly(methylene amine) was the hydrolysis of the precursor polymers, poly(1,3-diacetylimidazole-2one)(**6**) and poly(1,3-diformylimidazole-2-one)(**7**), to poly(methylene amine)(**8**). The process demanded hydrolysis of not only easily cleavable lateral acetyl or formyl groups but also strong C-N linkage of imidazolidone rings directly attached to the polymer backbone, as shown in scheme 3.1. Several attempts were made by a group of researchers from BASF to hydrolyse the polymer **6**. They tried to obtain poly(methylene amine)(**8**) by hydrolysis of polymer **6** under acidic and basic conditions. Hydrolysis of **6** was performed under basic conditions in the presence of NaOH as strong base and tetrahydrofuran (THF), 1,4-dioxan, N-methylpyrrolidone (NMP), PEG-400 or anisole as solvents. The reaction of the polymer **6** in a eutectic mixture of KOH/NaOH, at 200 ^{0}C, resulted only in partial hydrolysis[1]. Approximately 5% of the amine groups were generated. Also, this group of researchers from BASF has studied the hydrolysis of the polymer **6** under acidic conditions, in the presence of sulphuric acid at 120°C or with phosphoric acid at a concentration of 85%. All these attempts to hydrolyse the polymer **6** did not lead to poly(methylene amine) (**8**).
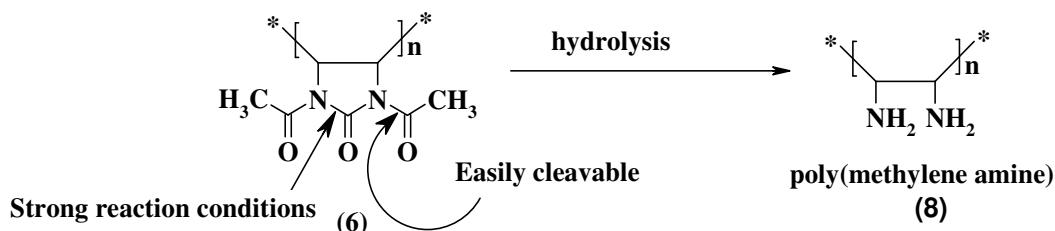
Scheme 3.1 Representation of cleavable sites on poly(1,3-diacetylimidazole-2-one)(**6**).

The transformation of the precursors, poly(1,3-diacetylimidazole-2-one)(**6**) or poly(1,3-diformylimidazole-2-one)(**7**), into poly(methylene amine)(**8**) required simultaneous hydrolysis of lateral acetyl or formyl groups as well as the hydrolysis of –N-C=O-N- bonds of imidazolidone rings. Thermal analysis of the precursor polymers **6** and **7** demonstrated a thermal stability up to 250 °C, which limited the use of temperature as one of the reaction parameters in facilitating hydrolysis. Since, further increase in

temperature above 250 °C would lead to scission of the polymer backbone, mild reaction conditions were employed to carry out hydrolysis.

3.2 Attempts to hydrolyse poly(1,3-diacetylimidazole-2-one)(6) to poly(methylene amine)(8) under mild conditions.

3.2.1 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) by using K_2CO_3 in ethanol.

In an attempt to hydrolyse polymer **6** under mild reaction conditions, a technical clue published in the literature was employed. The cited literature[2] revealed hydrolysis of lateral acetyl groups of 4,5-diimidazolidone moiety (scheme 3.2), a model very similar to the polymer under consideration. The literature procedure was embarked on the precursor poly(1,3-diacetylimidazole-2-one)(**6**)
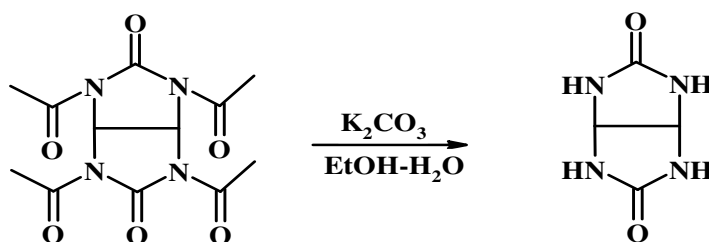
Scheme 3.2 Hydrolysis of 1,3,4,6-tetraacetyl-tetrahydro-imidazo[4,5-*d*] imidazole-2,5-dione.

In a typical experiment, polymer **6** and K_2CO_3 were suspended in a solvent mixture of ethanol and water (3:1 by volume) and refluxed for 6 hours (Scheme 3.3).
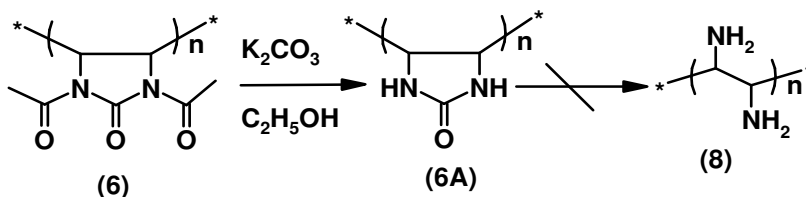
Scheme 3.3. Hydrolysis of polymer **6** in the presence of K_2CO_3 to yield **6A**.

The resulting poly(1,3-2H-4-imidazoline-2-one)(**6A**), was infusible and insoluble in organic solvents like chloroform, DMF or (NMP) with 6% LiCl. The polymer was stable up to 300°C. Their structure was characterized by solid state NMR and IR

spectroscopy. The solid state ^{13}C-NMR spectroscopy showed two signals at 52 ppm (arising from carbons on the main chain) and 153 ppm (arising from carbon of the carbonyl of imidazolidone ring). The small peaks at 100 ppm and 240 ppm represented spin bands of carbonyl carbon (Figure 3.1). The IR spectrum showed complete disappearance of band at 1774 cm^{-1} arising from carbonyl stretching of lateral acetyl groups while keeping the band at 1700 cm^{-1} from carbonyl of the imidazolidone backbone intact.
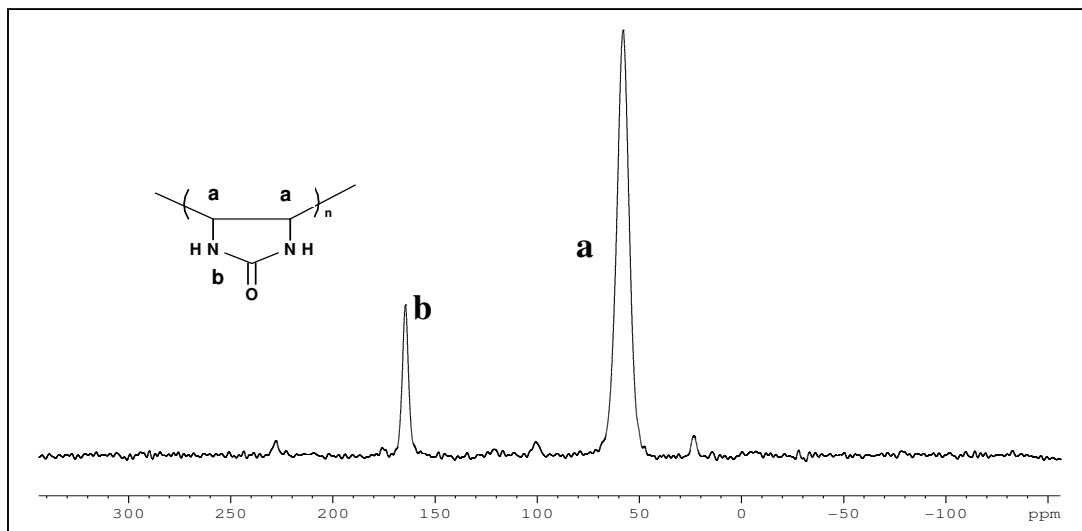
Figure 3.1. Solid-state ^{13}C-NMR of poly(1,3-dihydroimidazole-2-one)(**6A**)

The high insolubility of partially hydrolysed polymer **6A** was attributed to strong hydrogen bonding interactions between NH hydrogens of the rings. Thus, by using relatively mild conditions (K$_2$CO$_3$ as base and an aqueous ethanol solution as solvent) only the hydrolysis of acetyl groups of polymer **6A** took place. Further hydrolysis to obtain poly (methylene amine)(**8**) did not take place. The result was well in agreement with the study made by Hall *etal.* on the effect of heteroatom in the hydrolysis of five membered rings with and without nitrogen. Hall *etal*. found that the replacement of methylene group with oxygen adjacent to the carbonyl group had negligible effect on the rates of hydrolysis reaction (Figure 3.2). However, the replacement of the methylene group by -NH brought about strong interaction in (**c**), the consequences of which reflected in dramatic decrease of the rate of ring cleavage.
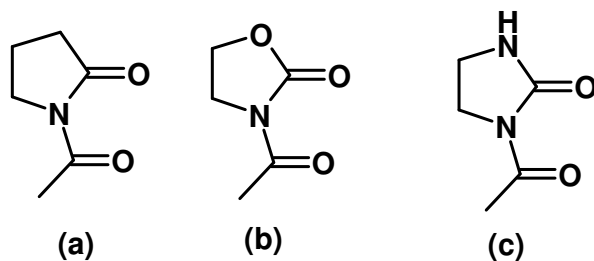
Figure 3.2. Influence of the ring structure on the hydrolysis conditions.

This fact derived from the literature and the results obtained from experiments conducted on the precursor polymer **6**, further, strengthened the view that mild reaction conditions are not suitable for the transformation of **6** into its completely hydrolysed analogue **8**. The studies on the solubility of the infusible polymer **6A** obtained after partial hydrolysis of the polymer **6** showed its solubility in concentrated HCl and H_2SO_4 at elevated temperature (i.e.$100^{°}$C). Nevertheless, it was insoluble in organic solvents due to strong hydrogen bonding between NH and CO of the heterocycle. At this stage, it was anticipated that further hydrolysis of the infusible polymer could operate in a heterogeneous medium by using strong reaction conditions.

3.2.2 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) in dilute solution of sulphuric acid

In this attempt sulphuric acid was chosen as a hydrolysing agent due to its ability to dissolve the partially hydrolyzed polymer **6A** at elevated temperature (i.e.100 °C). Thus, (0.5g, 2.976 x 10^{-3} mol) of polymer was refluxed in 10 ml of water and 0.2 ml H_2SO_4 (concentration of 97%) for 12 hours. The resulting polymer was partially soluble in N, N-dimethylformamide (DMF) and chloroform. The IR spectrum showed characteristic bands at 3400 cm^{-1} which was attributed to the NH groups of the imidazolidone units and concomitant reduced absorption intensity of carbonyl stretching vibration at 1780 cm^{-1} arising from carbonyl of acetyl groups. However, the stretching band from the carbonyl of imidazolidone units appeared as a strong band at 1700 cm^{-1} thereby confirming inadequacy of the method in hydrolysing the polymer. At this stage it was believed that mild reaction conditions are not appropriate for the

hydrolysis of the polymer. In order to achieve complete hydrolysis, strong reaction conditions must be employed.

3.3 Attempts to hydrolyse poly(1,3-diacetylimidazole-2-one)(6) under harsh reaction conditions

The investigations carried out so far on the hydrolysis of **6** have two conclusive remarks. The polymer could be hydrolysed either under very strong reaction conditions at elevated temperature and or in presence of a phase transfer catalyst in order to create a heterogeneous medium. The heterogeneous medium would enhance the solubility of intermediate formed and thus improve further hydrolysis.

3.3.1 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) at high temperature by using phase transfer catalyst

The procedure involved refluxing a mixture of polymer **6**, NaOH (as base), (N-neopentyl-4-(N,N´-dibutylamino) pyridinium chloride (as phase transfer catalyst), and diphenylether as solvent, under inert atmosphere. The solution mixture started turning brown on heating and at reflux temperature it turned completely brown. The mixture was kept under reflux for 6 hours, cooled to room temperature and poured into ethanol. No precipitate was obtained. The solution was treated with conc.hydrochloric acid to make the medium strongly acidic and was further refluxed for 4 hours. The resulting precipitate had dark brown colour. The IR spectrum showed strong absorption at 1700 cm^{-1} which was attributed to carbonyl of the imidazolidone rings. Thus, this attempt to hydrolyse the polymer in presence of phase transfer catalyst at elevated temperature remained unsuccessful.

3.3.2 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) in diethyleneglycol (DEG) at reflux temperature.

Following the literature, attempts were made to hydrolyse the polymer in DEG. In these attempts NaOH and KOH were used as hydrolysing agents. The summary of the experiments with concentrations of the reagents are listed in Table 3.1. DEG or EG

was used as high boiling solvents (reflux temperature 240°C) thus allowed to perform the hydrolysis at high temperature. The reaction was carried out by refluxing a mixture of polymer **6**, KOH and DEG for 6 hours (Entry1, Table 3.1). The concentration of the base KOH was around 7% by weight of total weight of the mixture. On heating, the reaction mixture turned brown. A small quantity of the polymer which was soluble in water was isolated at the end of the reaction. The change in colour of the reaction mixture was attributed to degradation of the polymer at high temperature (240°C). At this stage hydrolysis under acidic condition was considered worth investigating.

3.3.3 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) in acidic media at high temperature

The literature[3] on acid hydrolysis of similar systems showed hydrolysis of NCO bond of a cyclic urea into its diamine analogue, at elevated temperature, in the presence of 60% H_2SO_4, as shown in Scheme 3.4
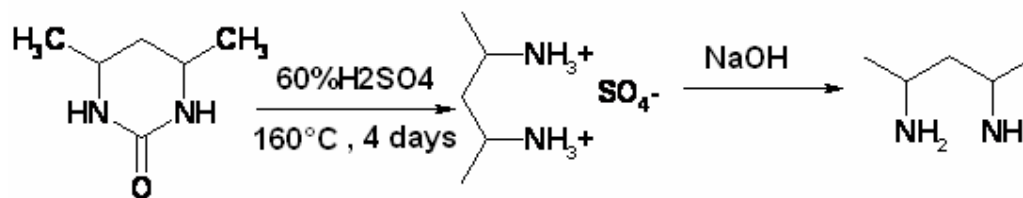
Scheme 3.4 Hydrolysis of cyclic urea in 60% H_2SO_4

Initial experiments to hydrolyse the polymer under acidic condition (Entry 2&3, Table 3.1) resulted in hydrolysis of only the lateral acetyl groups. Increase in the concentration of the acid yielded a black resin which could be due to some elimination or cyclisation processes.

Some reactions were also tried in concentrated hydrochloric acid. In this case the partially hydrolysed polymer **6A**, obtained by refluxing the initial polymer with potassium carbonate and a mixture ethanol/water, was used. In the first part of the reaction the polymer was soluble in concentrated hydrochloric acid solution, at

100°C, but after refluxing for few hours, it became insoluble. The structure of the resulting polymer seems to be unmodified. However, some reticulations catalysed by concentrated hydrochloric acid could be the reason of their insolubility.

3.3.4 Hydrolysis of poly(1,3-diacetylimidazole-2-one)(6) in ethylene glycol, in the presence of NaOH or KOH

The literature on the hydrolysis of amide linkages of urea revealed the use of a mixture of ethyleneglycol and water with NaOH to a tune of 15% by weight of total weight of mixture. The yield was quantitative.[4] The temperature of the reaction mixture depended on the quantity of water and concentration of NaOH. Since the reaction was carried out in a small scale, refluxing would bring about rise in the concentration of NaOH.

The hydrolysis of polyvinyl acetamide under basic conditions to polyvinylamine is described in the literature.[5-7] Strong conditions were used in this case, which involved high temperature and sometimes high pressure. It was mentioned that the maximum temperature that could be used was 170°C. By using a temperature higher than 170°C some degradation of the resulting polymer could appear. The time of the reaction was in the range of 1 to 48 h and the concentration of NaOH up to 20% by weight of total weight of mixture. The use of a large excess of base or high concentration tended to cause polymer precipitation. The concentration of the polymer in the hydrolysis mixture generally ranged from 5 to 20% by weight. Polymers with lower molecular weight may be hydrolysed at higher concentrations.

Taking into account the literature data, the hydrolysis of polymers **6** and **7** was performed in the presence of NaOH or KOH as hydrolysing agent and a mixture of ethylene glycol /water as solvent. NaOH and KOH were chosen on the basis of their commercial viability. A set of experiments were performed in order to optimise the parameters of this reaction. Few experiments were carried out in which the concentration of NaOH was in the range of 30-40%.

An increase in the concentration of the base led to an insoluble compound. The reflux temperature was kept in the range of 140-170°C. Some side reactions under strong conditions could occur and the resulting polymer containing amino groups could suffer an elimination reaction of ammonia with formation of a double bond or even scission of macromolecular chains.

Synthesis of Poly(methylene amine)

Table 3.1 Some experiments of hydrolysis of 6 using di(ethylene glycol) (DEG) or ethylene glycol(EG) as solvent.

Entry No	wt of 6 (g)		wt. of KOH		wt. of NaOH		DEG (ml)		EG (ml)		Water (g)		H$_2$SO$_4$ (97%) (ml)		LiCl (g)				Total Mix. (g)	Inf.
	(g)	Wt%	(g)	wt%	(g)	wt.%	ml (g)	Wt%	ml(g)	Wt%	(g)	Wt%	ml(g)	Wt%	(g)	Wt%	T (h)	Temp (°C)		
1	0.5	5.6	0.6	6.7	-	-	7(7.84)	87.7	-	-	-	-	-	-	-	-	6	240	8.94	IC
2	0.5	6.0	-	-	-	-	7(7.84)	93.7	-	-	-	-	0.2	-	-	-	6	240	8.36	IC
3	1.0	4.0	-	-	-	-	-	-	-	-	-	-	1.5	-	-	-			2.5	IC
4	1.0	6.3	-	-	1.7	10.74	-	-	10(11.13)	70.3	2	12.63	-	-	-	-	20	reflux	15.83	C
5	0.8	4.4	-	-	7.5	40	-	-	9(10.17)	55.6	5	27.32	-	-	0.8	4.37	12	reflux	18.3	IC
6	0.5	3.7	-	-	3	21.3	-	-	7(7.91)	59.5	2	15.0	-	-	-	-	20	160	13.29	C
7	2.0	7.6	-	-	5		-	-	7(7.91)	30.0	10	37.8	-	-	1.5	5.68	7	180	26.41	IC
8	2.0	5.6			10	28.2	-	-	7(7.91)	22.34	14	39.5	-	-	1.5	4.2	3.5	180	35.41	IC
9	2.0	5.6			12	32.0	-	-	7(7.91)	21.14	14	37.4	-	-	1.5	4.0	2	180	37.41	IC
10	1.0	5.0	6.0	30	-	-	-	-	7(7.91)	40.34	4	20.4	-	-	0.7	3.6	7	240	19.61	IC
11	1.0	4.6	8.0	37	-	-	-	-	7(7.91)	36.60	4	18.5	-	-	0.7	3.23	11	240	21.61	C
12	2.0	11.6	-	-	6.5	37.7	-	-	7(7.91)	45.9	4	23.2	-	-	0.8	4.6	17	170	17.21	C

6 = poly(1,3-diacetylimidazol-2-one) wt% = weight percentage of the component to that of total weight of the mixture. DEG=Di(ethylene glycol) (specific gravity=1.12);   EG = Ethylene glycol (specific gravity = 1.113) ; IC= Incomplete, C= complete

All the experiments of hydrolysis and their conditions are listed in Table 3.1. Based on literature survey, KOH was deployed as the hydrolyzing agent (Entry 1, Table 3.1). In this experiment, the mixture of polymer **6**, DEG and KOH were heated at 240°C for 6 hours under inert atmosphere. After being cooled to room temperature, the reaction mixture was acidified with 5ml of conc.HCl followed by reflux for 4 hours. Further addition of HCl was believed to facilitate hydrolysis and solubility of already partially hydrolyzed polymer. However, the IR spectrum of the isolated polymer showed a peak at 1700 cm^{-1} which could be due to the carbonyl of the heterocycle or urethane group that might appear in the process of hydrolysis. The incomplete hydrolysis of the polymer was attributed to inadequate amount of base i.e.KOH. Thus, successive formulations contained higher amount of KOH. With rise in the concentration of base (KOH) to a tune of 37% of the total mixture (Entry 11), the polymer was completely hydrolyzed and isolated in the form of its hydrochloride. Although, KOH and NaOH played similar roles in the process of hydrolysis, yet NaOH was found to be more efficient than KOH.

The temperature of 170°C appeared to be the highest value that may be effectively used. At temperatures above 170°C the degradation of the polymer, as evidenced by formation, of ammonia occurred. Therefore, it was decided to limit the conditions of the hydrolysis by increasing the reaction time and reducing the reaction temperature and concentration of NaOH. LiCl was added in to decrease the concentration of the base and the temperature of the reaction as shown in Figure 3.3. As it can be seen in the Figure 3.3, rise in the concentration of NaOH was compensated by fall in the concentration of LiCl to cause the same effect. LiCl in concentration up to 6%, increased the solubility of the partial hydrolysed polymer **6A** and allowed to use lower concentration of the base and lower
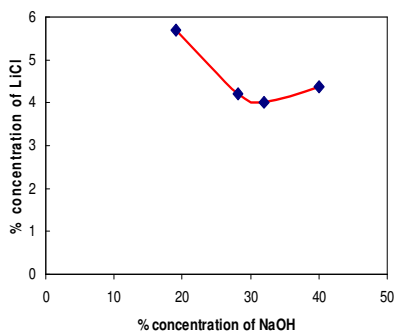

Figure 3.3 LiCl as a function of NaOH in the process of hydrolysis.

temperature for hydrolysis. The use of these ingredients reduced the possibility of some reactions leading to degradation and or reticulation.

3.4 Isolation and purification of crude poly(methylene amine) after hydrolysis

After hydrolysis, the reaction mixture was diluted with water to reduce the viscosity. The procedure followed acidification with concentrated hydrochloric acid. The precipitate formed contained a mixture of poly (methylene amine) **(8)** in the form of its hydrochloride, sodium chloride and sodium acetate. In order to eliminate the excess of salt, the entire mixture was stirred in ethanol-NaOH mixture to extract the polyamine and to remove the salts insoluble in ethanol. The ethanolic solution was concentrated to one third of its volume. Then it was transformed to poly (methylene amine) hydrochloride **(8A)** which was insoluble in ethanol. In this way bulk of the salts was removed. Poly (methylene amine) hydrochloride **(8A)** was further purified by dialysis.

3.5 Dialysis of poly(methylene amine)hydrochloride(8A)

Poly(methylene amine)hydrochloride**(8A)** was dialysed in water for five days, under inert atmosphere. A solution of **8A** was dissolved in water and was filled in the dialysis sack made of cellulose acetate membrane – (MW cut-off 1000 g/mol). The solution was dialysed in large volume of water (4 times the volume of dialysate) while replacing water twice a day. After dialysis, **8** was separated and stored as poly(methylene amine)hydrochloride**(8A)**. The complete preparation of poly (methyleneamine) is represented in Scheme 3.5. Poly(methylene amine) was kept in the form of its hydrochloride, as poly(methylene amine) on exposure to air reacts with carbon dioxide forming a cross-linked insoluble polymer.

Poly(methylene amine) was obtained after eluting poly(methylene amine) hydrochloride through a small column filled with anion exchange resin (Amberlite IRA-400 (Cl⁻).

3.6 Characterization of poly(methylene amine) and poly(methylene amine) hydrochloride

3.6.1 Solubility of poly(methylene amine)(8) and poly(methylene amine) hydrochloride(8A)

The solubility of amine containing polymers is largely driven by hydrogen bonding. Their susceptibility to react with carbon dioxide further limits their solubility. The immediate upper homologue of poly(methylene amine), polyvinylamine is reported to be soluble in water, dilute acids, alcohol and acetic acid, but insoluble in ether[1]. Poly(methylene amine)**(8)** is also soluble in water, methanol and ethanol. The solubility in these solvents is due to the presence of large number of amino groups in the polymer backbone. The corresponding hydrochloride compound was soluble in water and insoluble in methanol, ethanol and polar amidic solvents. The reason for further limited solubility could be attributed to strong hydrogen bonding due to presence of amino group in close proximity along the polymer backbone.
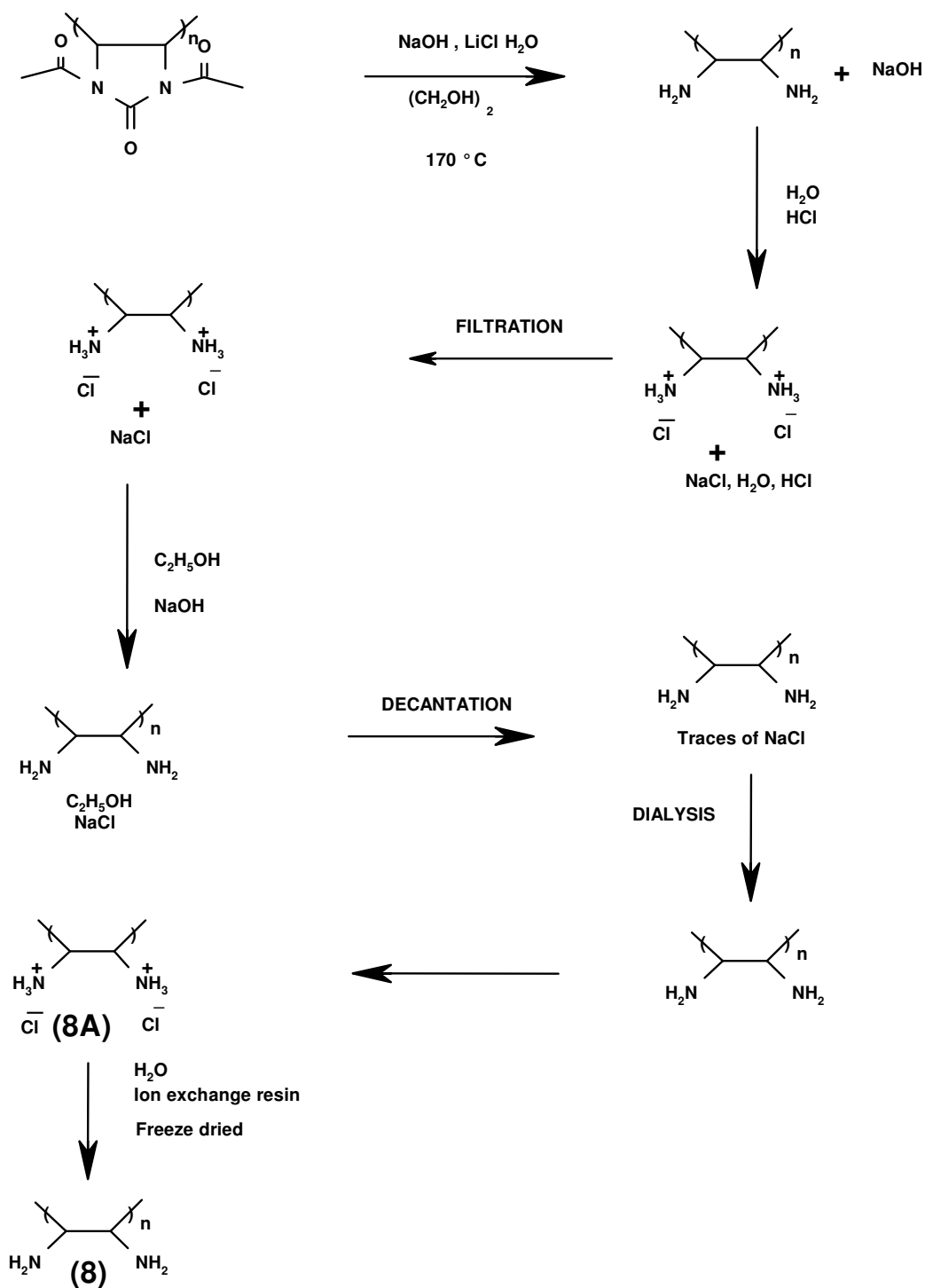
Scheme 3.5 Schematic representation of hydrolysis of poly(1,3-diacetylimidazol-2-one)(**6**)

3.6.2 Thermal properties of poly(methylene amine)(8) and poly(methylene amine)hydrochloride(8A)

The thermal properties of poly(methylene amine) were investigated by thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC). Due to presence of a large number of amine which are sensitive to thermal degradation, poly (methylene amine)**(8)** exhibited poor thermal stability. A sample of poly (methylene amine) left open to outside atmosphere turned into a globular mass, which became insoluble in methanol. The reason for insolubility is attributed to the reaction of free amino groups with carbon dioxide in atmosphere resulting in a cross-linked network. No glass transition temperature was observed for this polymer in DSC within the range of measurement.

3.6.3 Crystallinity

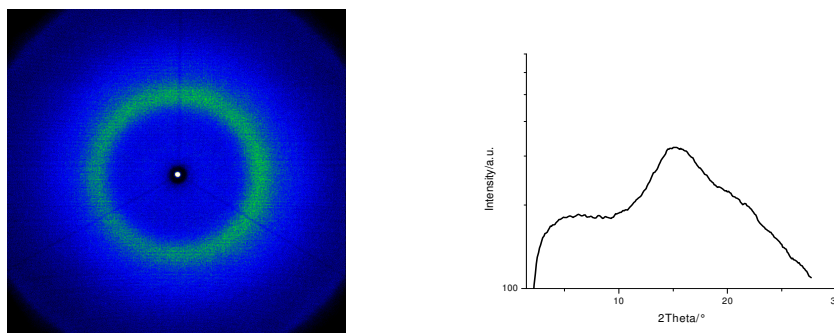Fig.3.4 shows the WAXD profiles of as-made powder poly(methylene amine) at room temperature.

Figure 3.4 X–ray diffraction of poly(methylene amine)**.**

The WAXS trace of the sample was dominated by the halo, indicating that poly (methylene amine) is amorphous.[8,9] The polymer chains within the envelope of halo are randomly packed.[9-12]

3.6.4 Structures of poly(methylene amine)(8) and poly(methylene amine) hydrochloride(8A)

The structures of the polymers, poly(methylene amine)**(8)** and poly(methylene amine)hydrochloride**(8A)** were confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Figure 3.5 shows juxtaposition of IR spectra of poly(methylene amine)**(8)** and poly(1,3-diacetylimidazol-2-one)**(6)**. The spectrum shows characteristic absorptions of poly (methylene amine) at 3420 cm^{-1}, 3330 cm^{-1} (NH stretching vibrations). 2930cm^{-1}(CH) 1595 cm^{-1} (NH). Complete disappearance of bands due to carbonyl absorption at 1774 cm^{-1} and 1700 cm^{-1} ensured complete hydrolysis of the parent polymer.

^{1}H-NMR spectrum of polymethyleamine showed a broad signal at 2.7 ppm (-CH of the backbone) and the ^{13}C NMR spectrum of poly(methylene amine) (1,4-dioxane as standard) showed a broad peak at 51.3 ppm. The IR spectrum of poly(methylene amine) hydrochloride**(8A)** showed absorption bands at 3415 cm,$^{-1}$ 2932 cm^{-1}(NH$_3^+$), 2500cm^{-1}(NH$_3^+$), 2000cm^{-1}(NH$_3^+$). The ^{1}H-NMR spectrum of poly(methylene amine) hydrochloride **(8A)** showed a broad peak at 4.0 ppm, however ^{13}C-NMR spectrum of poly(methylene amine) hydrochloride (using 1,4-dioxane as standard) showed a broad doublet centred at 55.9 ppm. The appearance of doublet was ascribed to the existence of considerable amount of non-protonated amine groups, hence two sets of environments for carbon on the polymer backbone. In order to study the protonation behavior of poly(methylene amine), shift in signal from –CH proton was monitored by ^{1}H-NMR of poly(methylene amine) hydrochloride in aqueous solution.

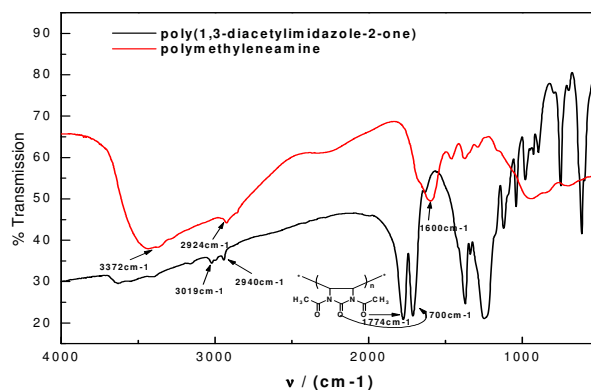**Figure 3.5** FT-IR spectrum of poly(1,3-diactylimidazol-2-one)**(6)** and poly(methylene amine)**(8)**

3.6.5 Study of the titration of poly(methylene amine)hydrochloride(8A) using ^{1}H-NMR spectroscopy

The titration process of poly(methylene amine)hydrochloride**(8A)** was studied with ^{1}H-NMR spectroscopy at different pH. The pH was adjusted with NaOH solution. Figure 3.7 shows the shift in CH signal as a function of pH. At the lowest pH, 1.5, the signal from –CH appeared at 3.84 ppm.The signal is shifted down field with the increase in pH. At the highest pH=12, the signal appeared at 2.85 ppm. This clearly explained the dependence of protonation of poly(methylene amine)**(8)** on the pH of the system. Figure 3.6 demonstrated a tentative variation in the conformation of poly(methylene amine) with respect to pH. At lowest pH most of the amine groups are protonated. Consequently, the electronegative character of protonated amine group close to the carbon atom deshields the -CH proton shifting the signal further downfield. With rise in pH, the ammonium sites are converted into the free amine resulting in shielding of the backbone. Thus the signal is shifted up-field. This leads to the fact that with variation in degree of protonation, the conformation of the polymer changes remarkably.
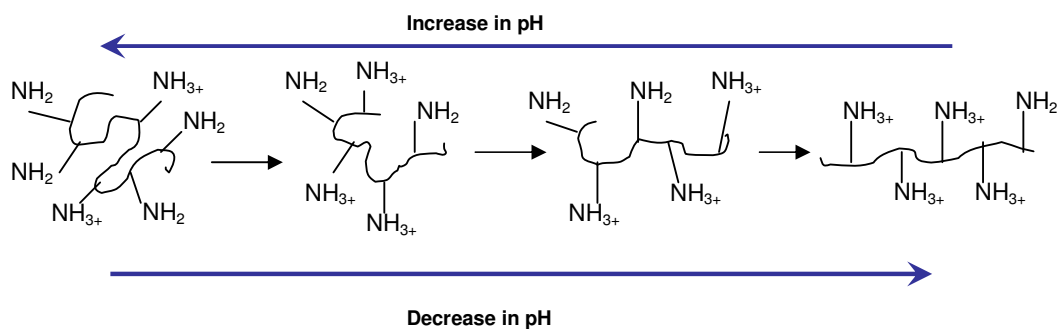

Figure 3.6 Schematic representation of poly(methylene amine) with variation in pH.
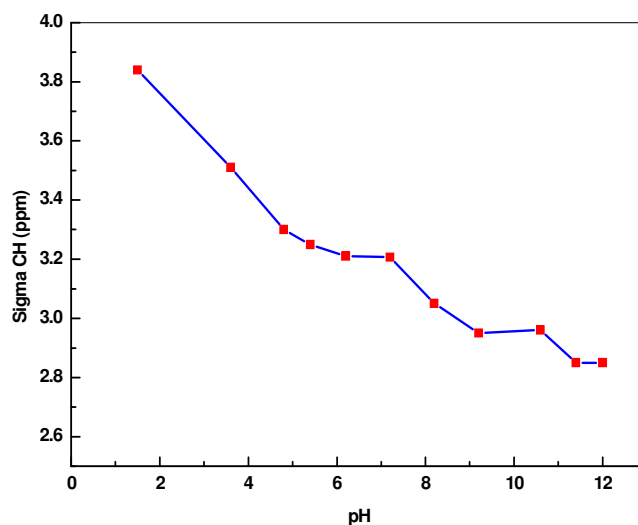
Figure 3.7 Shift in CH signal as a function of pH

3.7 Conclusions

1,3-diacetylimidazole-2-one and 1,3-diformylimidazole-2-one were polymerized by radical polymerisation in presence of peroxide initiator (t-Butylhydroperoxide 70%, solution in water) as well as azo initiator (1,1´-Azobis(cyclohexanecarbonitrile)).The polymerization was carried out in solution as well as in bulk. Attempts were made to increase the molecular weight by varying reaction parameters such as temperature, solvent and concentration of initiator. From all of the above experiments carried, it was concluded that highest molecular weight was achievable by polymerizing both the monomers in bulk. Poly(1,3-diacetylimidazole-2-one)**(6)** and poly(1,3-diformylimidazole-2-one)**(7)** were hydrolysed to poly(methylene amine)**(8)**, respectively**.** The hydrolysis of these polymers was performed under basic conditions. It was found that the polymers can be completely hydrolysed to poly(methylene amine)**(8)** by using a mixture of ethylene glycol/water as solvent and NaOH or KOH as strong base, in presence of LiCl. Poly(methylene amine)**(8)** was isolated from the reaction in the form its hydrochloride. The crude poly(methylene amine) hydrochloride was further purified by dialysis. Due to its greater reactivity towards CO_2 in atmosphere poly(methylene amine) was stored as its hydrochloride. Pure poly(methylene amine) was obtained by eluting a sample of hydrochloride through a

column of anion exchange resin (IRA 400 Cl⁻). The resulting solution was lyophilized to obtain poly(methylene amine) in solid state. The structures of poly(methylene amine) and poly(methylene amine)hydrochloride were confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

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SOLUTION PROPERTIES
OF POLY(METHYLENE AMINE)

4.1 Introduction

Amine containing polymers such as polyvinylamine and poly(ethyleneimine) demonstrate interesting properties in solution. Being polyelectrolytes, their aqueous solution properties display interesting behavior. In this chapter, the investigation into the solution properties of poly(methylene amine)(**8**) and its hydrochloride **8A** in aqueous solutions by viscosimetry, laser light scattering, GPC and GPC-MALLS. In addition, the precursor polymer poly(1,3-diacetylimidazole-2-one)(**6**) in THF has been investigated by the above mentioned techniques. Despite anomalous behavior of polyelectrolytes and their technological attributes, the study and understanding of this class of polymers is grossly inadequate. For obvious reasons, a blend of polymer and electrolyte properties makes the investigation of polyelectrolytes in solution rather complex.[1] However, the fully stretched conformation of a highly charged polyelectrolyte in the absence of foreign counter ions is widely accepted theoretically as well as experimentally. This feature was also used in a theoretical approach by Katchalsky,[2] where the polyelectrolytes are represented as rigid, uniformly charged rods, arranged in a parallel closed pack array. De Gennes *et al.*[3] applied scaling concepts to extend theoretical description to semi dilute solutions. They distinguish three different concentration regimes, each having a different polyion behavior, defined by the absolute ionic strength of the solution. At the lowest concentrations (dilute regime), the polyelectrolyte chains are widely separated and fully stretched and above a certain critical concentration the fully stretched chains can not orient freely any more and the electrostatic interaction between the polyions is expected to lead to a three dimensional periodic lattice. At higher concentration regime where the overlapping of chains is predominant, the formation of transient network with a characteristic correlation length similar to neutral polymers is suggested. The conformational change of the charged polyelectrolyte in the solution with respect to the polymer concentration was also investigated by Yu Chen *et al.*[4] through viscosimtery. They observed a sharp rise in reduced viscosity of polyvinylamine hydrochloride in aqueous solution below a certain concentration (dilute regime). In the higher concentration regime the variation of reduced viscosity demonstrated a plateau. The dramatic rise in viscosity in dilute regime is attributed to poor shielding

of the backbone charges by the counter ion leading to straightened polymer backbone, consequently rise in reduced viscosity. This phenomenon was qualitatively explained by coil –to- rod transition of the polyions up on dilution due to increasing electrostatic interactions along the chains with decreasing ionic strength.[5-8] Extensive literature survey revealed controversial arguments to the aforementioned behavior of polyelectrolyte in dilute solution. The rise of reduced viscosity is always followed by a maximum with a subsequent steep decrease at the lowest concentrations.[9-11] The concentration corresponding to the maximum reduced viscosity is independent of molecular weight and depends only on the ratio of C_{pe}/C_s (concentration of polyelectrolyte to salt in moles). Apart from viscosimetry, laser light scattering has remained an indispensable method for investigating dynamics of a polymer chain, neutral and charged, over the past few decades. Besides, determination of basic characteristics of a polymer viz. molecular weight, hydrodynamic radius etc, helps unravel the intricacies associated with diffusion of a polymer chain in solution at different concentrations. However, the picture of polyelecetrolytes laid by various researchers investigated through light scattering does not fit into a common framework. The diffusion behavior of macro ions in aqueous solutions especially at low salt concentrations aroused curiosity since Schurr *et.al.* found slow mode in 1978.[12]They found rather an interesting behavior for diffusion of polyelectrolytes in aqueous solutions. They measured diffusion coefficients of poly L-lysine in solution by dynamic light scattering (DLS) as a function of salt concentration. The apparent diffusion coefficient first increased with decreasing salt concentration, but it dramatically dropped off at a certain salt concentration. This phenomenon has been called "ordinary – extra ordinary transition." Drifford *etal.* found that the diffusion coefficient does not simply drop-off but separates into two dynamic modes with decreasing salt concentrations. These two modes have been called "fast mode" and "slow mode " respectively.[13] The origin of slow mode has been proposed to be an existence of some kind of (temporal) cluster or domain of macro ions even in solution by Schmitz *etal.*[14,15] Drifford and Dalbeitz interpreted the slow mode by some macroscopic fluctuations of short structural domains with large correlation length giving oscillations in the structure factor by a long range repulsive interaction.[13] Although Drifford *et al* claimed that this phenomenon was typical for "linear " polyelectrolytes, Matsuka et al found similar behavior for solutions of the "globular "

protein bovein serum albumin (BSA), which is an ellipsoidal protein with an axial ratio of 140:40 A°. They carefully examined pH dependence of diffusion coefficients of BSA in aqueous solutions and found both the fast and slow modes in addition to middle mode which was insensitive to pH and was very close to the calculated value from its geometry. The extensive origin of fast and slow modes has been studied in detail by Sedlak and Amis.[16,17] For example they carefully examined the molecular weight dependence of these two modes, and found that the fast mode did not depend on molecular weight where as the slow mode did. Again, the origin of the slow mode was thought to originate from some kind of cluster. Further, the existence of cluster was confirmed by small angle neutron scattering experiments.[18,19]

From the above discussion it is apparent that the polymer chain dynamics in polyelectrolyte solutions is poorly understood. The behaviour is greatly affected by the architecture, charge density and the rigidity of the polymer backbone and require more detailed investigation. Following its synthesis, the prospect of using poly(methylene amine)**(8)** as a cationic polyelectrolyte was investigated by static and dynamic light scattering in aqueous solution with and without low molecular weight electrolyte (salt). In addition to this, the precursor polymer to poly(methylene amine) poly(1,3-diacetyl-imidazole-2-one)**(6)** has also been investigated by static, dynamic light scattering, GPC and online GPC-MALLS.

4.2 Viscosimetry

One of the most characteristic features of a dilute polymer solution is that its viscosity is considerably higher than that of the pure solvent. This arises because of the large differences in size between polymer and solvent molecules, and can be significant even at very low concentrations, especially for polyelectrolytes and polymers with high molecular weights. Dilute solution viscometry is concerned with accurate quantitative measurement of the increase in viscosity and allows determination of the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature. This quantity provides a wealth of information relating to the size of the polymer molecule in solution, including the effects up on chain dimensions of polymer structure, molecular shape, degree of polymerization and polymer solvent

interaction. In addition, it also has the advantage that it is applicable over the complete range of attainable molecular weights. For these reasons, dilute solution viscometry has long been a widely used method for polymer characterization and continues to be used today.

4.2.1Types of viscometers

There are roughly three classes of viscometers available, the capillary viscomter, the rotational viscometer, and the falling ball viscometer. Both the capillary and the rotational viscometers are built in different versions that allow for the exact determination of the viscosity in well-defined flow fields.

Capillary viscometers are the most commonly used viscometers for the determination of the intrinsic viscosity. Commonly used capillary viscometers include **a**. Ostwald viscometer, **b**. Ubbelhode viscometer, **c**. Cannon-Fenske viscosimeter **d**. multi-level viscosimeter for different average heights `h` and different average shear rates in one experiment.

4.2.2 Theory

The flow of the examined liquid sample is achieved through gravity. The sample flows under its own weight through a known capillary length ´l´ with a defined radius ´**R**´. The running times of a known sample volume between two measurement points. (M_1 and M_2) are measured. With the help of these running times, the kinematic viscosity can be calculated. Viscosities of all the polymers mentioned in this chapter were measured by Ubbelhode viscometer.

4.2.3 Calculation of viscosity measured by Ubbelhode Viscometer

The number of seconds stated for the various capillaries in the tables for Hagen Bach corrections are subtracted from the determined efflux time. Intermediate values are interpolated. For absolute measurements, the corrected efflux time multiplied by the constant k printed on the viscometer, gives the kinematic viscosity in cSt.(mm^2/s)

$\nu = K \,(t - \sigma)$ --(1)

Where: ν = Kinematic viscosity, K= Capillary constant, t = average flow time, σ = Hagen Bach correction for the average flow time.

Dynamic viscosity $\eta = \nu / \rho$ Where η = Dynamic viscosity, ρ = Density of the solution (Kg/m^3)

The ratio of viscosity η of a solution to that of pure solvent η_s is the relative viscosity and is called η_r

$\eta_r = \eta/\eta_s$ --- (2)

If the viscosity is conceived as the sum of the solvent viscosity η_s and the viscosity from the dissolved polymer ´η_p`

$\eta_r = \eta_s + \eta_p$ ---(3)

The ratio of the dissolved polymer viscosity η_p to the solvent viscosity η_s can be called the specific viscosity η_{sp} of the polymer in solvent.

$\eta_{sp} = \eta_p / \eta_s = (\eta - \eta_s) / \eta_s = \eta_r - 1$, Reduced viscosity = $\eta_{red} = \eta_{SP} / c$ For the under mentioned measurements: K = 0.005

4.2.4 Viscosity of poly(methylene amine)(8) and poly(methylene amine) hydrochloride(8A).

The viscosity of the polymers poly(methylene amine) and poly(methylene amine) hydrochloride was determined in water at 20^0C and at different concentrations, by using an Ubbelohde viscometer. poly(methylene amine) hydrochloride was measured at pH = 2 and poly(methylene amine) at pH=9.5. The inherent viscosity was calculated by using the formula

$\eta_{inh} = \ln (\eta_r)/C = \ln (t/t_0)/C$

Where t = efflux time of the solution t_0= efflux time of the solvent

Table 4.1 Inherent viscosity of poly(methylene amine)**(8)** (pH=10.5) t_0=107.34 at varying polymer concentration.

Efflux time of solution (t) (sec)	Concentration (g/L)	Inherent Viscosity (dl/g)
123.43	8.36	0.166
123.01	8	0.17
121.5	7	0.177
118.5	6	0.183
117.04	5	0.172
114.8	4	0.167
113.4	3	0.183

The inherent viscosities of poly(methylene amine)**(8)** and poly(methylene amine) hydrochloride**(8A**) at different concentrations are listed in Table 4.1 and Table 4.2 respectively. The inherent viscosity of poly(methylene amine)**(8)** increased from 0.166 dl/g at a polymer concentration of 8.36 dl/g to 0.183 dl/g at a polymer concentration of 3g/L. The inherent viscosity of poly(methylene amine) hydrochloride **(8A)** followed a similar trend. However, the viscosity values for poly(methylene amine) hydrochloride were higher in comparison with poly(methylene amine) at the same polymer concentration. Poly(methylene amine)hydrochloride exhibited an inherent viscosity of 0.256 dl/g at a polymer concentration of 8.36 g/L in comparison to poly(methyleneamine), which attained a viscosity of 0.166 g/dl at the same polymer concentration. The viscosity value at lowest measured concentration, 3g/L for poly(methylene amine) and poly(methylene amine)hydrochloride was 0.183 dl/g and 0.291 dl/g respectively. Although, both the polymers demonstrated a rise in the values of viscosity with decrease in concentration yet the variation was negligible. In conclusion, higher viscosity of Poly(methylene amine)hydrochloride against poly(methylene amine) at same polymer concentration was result of better stretched conformation due to like charge repulsion placed in the vicinity. Further, increase in viscosity with decrease in polymer concentration of poly(methylene amine) can be explained in terms of partially protonated structure the polymer in aqueous solution. To understand the effect of typical polyelectrolyte behaviour which is manifested by both the polymers, inherent viscosities were measured in presence of KCl.

Furthermore, reduced viscosities of poly(methylene amine)hydrochloride was measured to gain better understanding

Table 4.2 Inherent Viscosity of poly(methylene amine)hydrochloride(**8A**) at pH = 2.0 at varying polymer concentration. t_0 = 107.65

Time solution(sec)	Concentration(g/l)	Inherent viscosity(dl/g)
132.81	8.36	0.256
132.29	8	0.261
131.06	7.5	0.266
129.8	7	0.271
128.57	6.5	0.277
127.28	6	0.283
126.03	5.5	0.291

4.2.5 Study of the influence of salt on the inherent viscosity of poly(methylene amine) and poly(methylene amine)hydrochloride at varying concentration of salt KCl.
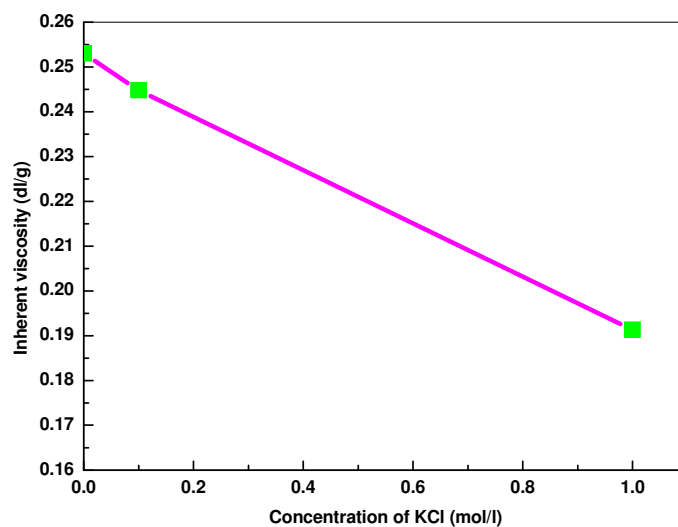
Figure 4.1 Inherent viscosity of poly(methylene amine) as a function of salt (KCl) concentration.

The behavior of poly(methylene amine) and poly(methylene amine)hydrochloride in aqueous solutions was investigated by determining their inherent viscosities at two

different concentration of salt (0.1 mol/L, 1 mol/L of KCl) of aqueous solution of polymer. The temperature of the solution was maintained at 25^0C and the pH 10.4. Figure 4.1 shows the variation of inherent viscosity of poly(methylene amine) with salt concentration. As it is clearly seen, the inherent viscosity decreases with increase in
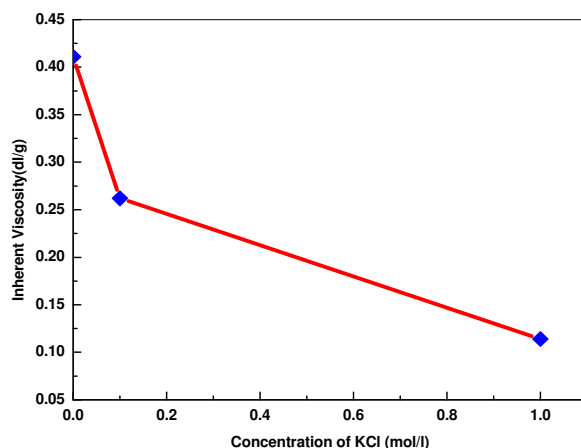

Figure 4.2 Inherent viscosity of poly(methylene amine)hydrochloride as a function of salt (KCl) concentration.

concentration of salt i.e. KCl. Figure 4.2 reveals a similar trend in the behavior of poly(methylene amine) hydrochloride in aqueous solution in the presence of KCl. However, careful examination of both the figures gives an insight into the difference in the behaviour of these polymers while exhibiting similar trends in inherent viscosities. Poly(methylene amine)**(8)** (Figure 4.1) showed an inherent viscosity of 0.255 dl/g in the absence of salt, in comparison with poly(methylene amine) hydrochloride that had a viscosity of 0.425 dl/g. Higher inherent viscosity of poly(methylene amine)hydrochloride is attributed to fully extended chain conformation due to repulsion of positively charged ammonium ion located in close proximity. On addition of salt the viscosity dropped in either of the cases. Viscosity of poly(methylene amine) dropped to 0.2448 dl/g against poly(methylene amine) hydrochloride 0.25 dl/g up on addition of 0.1 mol of KCl per litre of polymer solution under investigation. Further, increase in the concentration of salt reduced the viscosity to a tune of 0.1993 dl/g in case of poly(methylene amine) and 0.102 dl/g in case of poly(methylene amine)hydrochloride. The dramatic viscosity drop observed in

poly(methylene amine)hydrochloride in contrast with poly(methylene amine) on addition of salt was due to collapse of counter ions on the polymer backbone which contributed to rise in viscosity. Consequently, the highly charged poly(methylene amine)hydrochloride acquired a conformation similar to the neutral polymer, poly(methylene amine).

4.2.6 Reduced viscosity of poly(methylene amine)hydrochloride as a function of polymer concentration.

Figure 4.3 represents the relationship between reduced viscosities as a function of concentration of aqueous solution of poly(methylene amine)hydrochloride. The increase in reduced viscosity with decrease in concentration demonstrated a typical polyelectrolyte behavior. The reduced viscosity rises gradually from the region of higher concentrations (10 – 6 g/L) towards the region of lower concentrations, increasing sharply below 5 g/L. This behaviour is ascribed to a change in the conformation of the polymer chain with dilution. At higher concentrations the apparent shielding of positively charged species on the backbone by the counterions result in weak electrostatic repulsion. Thus the polymer chains remain in the form of globular networks with minimum electrostatic repulsion. However, dilution liberates the positively charged species from the shield of the counter ions. As a result, the strong electrostatic force of repulsion operating between neighbouring positive charges lead to
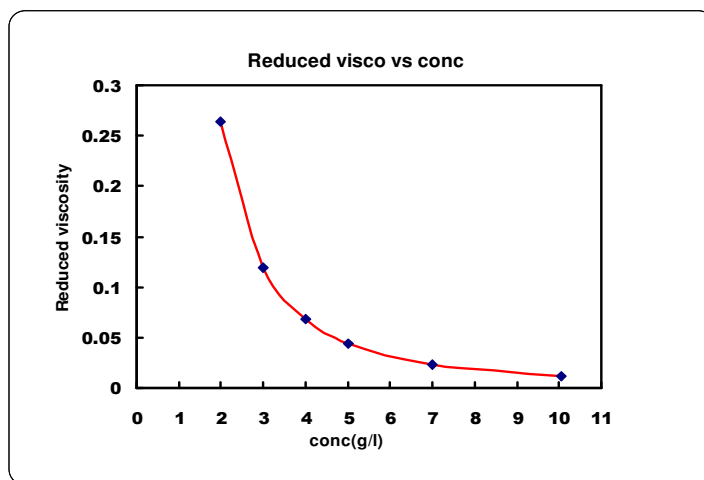

Figure 4.3 Reduced viscosity of poly(methylene amine)hydrochloride as a function of polymer concentration.

straightening of the polymer backbone. The long straightened conformation of the polymer chain arising from electrostatic repulsion results in the rise of reduced viscosity of the polyelectrolyte in solution. A similar trend in the behaviour of reduced viscosity with concentration has been observed with the upper homologue of poly(methylene amine), polyvinylamine hydrochloride and diallyl dimethymammonium hydrochloride.[1,2] In order to study the influence of maximum number of amine groups on reduced viscosity; poly(methylene amine)hydrochloride was compared with its upper homologue polyvinylamine hydrochloride under similar experimental conditions.

Table 4.3 Reduced viscosity of poly(methylene amine)hydrochloride and polyvinylamine hydrochloride as a function of polymer concentration.

Concentration (g/L)	Poly(methyleneamine) Hydrochloride (dl/g)	Polyvinylaminehydrochloride (dl/g)
10	0.012	0.016
7	0.023	0.028
5	0.044	0.047
4	0.119	0.068
3	0.264	0.110
2	0.263	0.219
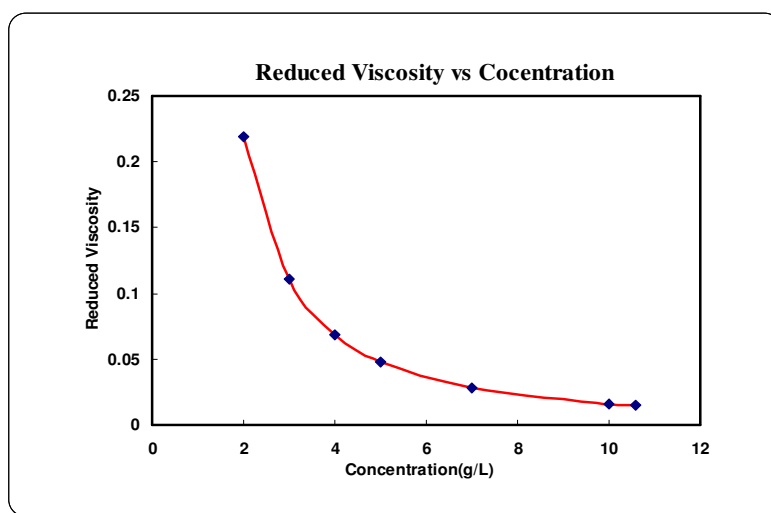
Figure 4.4 Reduced viscosity of polyvinylamine hydrochloride as a function of polymer concentration.

The reduced viscosities of poly(methylene amine)hydrochloride and polyvinylamine hydrochloride in their aqueous solutions measured under similar conditions are listed in Table 4.3. At a concentration 10g/L the hydrochlorides of poly(methylene amine) and polyvinylamine exhibited nearly the same viscosity. With rise in dilution the viscosity of both the polymers increased, manifesting a typical polyelectrolyte behavior. Below the concentration 5g/L, the viscosity increased rapidly in either of the cases. However, the rise was comparatively higher in case of poly(methylene amine)hydrochloride. This indicated greater polyelectrolyte effect due to maximum charge density on the polymer backbone in case of poly(methylene amine) hydrochloride.

4.3 Charge Density

4.3.1 Determination of surface charge density

Electro kinetic techniques are widely used to characterize the charge distribution around aqueous colloid particles. The distortion of counterions resulting from movements of charged ions leads to the electro kinetic effect.
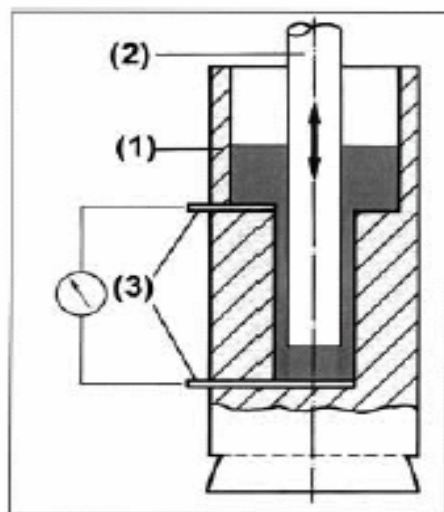
(1) PTFE cup (2) Oscillating PTFE –piston (3) gold electrode

Figure 4.5 Schematic representation of Particle charge detector PCD

Consequently, a dipole is formed around each particle, which affected the speed of the particles in an electric field (electrophoretic mobility) or for particle movement, forms an electric potential within the suspension (sedimentation potential or streaming potential). Whereas surface charge determined by titration or exchange techniques measures the amount of total charge, electro kinetic techniques furnish information about the mobile and weakly bound fraction of the counter ions.

4.3.2 Methods

The principle of charge indication is based on the generation of streaming potential, which is induced by the oscillating movement of a plunger in a PTFE cell (Figure 4.5). Two gold electrodes placed in the cell record the electro kinetic signal. The positive surface charge was then quantified by titration with 10^{-3}M PES-Na (sodium polyethylenesulfonate). Addition of the titration solution is performed across the point of zero charge i.e. the point at which the electro kinetic potential is zero. For each measurement 10 ml of the poly(methylene amine) hydrochloride solution was used.

The electro kinetic charge (**Qek**) of a colloidal system is calculated from the required titrant polyelectrolyte by using the following equation:

 Qek = V.c / w.

Where V is volume of titrant added (L), c charge of the titrant (mol L^{-1}), w is the amount of the titrated substance (kg).

4.3.3 Determination of charge density of poly(methylene amine)hydrochloride at different pH.

Figure 4.6 shows a typical PCD titration curve. With increase in the volume of titrant the PCD signal reaches a quasi plateau followed by a sharp decrease across the isoelectric point (IEP), marking the end of the titration. Interpretation of both the initial PCD signal and the shape of the titration curve is rather difficult. Several investigations have been conducted to correlate the electro kinetic signal from the SCD or PCD with those obtained by other electro kinetic techniques. Although satisfactory linear correlations have been found, the calculation of zeta potentials from

the signal is highly dependent on the type of model selected. Besides, the general criticism of deducing zeta potentials from electro kinetic signals, the principal mechanism of the generation of the PCD signal is still poorly understood. More reliable information is obtained if only the sign of PCD signal is used. For the polyelectrolyte titration in the PCD, the point at which the sign of signal gets reversed is of sole interest. This point can be interpreted as the isoelectric point(IEP) of the solution or the suspension, when the charge of the sample is balanced by counter ions. The amount of titrated polyelectrolyte can be accurately calculated by linear interpolation at the IEP.
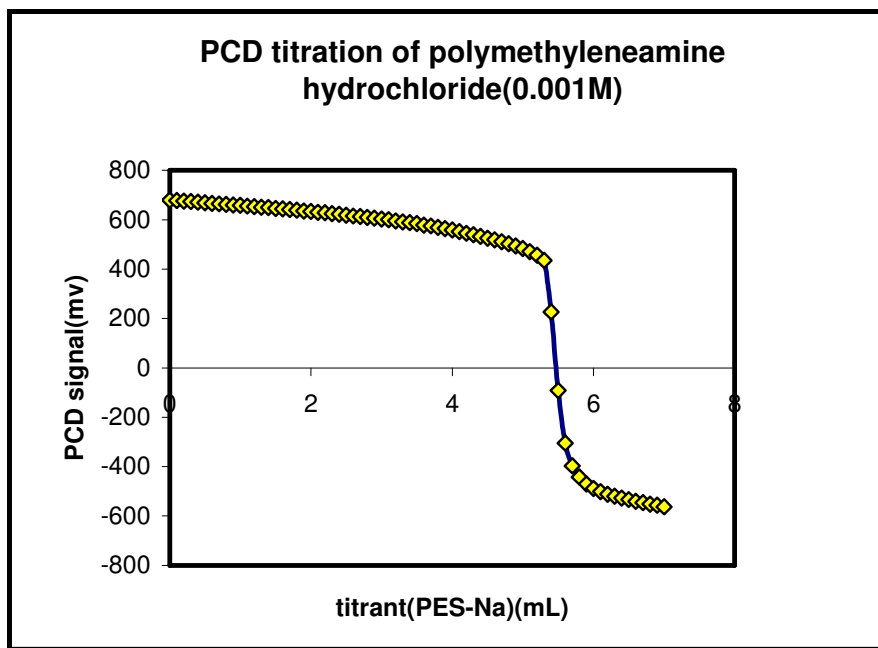
Figure 4.6 A typical curve representing titration of poly(methylene amine) hydrochloride (0.001 M) against PES-Na (0.001M) by PCD (Particle charge Detector)

Figure 4.7 shows the influence of pH on the electro kinetic surface charge of poly(methylene amine)hydrochloride in water. The electro kinetic charge increases with decrease in pH. The percentage charge density of 6.07 at pH 9.38 increases to 24.5 at a pH of 6.97, which is nearly neutral (Table 4.4). Although the decrease in pH from 6.97 to 1.78 displays an increase in charge density the rise is not steady and linear unlike in the higher pH regimes.

Table 4.4 % Charge density of poly(methylene amine)hydrochloride at varying pH

Sample No	pH	Electro kinetic charge (mol^{-1}Kg)	%Charge Density
1	1.78	8.598	55.89
2	3.71	8.412	54.71
3	3.75	8.060	52.4
4	6.97	3.742	24.32
5	9.38	0.934	6.07

The surface charge density increases rapidly below pH 5 and attains the maximum value (55.89%) at a pH of 1.78. The variation of % charge density is presumably negligible in the pH range of (4 – 2). Thus pH plays a pivotal role in the distribution of positive charges on the back bone of the polymer. The distribution and the density of charge on the polymer backbone are governed by the solution pH. Hence, pH of the solution is an important factor which decides the conformation of the wiggling polymer chain in the solution. The shape and size of the
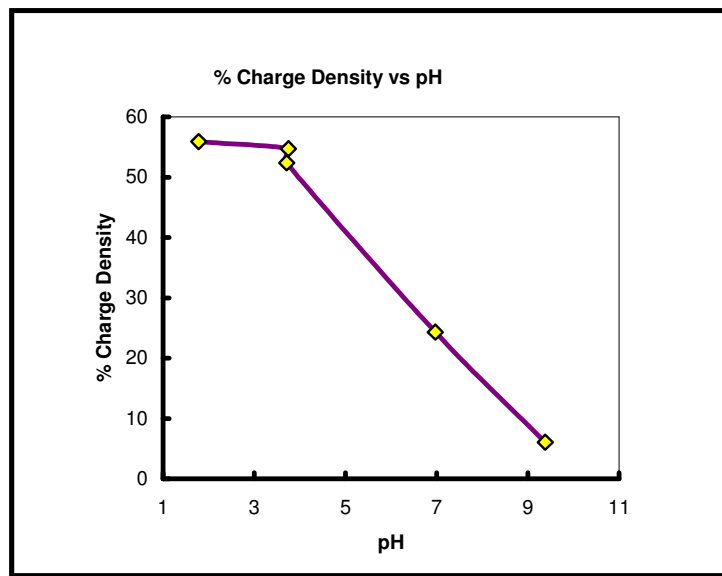
Figure 4.7 % charge density of poly(methylene amine)hydrochloride as a function of pH

polymer chain largely influences its solution properties like reduced viscosity, hydrodynamic radius etc. From the above set of experiments, a surface charge density

of 56% at a pH of 1.78 was obtained by PCD titration. Furthermore, the titration curve looks like a typical titration curve for a strong polyelectrolyte.

4.4 Laser Light Scattering

4.4.1 Light scattering Measurements

Light scattering experiments were performed with an ALV-5000 correlator. A Kr –ion laser at 647.1 nm wavelength was used as light source. The scattering angle was in the range of 15 -150 ^{0}. The light scattering cells were cleaned in acetone fountain prior to use. The refractive index increment of the solution after dialysis was measured with Michelson interferometer, (wavelength-633nm). In dynamic light scattering experiments, the time auto correlation function of the scattered intensity *g2(t)* was measured by homodyne method, which was converted to the scattered field autocorrelation function *g₁(t)* .

4.4.2 GPC- MALLS

The size exclusion chromatography was equipped with a refractive index detector (Wyatt Technology Europe, Flow cell serial Number K5, chromatography solvent sample: Toluene/2000 KD, 30KD Polystyrene) and an ALV 1800 multiage laser light scattering detector (MALLS) operating at 684 nm and 300 Mw power.

4.4.3. Data Analysis

A. SLS (Static Light Scattering)

A Zimm plot was employed to evaluate the weight average molecular weight (M_w), the second virial coefficient (A_2) and radius of gyration $<R_g>$, by using following equation (**1**)

$$K_c/ R (\theta) = 1/ M_w P (\theta) (1+ 2A_2C) \tag{1}$$

Where, K is the optical constant (K = 1.33 x 10 $^{-7}$ cm^2 g $^{-2}$ mol). c, A_2 and P(θ) are the concentrations of polymer in g cm^{-3}, second virial coefficient and particle scattering function respectively. q is the wave vector q = 4πn sin (θ/2)/λ. P(θ) depends on the dimensions of the polymer and is related to the radius of gyration R_g as follows,

$$1/ P(\theta) = 1 + 1/3 \, q^2 <Rg^2 > +............ \tag{2}$$

B. DLS (Dynamic Light Scattering)

The autocorrelation functions of scattered light intensity, $g^{(2)}$ (q, t) obtained by the homodyne mode were analysed by CONTIN methods. $g^{(2)}$ (t) has the following form related to the normalized electric field correlation function, $g^{(1)}$ (t)

$$g^{(2)} (q,t) = A \{ 1 + ß \mid g^{(1)} (q, t) \mid^2 \} \tag{3}$$

Where q is the scattering vector defined by $q = 4\pi n \sin (\theta/2)/\lambda$ with the scattering angle θ, wavelength λ, the refractive index n, and A is the base line and ß is a machine constant relating to the coherence of detection. Generally $g^{(1)}$ (t) is expressed by the distribution function G (Γ) of the decay rate Γ as

$$g^{(1)} (q, t) = \int G (\Gamma) \exp (-\Gamma t) \, d\Gamma \tag{4}$$

Where $\int G (\Gamma) d\Gamma = 1$, $\Gamma = 1/\tau$, τ = Decay time. If the fluctuation of the scattered light intensity is due to the translational diffusion of the polymer chains, the decay rate has the form

$$\Gamma / q^2 = D_0 (1 + k_d c + \ldots\ldots) \tag{5}$$

Where, D_0 is the translational diffusion coefficient at infinite dilution and k_d is a constant for the effect of polymer concentration. The hydrodynamic radius R_h is related to D_0 by Stokes- Einstein's equation,

$$R_h = kßT / 6\pi \eta D_0 \tag{6}$$

Where $k_ß$ = Boltzmann's constant $(1.4 \times 10^{-23}$ $JK^{-1})$ T = Temperature in °K η = Viscosity of the solvent (Pa Sec)

4.4.4. Conventional Static Light Scattering (SLS) of precursor polymer(Poly(1, 3-diacetylimidazol-2-one)(6)

The weight average molecular weight (M_w), second virial coefficient (A_2) and the radius of gyration (R_g) were deduced from Zimm Plot by using equation (1). Various parameters evaluated from conventional static light scattering, dynamic light scattering, GPC and MALLS (multi angle laser light scattering) - GPC are listed in Table 4.5. The selection of a reliable calibration for a specific polymer is a basic problem with GPC. As it is seen from the generated data listed in Table 4.5, the molecular weight determined by GPC with PS standard ($M_w = 1.18 \times 10^5$ g/mol), for the sample **2**, is nearly half the molecular weight determined by GPC-MALLS (2.82×10^5 g/mol). On the other hand, the weight average molecular weights (M_w),

determined by MALLS-GPC and conventional static light scattering (3 x 10 [5] g/mol) are nearly equal. This clearly indicates the limitation of GPC as a characterization technique for evaluation of molecular weight of the polymer poly(1,3-diacetylimidazol-2-one). The reliability of results determined by GPC depends on the appropriate selection of the standards. GPC coupled with MALLS takes care of this problem to a large extent for at least homopolymers. Thus in the ongoing study the generated data shows that PS is not the appropriate standard for the determination of molecular weight of poly(1,3-diacetylimidazole-2-one). Radius of gyration (R_g) of the sample **2** in THF was found to be 19.5 nm determined by GPC –MALLS and 24.6 nm. by conventional SLS.
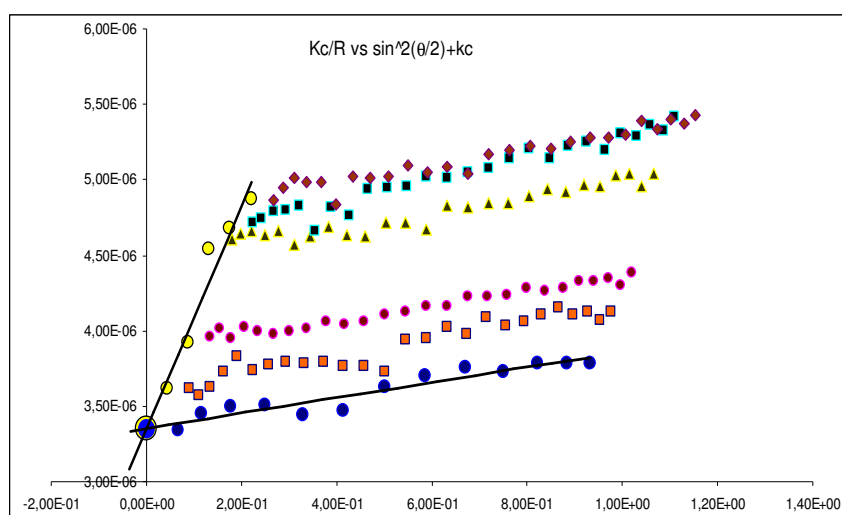
Figure 4.9 Zimm Plot of poly(1,3-diacetylimidazol-2one) (Precursor II in Table 4.5) in THF M_w =3.0 x 10^5 g/mol, R_g = 24.6 nm, A_2 = 1.14 x 10^{-3} cm^3 mol/gm^2

Table 4.5 Characteristics of polymers investigated by GPC, GPC-MALLS and SLS and DLS

	GPC			*GPC – MALLS*				*SLS*			*DLS*		
	Mw (g/mol) x 10^{-5}	Mn (g/mol) x 10^{-5}	PDI (M_w/M_n)	Mw (g/mol) x 10^{-5}	Mn (g/mol) x10^{-5}	PDI (g/mol) (M_w/M_n)	R_g (nm)	M_w (g/mol)	R_g (nm)	A_2 cm^{3}mol/gm^2	Do	R_h (nm)	K_d
1. Precursor (I)	1.52	0.52	2.94	-	-	-	-	-	-	-	-	-	-
PMA	-	-	-	-	-	-	-	21,300	22.42	-1.063 x 10^{-2}	3.69 x 10^{-11}	7.67	-5.051 x 10^{-12}
2. Precursor (II)	1.18	0.44	2.63	2.82	1.09	1.65	19.5	3 x 10^5	24.6	1.14 x 10^{-3}	3.6 x10^{-11}	11.8	1.0115 x10^{-12}
PMA	-	-	-	-	-	-	-	9200	18.3	-1.55 x10^{-2}		7.99(1g/l) 7.68(0.8g/l)	
3. Precursor (III)	1.05	0.37	2.76	2.71	1.19	2.28	18.5						
PMA	-	-	-	-	-	-	-	6700	4.357	-4.392 x 10^{-2}	3.63 x 10^{-11}	2.955 x 10^{-11}	

M_w = Weight Average Molecular Weight, M_n=Number Average Molecular weight, PDI= Poly dispersity Index, D_0= Translational diffusion coefficient, A_2= Second virial coefficient, R_h= Hydrodynamic Radius, R_g= Radius of gyration, K_d= a constant for effect of polymer concentration.

4.4.5 Dynamic Light scattering of poly(1,3-diacetylimidazole-2-one) (Precursor II in Table 4.5)

The Figure 4.10 shows a plot of the autocorrelation function $g^{(2)}(t) - 1$ as a function of time. The plot of distribution function $G(\tau)$ provides the average decay time (τ). This in turn gives the decay rate by using the equation (Γ (Decay rate) = $1/\tau$). The plot of decay rate (Γ) vs. q2 is shown in Figure 4.12 (b). Γ showed excellent linearity passing through the origin in this plot, indicating that the mode is translational. The slope gives the diffusion coefficient at a particular concentration. Figure 4.12 (a) shows the plot of diffusion coefficient vs. concentration
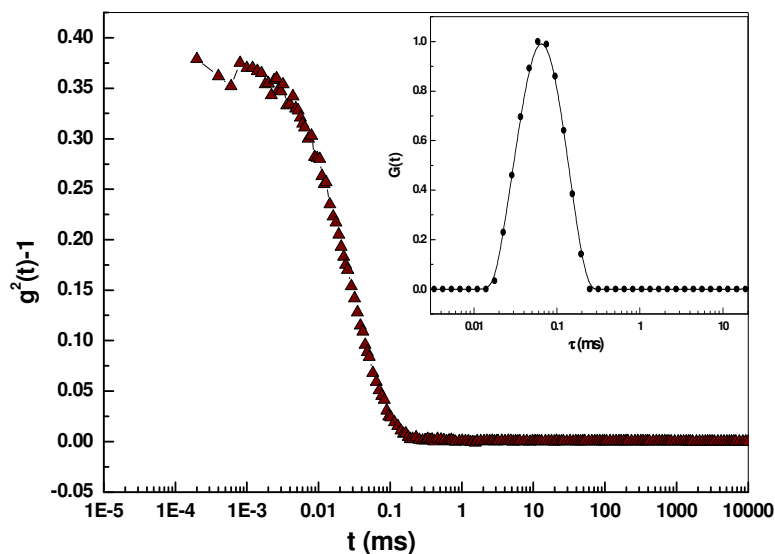
Figure 4.10 Autocorrelation function $g^2(t) - 1$ as a function of decay time(t)

At zero concentration D= D_0 (translational diffusion coefficient). The value D_0 is used to calculate the hydrodynamic radius R_h by stokes Einstein's equation. R_h of the parent polymer, poly(1,3-diacetylimidazole-2-one)(precursor II, Table 4.5) was found to be 11.8 nm where as R_g of 24.6 nm was determined by static light scattering. The ratio ($\rho = R_g/R_h$) 2.09 gives a tentative idea about the shape of the polymer in solution and the polydispersity index. However, at the same time the higher second virial coefficient (A_2) (1.14×10^{-3}) accounts for greater segment solvent interaction leading to good solubility. Under such condition a polymer is expected to behave like a random coil in good solvent. Thus combining the above facts it can be said that the polymer under consideration behaves like an expanded swollen chain with stiff backbone.

Figure 4.11(a) and (b) represent the distribution function G(t) for various concentrations and at different angles for the concentration 0.4g/l.
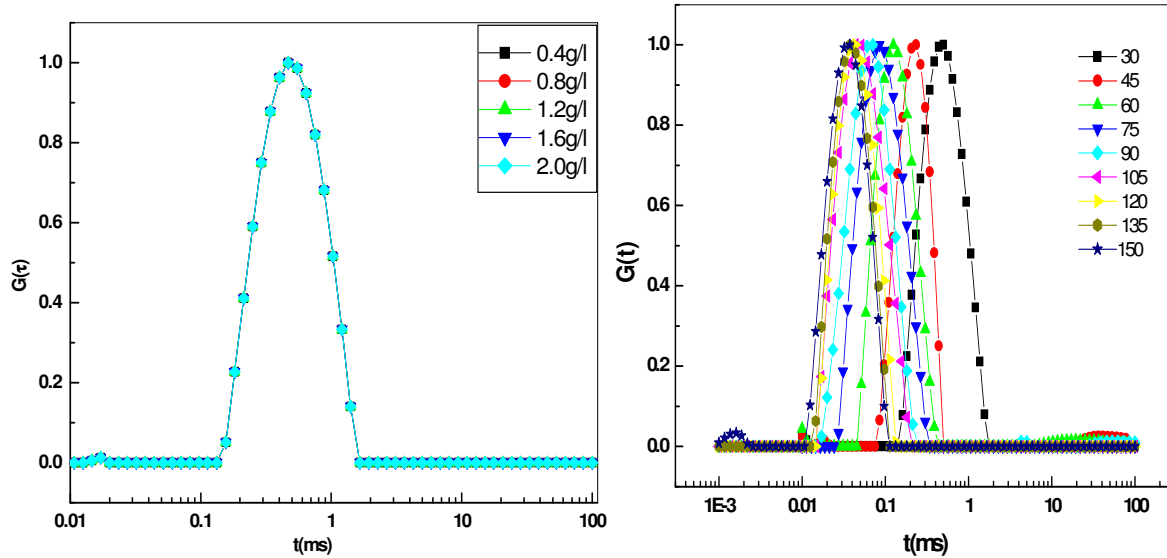
Figure 4.11 Distribution function $G_{(t)}$ as a function of decay time (t) in milliseconds **(a)** at different concentrations at scattering angle 90° **(b)** at different angles for the concentration 0.4g/l respectively.

It is evident from the graph that the decay time is independent of concentration of polymer However, at a particular concentration (0.4g/l) decay time decreased with increase in angle. The amplitude at different concentrations is same indicating equal contribution at different concentration. On comparison with the distribution function vs. decay time for corresponding poly(methylene amine)**(8)** at different concentrations, a bimodal distribution existing at all concentration is seen unlike the parent polymer.
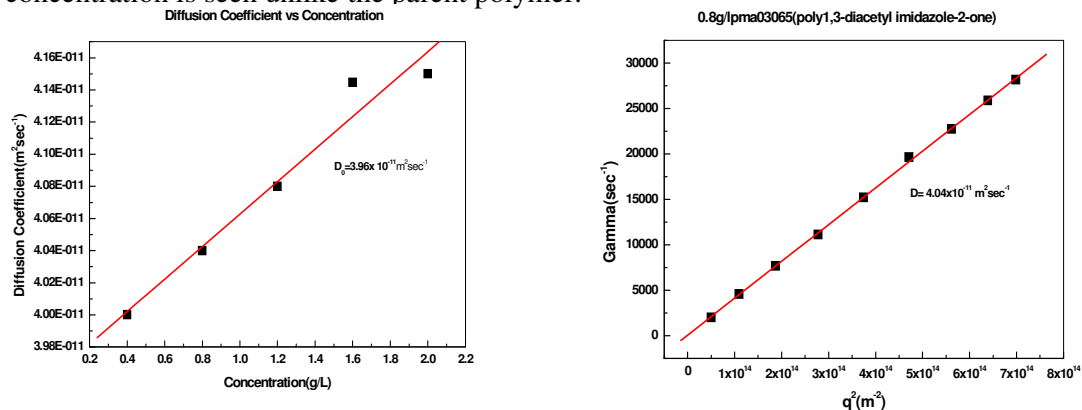
Figure 4.12 (a) Diffusion coefficient as a function of concentration **(b)**Decay rate (Gamma) as function of q^2

With increase in concentration the decay time of both the modes increases. However, rise in concentration results in reducing the relative amplitude of the fast mode while the slow mode remains unaffected. This clearly explains the association behavior of poly(methylene amine), a polyelectrolyte, in aqueous solution unlike its precursor, which is a neutral polymer, poly(1,3-diacetylimidazol-2-one)**(6)**.

4.4.6 MALLS–GPC studies of poly(1,3-diacetylimidazol-2-one)(6):An insight into branching in polymer chains.

Poly(1,3-diacetylimidazol-2-one)**(6)** in THF was investigated by Multiangle Laser Light Scattering. Multiangle laser light scattering coupled with GPC was used to determine the molecular weight, root mean square radius and conformational information of poly(1,3-diacetylimidazole-2-one). The molecular weights of the samples were calculated by using dn/dc Method using the ASTRA software.[20] The method requires values for RI detector instrument constant and the dn/dc of the polymer. The polymer concentration is calculated from the sample RI detector signal, the RI detector constant and the value of dn/dc. This method is quite useful because it calculates a theoretical mass eluted through the columns (and detectors). Percent recovery of the polymer through the SEC can then be determined. The method was used to examine three different samples of polymer **6.** The results are listed in Table 4.6.

The conformational behavior of the polymer is examined by using the values of Molecular weights and corresponding RMS radius from the relationship (8).[21-23] By plotting the RMS radii of gyration as a function of molar mass in a double logarithmic way, the gross molecular information can be investigated according to the following equation:

$$\text{RMS} = k \, M^{\alpha} \qquad\qquad (7)$$

$$\log \text{RMS} = k + \alpha \ \log M_i \qquad\qquad (8)$$

where α is the conformational coefficient, k is the proportionality constant (the y axis intercept), M_i a molar mass and RMS is the Root mean square radius of gyration.[24] It is known that for a rigid rod $\alpha = 1.0$, for a random coil in theta solvent α is 0.5 and for a sphere it is 0.33. Flory has shown that the value for α of a polymer in a good solvent is 0.55 – 0.60.[25]The conformational coefficient is determined from the slope of a log-log plot of RMS radius vs molecular weight.

Table 4.6 MALLS Data for poly(1,3-diacetylimidazol-2-one)**(6)** in THF

Sample	Molecular Weight.(M_w)	RMS Radius,(nm)	α
PI(pma/03/021)	2.72 x 10 ^{5}	18.8	0.32 ± 0.01
PII(pma/03/065)	2.82 x 10 ^{5}	19.5	0.329 ± 0.005
PIII(pma/03/063)	2.79 x 10 ^{5}	18.3	0.330 ± 0.005

Table 4.6 compiles the data including the conformational coefficient α, of three samples of poly(1,3-diacetylimidazol-2-one) in THF prepared under similar experimental conditions. Although the increase in the value of α is not significant from the data listed in the Table 4.6 yet an analogy can be drawn in comparison with literature.[20] Samples prepared under similar experimental conditions are anticipated to produce same or nearly same results on investigation with MALLS.

As already mentioned earlier, the value of α denotes the conformational characteristics of a polymer in the given solvent. A value less than 0.5 indicates the presence of branched molecules, [26-28] while higher values are indicative of rod like polymer chain arrangements. The α value of 0.32-0.33 suggests a more compact or tightly coiled structure for poly (1,3-diacetylimidazol-2-one)**(6)** at higher molecular weight, possibly due to branching.Wittmar *etal*. compared linear unbranched pullulan to branched polyesters. Pullulan[29] (a water soluble polysaccharide with a repeat unit of myltotriose condensed through alpha 1,6-linkage) showed a typical slope value of random coil polymers (0.55). In contrast, the slopes of the polyesters were much smaller (0.28-0.35), demonstrating highly branched, tightly bound compact character.[30] This observation is consistent with the fact that highly branched commercial dextran has an α value of 0.38.[31] A typical curve of Molecular weight vs. RMS Radius of poly(1,3-diacetylimidazole-2-one) is represented in Figure 4.13
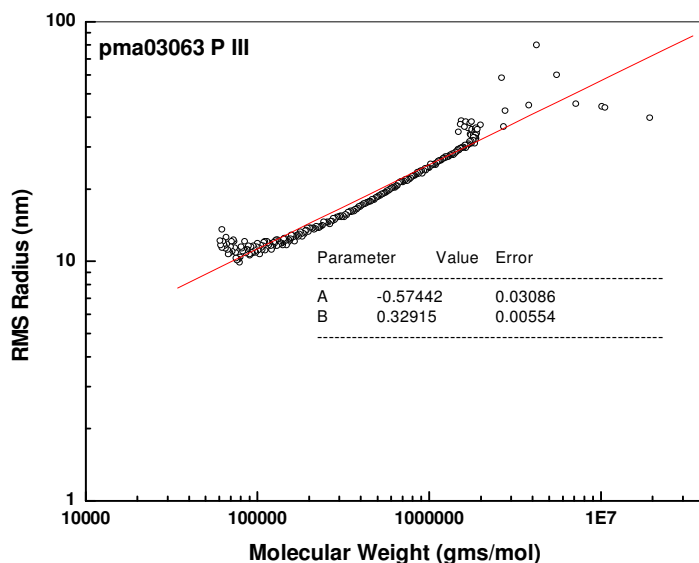
Figure 4.13 Double logarithmic plot of RMS radius of gyration vs. Molecular weight for poly(1, 3-diacetylimidazol-2-one)**(6),** sample P III; slope = 0.329 ± 0.005

The presence of branched molecules in a polymer sample can be examined further from a plot of Molar mass vs. volume. At a given elution volume, the molar mass increases with increased branching, because the branched molecules tend to be more compact i.e. tightly bound within the molecule. Thus, the size of the macromolecules of branched polymers are smaller than those of macromolecules of linear polymers with the same molecular weight.[20]Figure 4.14 shows a plot of molecular weight as function of elution volume of three different samples viz. PI, PII and PIII of poly(1,3-diacetylimidazol-2-one)**(6)**. As it is evident from the plot, **P I** is the most branched among all three samples under investigation. Further, the extent of branching in the sample **P I** is maximum in low and high molecular weight regime as seen from the deviation of the curve from linearity at both the ends. This implies that the concentration of branched macromolecules is higher in low (10,000– 70,000 g/mol) molecular weight region as well as in high molecular weight region (> 1000,000 g/mol).
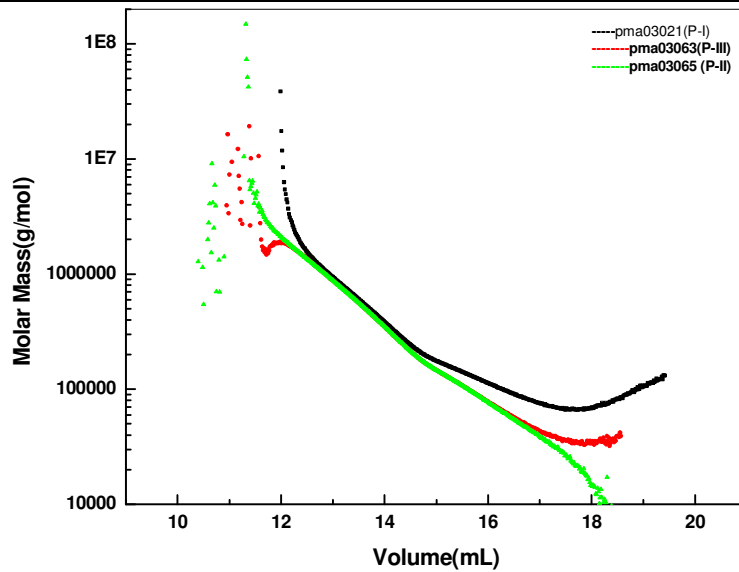
Figure 4.14 Molecular weight vs. elution volume for poly(1,3-diacetylimidazol-2-one)**(6),** samples; PI (pma/03/021), PII (pma/03/063), and PIII (pma/03/065)

4.4.7 Dynamic light scattering (DLS) studies of poly(methylene amine)(precursor II in Table 4.5)

Since the data obtained in the study was a superimposition of several decay rates CONTIN program was used for the analysis of data. Figure 4.15 shows correlation functions of poly(methylene amine)**(8)** at different concentrations obtained from CONTIN analysis**.** In subsequent discussions the amplitude of all auto correlation functions $g^2(t)$-1 are normalized to unity.
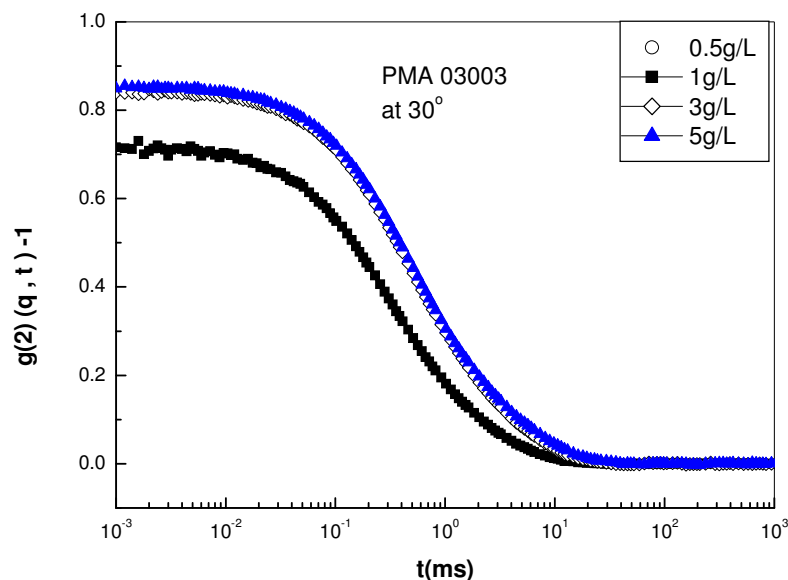
Figure 4.15 Correlation functions of poly(methylene amine) at different concentrations.

4.4.8 Concentration dependence in the absence of salt

Figure 4.16 shows a typical plot of decay time distribution; **G(τ)** at various concentration of poly(methylene amine) in water at a scattering angle of 30 ° obtained from CONTIN analysis. The decay time distribution obtained at different concentrations of poly(methylene amine) in salt free condition at different angles, demonstrated two relaxation processes that resembled bimodal distribution. This kind of distribution has previously been reported with other polyelectrolyte systems and assigned as slow and fast mode respectively. The relative amplitude of the slow mode in CONTIN analysis is defined as the area under the slow mode peak divided by the total area under slow and fast mode peaks. It is interesting to note that the aqueous solution of poly(methylene amine) manifests a bimodal distribution in the absence of a foreign counter ion unlike other existing and well-studied polyelectrolytes.
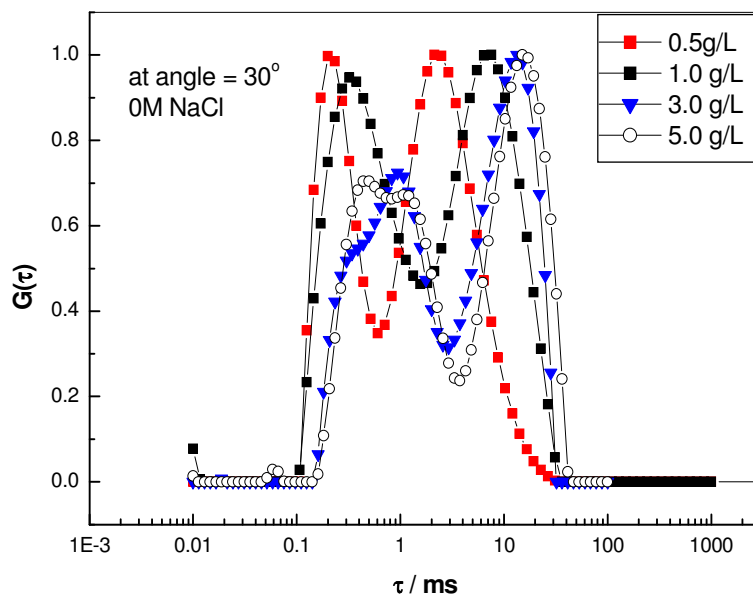
Figure 4.16 Decay time distributions at various concentration of poly(methylene amine)

This strange phenomenon can be attributed to the existence of an appreciable number of charged amine functionalities (partially protonated) in aqueous solution that renders the polyelectrolyte effect. From the above observation it is apparent that poly(methylene amine) in aqueous solution is basic and abstracts protons from surrounding water there by producing self-generated counter ions (hydroxyl ions). Further, it is qualitatively observed that with increase in concentration decay time of both the processes increases. The relative amplitude of fast relaxation decreases with increase in concentration. This observation reflects greater association between polymer chains rather than interaction with solvent molecules, with

increase in polyelectrolyte concentration. However, above 3 g/L it remains nearly constant. Thus, the cluster formation that contributes towards slow mode gets prominent with rise in polyelectrolyte concentration. However, beyond a limit (3g/L) the contribution is almost negligible.

4.4.9 Salt Concentration Dependence

Figure 4.17 shows the salt concentration dependence of the decay time distribution of the polymer at scattering angle $\theta = 90°$. As evident from the distribution curve, with increase in salt concentration the contribution from slow mode diminished gradually, and eventually subsides at higher salt concentrations (1M NaCl). The relaxation time of the fast mode increased. The slow mode perhaps originated from agglomeration of individual polymer chains. Addition of salt led to shielding of charges and hence weakening of electrostatic attraction. This resulted in disentanglement of large clusters.
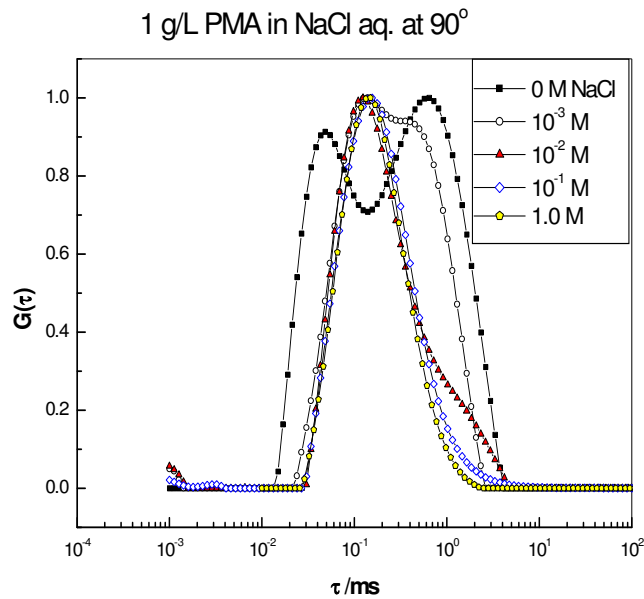
Figure 4.17 Salt concentration dependence of poly(methylene amine) at scattering angle 90**.**

Further, it was observed that at a constant scattering angle, the increase in salt (NaCl) concentration led to gradual disappearance of slow mode. Finally, it disappeared at NaCl concentration of 1M. This behaviour of the aqueous solution of poly(methylene amine) in presence of low molecular weight electrolytes (NaCl) confirmed the appearance of slow mode as a result of polyelectrolyte effect arising from some kind of temporal clusters[15] and the fast mode due to translational diffusion of polymer chain.

4.4.10 Plot of apparent diffusion coefficient vs.pH

Figure 4.18 shows the plot of apparent diffusion coefficient vs. pH. The diffusion behavior of poly(methylene amine) changes with change in pH. However, as seen from the plot above, the apparent diffusion coefficient is maximum in the pH range of 6-7. With increase or decrease in pH the apparent diffusion coefficient of the fast and slow mode decreases to a minimum. Further, the diffusion coefficient of the fast mode is much larger than the slow modes. Apparently, the middle mode remained unaffected. The decrease in Diffusion coefficient along both sides of neutral region of pH can be explained by shielding effect of
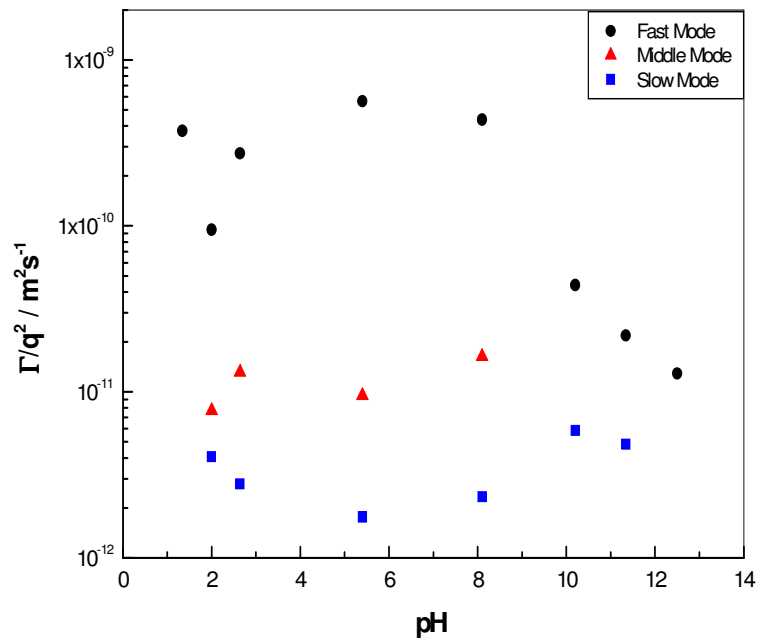
Figure 4.18 Apparent diffusion coefficient as a function of pH

counter ions. It is already shown earlier that poly(methylene amine) remains in partially protonated form there by generating its own counter ion i.e.OH⁻. from water. Thus, increase in pH resulting from addition of NaOH increases the concentration of counter ions (OH⁻). Consequently, the shielding effect becomes prominent and the ionic cloud gets larger. This eventually lowers the mobility of polyion. On the other hand, the decrease in apparent diffusion coefficient along the lower range of pH can be explained in an analogous way. The decrease in pH achieved by addition of HCl leads to protonation of poly(methylene amine) where Cl⁻ is the foreign counter ion. With decrease in pH resulting from increase in HCl

concentration, the shielding effect gets prominent and the ionic cloud gets larger thereby reducing the mobility of polyion. In a similar system, it was also reported that diffusion behavior of polyion depends on the diffusion of counter ion.[23]

4.5. Conclusions

Poly(methylene amine)**(8)**, a novel cationic polyelectrolyte was prepared by basic hydrolysis of poly(1,3-diacetylimidazol-2-one)**(6).** Both the polymers were investigated by conventional dynamic and static light scattering, GPC, and GPC-MALLS. Discrepancies in the molecular weight of the precursor polymer (poly (1, 3-diacetylimidazole-2-one)**(6)** determined by GPC and conventional light scattering and GPC-MALLS showed that polystyrene was not the right GPC standard for the polymer under investigation. The diffusion behavior of both the polymers was studied by dynamic light scattering. The ratio ($\rho = R_g/R_h$) for the precursor polymer II in Table 4.5, poly(1,3-diacetylimidazol-2-one) was found to be 2.09, which showed that the polymer takes the shape of a swollen rigid rod in THF solution. The diffusion behavior of the poly(methylene amine) was investigated in aqueous solution at different salt (NaCl) concentrations. It was found that with increase in salt concentration the fast mode became prominent where as the slow mode diminished gradually. At a concentration of 1M NaCl, the slow mode diminished completely leaving aside a single prominent fast mode. The plot of diffusion behavior of poly(methylene amine) as a function of pH in the absence of salt, investigated in aqueous solution demonstrated an interesting trajectory. The diffusion coefficients dropped off gradually along both the sides to the neutral pH regime (pH 7.0).This behavior of rise and fall of diffusion coefficient along both sides of pH 7.0 signified the increase in the size of ionic cloud due to rise in the concentration of counter ion. The large ionic clouds slowed down the mobility of polyion and hence decrease of diffusion coefficient.

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Chapter 5 **MODIFICATION of   POLY(METHYLENE**

AMINE)

5.1 Introduction

Amines can act both as a base as well as a nucleophile. A linear aliphatic polyamine can be assumed to undergo reactions similar to a monomer. This opens up the possibility to access a broad range of new materials through polymer analogous reactions with electrophiles such as methyl iodide, acid chlorides, acrylic acid derivatives etc. Polymer analogous reactions of amino containing linear polymers viz-PVAm and polyethyleneimine(PEI) with electrophiles have been well studied and reported.[1] Adjacent amino groups in PVAm (Figure 5.1(a)) and polyallylamines (Figure 5.1(c)) are separated by one and two carbon atoms, respectively. This renders enough space for protonation and helps prevent steric hindrance during nucleophilic substitution up on reaction with electrophiles. On the contrary, the polymer under investigation, Poly(methylene amine) (Figure 5.1 (b)), bearing an amino group on every carbon atom enhances the possibility of maximum functionalization while gradually making the polymer sterically hindered. Consequently, the polymer is expected to strike a balance between nucleophilicity and steric hindrance while trying to maximize functionalization. Studies on the functionalization of poly(methylene amine) is described in detail in this chapter.

(a)   **(b)**   **(c)**
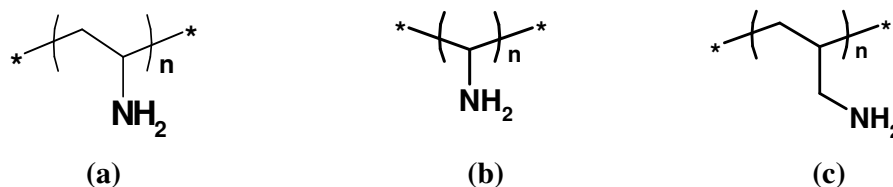
Figure 5.1 The structures of polyvinylamine(a), poly(methylene amine)(b) and polyallylamine(c)

A schematic representation of a few important reactions of poly(methylene amine) such as protonation with acid, alkylation with methyl iodide, acylation with aliphatic and aromatic acid chlorides and Michael addition reaction with unsaturated aliphatic esters is depicted in Figure 5.2.

5.2 Degree of functionalization

The degree of functionalization was determined by elemental analysis and is defined as percentage of substituted monomer units relative to all monomer units. The degree of substitution (in %) = [m / (m + n)].100

Where m = substituted monomer units, n = unsubstituted monomer units

m + n = Total number of monomer units.

5.3 Poly(N-methyl-ammonium-iodide-methyleneamine)(10)

One of the important applications of polyamines by virtue of their cationicity involves their interactions with anionically charged colloidal particles in aqueous media in nature. The cationic character of polyamines is pH dependent. This means, a polyamine that could flocculate particulates from water at a pH below 7 via charge – neutralization mechanism might be expected to be less effective at pH above 10. Because the primary amine functions in polyamines loose a significant amount of cationic charge during neutral conversion. The negative impact of increased pH on fixing properties has been confirmed by Richardson and Pruszynsky[2] in the laboratory and based on the paper machine application. They observed a loss of 6% of machine efficiency during neutral pH conversion with PEI – based fixative programme, was recovered when switched to quarternized product. Therefore, the underlying work deals with quarternization of poly(methylene amine) and its comparison with polyvinylamine. Partially methylated poly(methylene amine) was synthesized by treating methanolic solution of poly(methylene amine)**(8)** according to a procedure reported in the literature.[3-5] The product was insoluble in methanol but soluble in water.^{1}H-NMR spectrum of **10** showed two broad peaks, one in the region 2.5-2.85 ppm which can be due to the protons of methyl groups from N-CH_3 units, the other peak was broader, in the region 3.1-3.8 ppm and was ascribed to the protons of –CH- groups of the main chains and from the protons of methyl groups of N^+-CH_3 with methyl iodide. ^{13}C-NMR spectrum of this polymer showed two broad peaks, one in the region 32-37 ppm attributed to N-CH_3 units and another broad signal in the region 47-57 ppm ascribed to the presence of N^+-CH_3 and CH units.[6] The extent of methylation was determined from elemental analysis. It was found that on varying molar ratio of PMA/MeI between 1:1 and 1:10 there was an increase in degree of substitution. The degree of substitution varied from 32 % for 1:1 molar ratio to 40 %

for 1:10 molar ratio. In order to investigate the influence of amino groups placed in close proximity on the degree of substitution, a set of methylation experiments was performed with PVAm under similar conditions. It was found that with variation in molar ratio PVAm/MeI from 1:1 to 1:10, the degree of substitution varied from 34 % (1:1) to 56%(1:10) through 44%(1:2). From the above set of experiments one concludes that degree of alkylation is higher in case of polyvinylamine in comparison with poly(methylene amine).

5.4 Poly(4-acetamido-N-methylenebenzensulfonamide)(11)

Poly(4-acetamido-N-methylenebenzenesulfonamide)(**11**) was prepared from poly(methylene amine)hydrochloride and *p*-acetamido-N-benzenesulfonylchloride, in water. The pH of the solution was adjusted during the reaction to 10.5 and tetrahydrofuran (THF) was added to increase the solubility of the resulting polymer upon amidification with acyl chloride. The volume of THF was increased with the expected amidification ratio in order to have convenient solvating properties of the reaction medium.[7] It was estimated from the C/N ratio from elemental analysis that 70% of amine groups have reacted. On comparison of the IR spectra of the polymer **11** with the starting polymer, poly(methylene amine)(**8**), a decrease of the broad NH stretching band at 2900 cm^{-1} was observed and the appearance of a new band at 1670 cm^{-1} which was assigned to C=O stretching vibration of the amide groups. The structure of the polymer **11** was confirmed by ^{1}H-NMR spectroscopy.
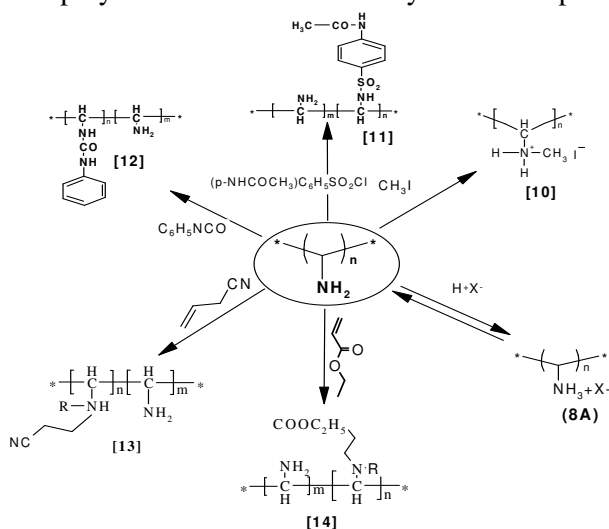
Figure 5.2 Few chemical modifications of poly(methylene amine)

^{1}H-NMR spectrum of the polymer displayed a broad signal at 8.5-7.2 ppm characteristic of aromatic protons and the signal at 2.2-ppm characteristic for the protons of methyl groups. The signal characterizing the protons connected with the carbon atoms on the main molecular chains was masked by the solvent peak (THF). The ^{13}C-NMR spectrum of **11** is presented in Figure 5.3 with the corresponding assignments. The peak which characterized methine groups on the main chains appeared between 50-60 ppm region. This was even broader than the unmodified poly(methylene amine) owing to the complex microstructure arising from partial amidification. The NMR measurements were performed in a mixture of THF/H_2O (1:1) in which the polymer was soluble. The polymer was insoluble in organic solvents and water.
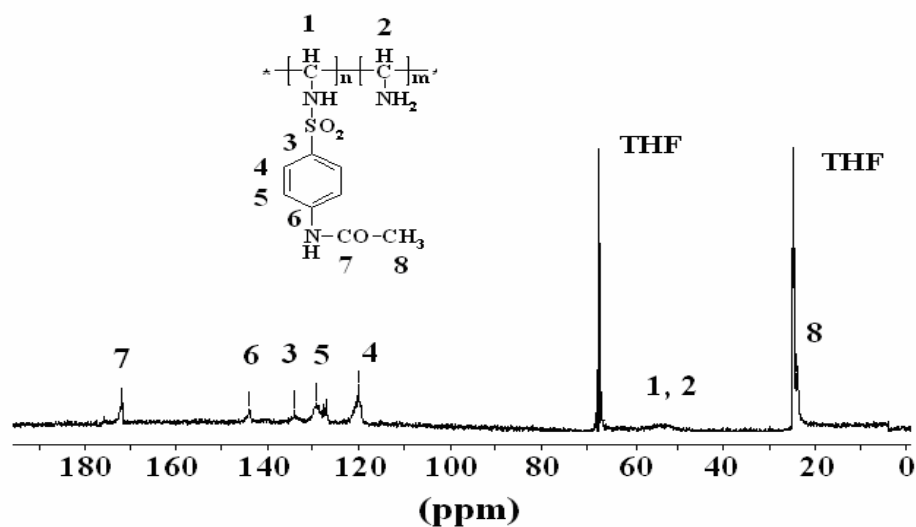
Figure5.3 ^{13}C NMR of poly(4-acetamido –N-methylenebenzene sulphonamide)**(11)**

The TGA curve of **11** showed two steps of degradation.The first step of degradation, in the range of 120-250°C, was assigned to the degradation of unreacted amino groups. The second step, in the range of 280-400°C, and was ascribed to the degradation of the main chains of the polymer. Polymer **11** did not show any glass transition temperature upto the temperature where the degradation process began.

5.5 Poly(N-methylene-N-phenylurea)(12)

Poly(N-methylene-N-phenylurea)**(12)** (Figure.5.4) was obtained by reacting phenyl isocyanate with methanolic solution of poly(methylene amine), as described in the literature. The elemental analysis revealed the degree of substitution to be 80%. The structure of the modified polymer **12** was confirmed by IR and solid state NMR. The IR spectrum of the polymer exhibited characteristic absorption bands at 3335 cm^{-1} (NH stretching vibration), 1670 cm^{-1} (C=O stretching vibration), 1530 cm^{-1} (C-N stretching vibration), 1600 cm^{-1}, 1500 cm^{-1}, 900 cm$^{-1,}$ 720 cm^{-1}, 684 cm^{-1} (aromatic). As the resulting polymer was insoluble in all the solvents tested, the structure was elucidated with the help of solid state NMR. In the ^{1}H-NMR spectrum of the polymer the aromatic protons appeared as a large peak having a maximum around 7 ppm. and the protons of methine groups H$_a$ and H$_e$ are hidden by the peak appearing around 3.8 ppm that characterized the protons of amine groups(Figure.5.5 (a))
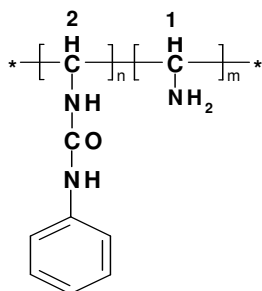
Figure 5.4 poly (N-methylene-N-phenylurea)

(a)   (b)
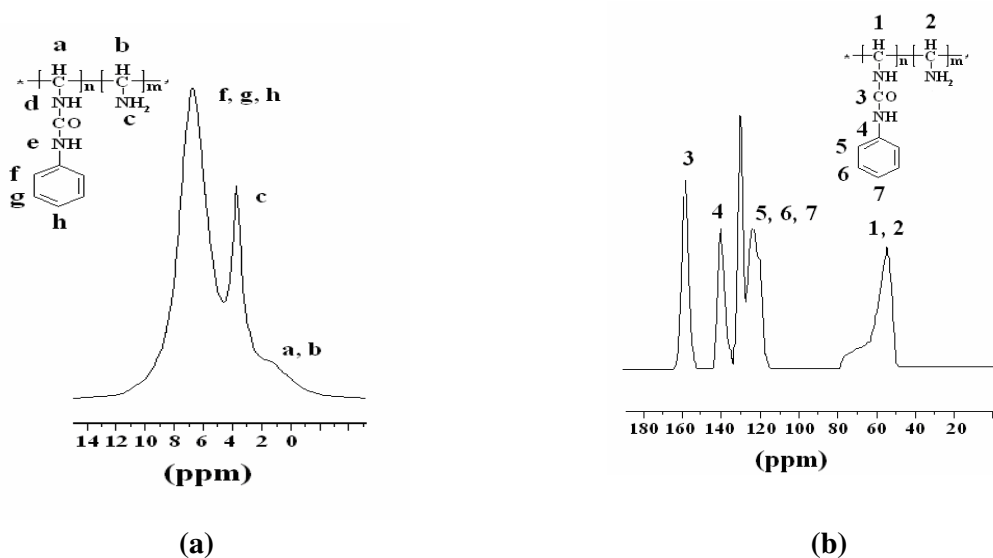
Figure 5.5 ^{1}HNMR (a) and ^{13}C NMR (b) of poly(N-Methylene-N-phenylurea)**(12)**

In the solid state ^{13}C-NMR of the polymer (Fig.5.5.(b)) the peak that characterized carbonyl groups appeared at 160 ppm. The characteristic peak of the methine groups (carbons 1 and 2) was very broad (80-50 ppm) due to the complicated microstructure formed by different sequences. The polymer was insoluble in organic solvents as well as in water. The TGA of the polymer demonstrated high thermal stability with onset of degradation at 260 $^{\circ}$C. However, no clear glass transition (T_g) was observed for the polymer in the DSC curve until it started to degrade.

5.6 Poly(methylene amine)acrylic acid derivatives (13) & (14)

Poly(methylene amine) was modified by reacting it with acrylic acid derivatives acrylonitrile and ethylacrylate. The structures of the resulting acrylonitrile modified poly(methylene amine) **13** and ethylacrylate modified poly(methylene amine) **14** are presented in Figure 5.6 and the conditions of the synthesis in Table 5.1. The structure of the polymers was identified by elemental analysis, IR and NMR spectroscopy. In the IR spectra of polymers **13** and **14** absorption bands appearing at 2953 cm^{-1}, 2920 cm^{-1} and 2853 cm^{-1} were attributed to the CH$_3$, CH$_2$ and CH groups respectively. In the case of polymers **13** characteristic absorption bands for CN groups appeared at 2245 cm^{-1}.

The characteristic absorption band appearing at 1735 cm^{-1} is due to the presence of carbonyl group from ester units present in the structure of **14.** All the spectra demonstrated reduction in peak intensity arising from NH$_2$ stretching. In the ^{1}H-NMR spectrums of polymers **13** some of the peaks were masked by other broad peaks. In the ^{13}C-NMR spectrum the peak that characterized the methine units from the main chains was broad because of the complicated microstructure of this modified polymer. The analysis was supplemented by ^{13}C-^{1}H COSY. From this spectrum it was seen that for the peak which appeared in ^{13}C-NMR spectrum at 71 ppm correspond in ^{1}H-NMR spectrum corresponded a peak which

(13)

(14)

(13) R = H, CH$_2$-CH$_2$-CN

(14) R = H, CH$_2$-CH$_2$-COOC$_2$H$_5$
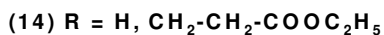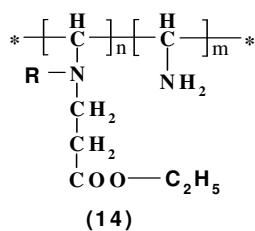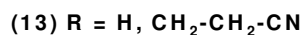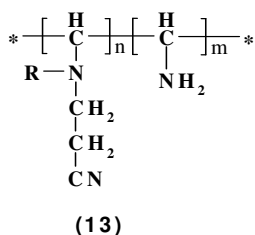
Figure 5.6 Structures of polymers modified with acrylonitrile**(13)** and modified with ethylacrylate**(14)**

appeared at 3.5 ppm. These two peaks were assigned to N-CH$_2$ groups. Also, for the peak appearing in the ^{13}C-NMR spectrum at 62 ppm corresponded in ^{1}H-NMR spectrum a peak at 3.3 ppm. These two peaks were assigned to be due to the presence of the CH groups from the main macromolecular chains. For the peak appearing in ^{13}C-NMR spectrum at 25 ppm, a corresponding peak was observed in the ^{1}H-NMR spectrum at 2.8 ppm. These peaks were assigned to be due to the presence of CH$_2$-CN groups. For compound **14** the assignment of the peaks is complicated due to the fact that most of them are broad and some of them are hidden due to the presence of the other peaks. The peak that characterized methyl groups appeared at around 0.8 ppm, the characteristic peak of O-CH$_2$ groups appeared around 3.6 ppm and the characteristic peaks for the groups CH$_2$-CH$_2$-CO is broad and appeared in the range of 3.2-1.7 ppm. The peak that characterized the protons of CH$_2$-CH$_2$-CO from the main macromolecular chains is hidden by the presence of the characteristic peak of CH$_2$-CH$_2$-CO groups.

Table 5.1 Characteristic of compounds **13** and **14**.

Polymer	Reactant	Molar ratio PMA/Reactant	Reaction time (h)	Conv[a] (%)	η^b_{inh} (g/dL)	T^d_5 (°C)	T^e_{10} (°C)	T^f_{20} (°C)	T^g_{50} (°C)
13a	Acrylo nitrile	1:2	24	64	0.3	185	212	225	390
13 b	Acrylo nitrile	1:100	24	100	0.4	213	230	252	305
14	Ethyl acrylate	1/5	24	87	0.35	150	160	185	360

[a] = conversion of the amino groups (100% indicates that 2 mols of reactant reacted with one NH_2 group) calculated from elemental analysis; [b] = inherent viscosity at 20°C, 0.5 g/dL, in DMF; [c] = glass transition temperature; [d] = temperature of 5% weight loss; [e] = temperature of 10% weight loss; [f] = temperature of 20% weight loss; [g] = temperature of 50% weight loss

In [13] C-NMR spectrum of the polymer **13** characteristic peaks of methine groups appeared at 50 ppm and was broad. The DSC curve of this polymer did not show a clear glass transition temperature. Polymer **14** was less thermostable when compared with poly(methylene amine) modified with acrylonitrile **13**. Polymer **13b** exhibited higher initial decomposition temperatures when compared with **13a**. Probably polymer **13a** had higher concentration of amine groups more sensitive to degradation. The degrees of substitution were determined from elemental analysis and are listed in Table 5.1. Acrylonitrile modified poly(methylene amine) showed 64% conversion at a molar ratio of PMA/Reactant = 1:2. With increase in molar ratio to (1:100); the degree of substitution was determined to be 100%. On the other hand, ethyl acrylate modified poly(methylene amine) showed 87% extent of conversion at a molar ratio of 1:5.

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5.7 Acid functionalised polymers (Polymethylene-N-propanesulfonic acid)(15)

Sulfonic acid derived polymers have been evaluated as host matrices in polymer electrolyte membrane fuel cells[8]. These polymers can also be used as plasticizers for concrete to improve the flow ability or work life of the concrete[9]. However, the described work deals with the evaluation of the degree of substitution and its comparison against polyvinylamine.
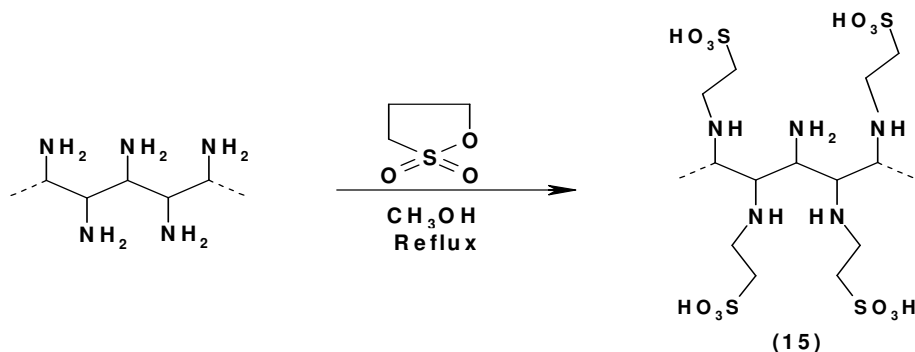
Scheme 5.1 Synthetic scheme for poly(N-methylene-N-propanesulfonic acid)**(15)**

Poly(N-methylene-N-propanesulfonicacid) was obtained by reacting a methanol solution of poly(methylene amine) with 1,3-propanesulfone, at reflux temperature (scheme 5.1). The reaction was carried out by using different molar ratios of poly (methyleneamine)/1,3-propanesulfone. Unreacted 1,3-propanesulfone was removed by dialysis. The resulting polymer was well soluble in water and was separated from the solution by freeze-drying. The IR spectrum of the polymer showed characteristic absorption bands at 3430 cm^{-1} (NH), 1618 cm^{-1} (NH), 1192 cm^{-1} (S=O symmetric vibration) and 1035 cm^{-1} (S=O asymmetric vibration). The degree of substitution was calculated from elemental analysis. With variation in molar ratio of PMA/1,3-propanesulfone the degree of substitution varied. At a proportion of 1:1 the degree of substitution was 44% and it rose to 54% at molar proportion of 1:10. In order to compare the degree of substitution, polyvinylamine was reacted with 1,3-propanesulfone under similar experimental conditions. PVAm showed a percentage conversion of 66% at PVAm/ 1,3-propanesulfone molar ratio (1:2) and the degree of substitution increased to 75% with increase in PVAm / 1,3-prpanesulfone ratio (1:10). The low percentage of conversion in case of poly(methylene amine) in comparison to PVAm can be explained in terms of steric hindrance. While, increased number of

amino groups in poly(methylene amine) offers room for maximizing substitution, their presence in close proximity generates steric hindrance. Consequently, the nucleophillicity of the amino groups competes with the steric hindrance posed by mono substituted amino groups; which limits the degree of substitution in case of poly(methylene amine).

5.8 Photocrosslinkable Polymers

During the last decades, several significant developments in polymer science have involved the use of cinammic derivative photochemistry for modifying macromolecular structures and materials. Interestingly, for some of these applications the expected dominant effect is not conventional cross-linking. Stepwise photo coupling of low or medium molecular weight compounds to polymeric surfaces or in to polymer matrices was achieved and studied for improving the biocompatibility of synthetic implants and for improving the durability and performances of non-linear optics materials. E-Z isomerisation of cinnamic and other aryl propeonic acid derivatives has been selected as the photochemically driven process leading to substantial changes in polymer solvent interactions. The designed polymers including these photosensitive moieties as side groups, exhibited the desired photoresponsivity with much reduced risk of thermal reversibility compared with azobenzene, stilbene or spiro benzopiran chromophore. The aim of the present work is to evaluate the degree of substitution of cinnamoyl functionality in the poly(methylene amine) polymer backbone and to investigate the phenomenon of photocrosslinking on exposure to UV light.
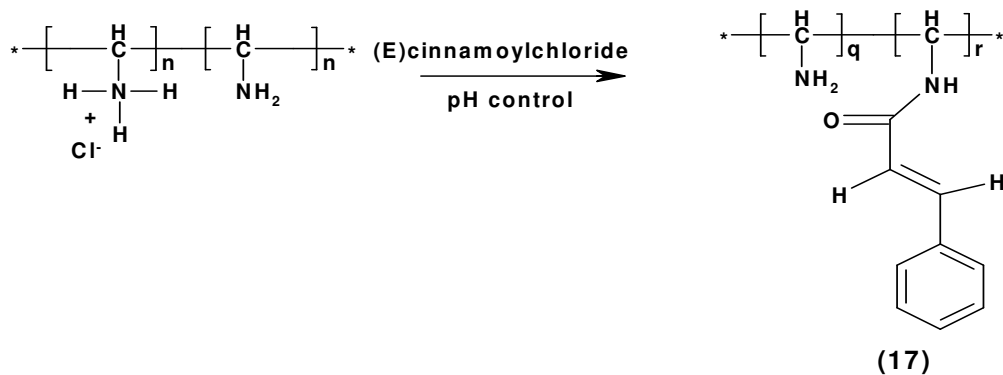
Scheme 5.2 Synthetic scheme for poly(methylene-N-cinnammoylamide)**(17)**

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5.8.1 Photochemical Reactivity

The photocrosslinking behavior of the cinnamoylated polymer was carried out by irradiating a solution of the polymer by fluorescent lamp centred at 254 nm. Irradiation times at constant light intensity were controlled by means of an electronic shutter. The photocrosslnking of the polymer was monitored by recording UV at regular time intervals.

5.8.2 Preparation of photosensitive poly(methylene amine) copolymers

The photosensitive polymers derived from poly(methylene amine) were obtained by adopting standard Schotten Bauman reaction as described by Cocquert *etal*.[10,11] The addition of increased portion of THF was made, tentatively, based on the expected amidification in order to ensure better solubility of the resulting cinnamoylated polymer. Cinnamoylation was performed at three stoichiometric combinations viz.1:1, 1:0.25,1:0.1.of poly(methylene amine) to cinnammoyl chloride (scheme 5.2). The characteristics of the resulting modified polymer are listed in Table 5.2. The increase in content of cinnamoyl chloride led to an increase in the degree of substitution. The maximum conversion of 43.24% was achieved at a stoichiometry of 1:1. The incorporation of cinnamoyl moiety in the polymer backbone affected the solubility dramatically. At a ratio of 1:1 the resulting polymer was insoluble even in pure THF. The modified polymers were characterized by IR, NMR and UV spectroscopy.
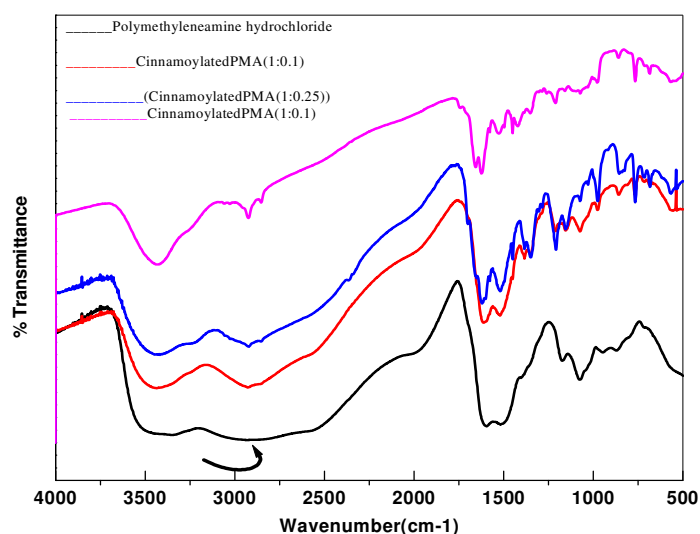
Figure 5.7 IR spectra of cinnamoylated poly(methylene amine)s.

Figure 5.7 shows, the change in the IR spectrum of the poly(methylene amine) hydrochloride and its cinnamoyl derivatives at varying degree of substitution. The gradual disappearance of NH stretching at 2900 cm^{-1} with increase in substitution followed by concomitant appearance of new bands at 1623 cm^{-1} and 1655 cm^{-1} assigned to cinnamoyl double bond and carboxamide respectively that overlaps the deformations bands of ammonium groups at 1511 cm^{-1} and 1603 cm^{-1}. The proton NMR of the modified polymers showed a broad signal at 7.4 ppm, which is attributed to aromatic protons of the cinnamoyl group. The –CH proton of the polymer backbone appeared at 3.5 to 4.0 ppm. However, the CH double bond protons are presumably merged with the broad signal from the aromatic protons.

Table 5.2 Characteristics of cinnamoylated poly(methylene amine)

stochiometry [PMA.HCl]/ [Cinnammoyl Chloride]	solubility (THF:water)	Degree of substitution (%)
1:1	Insoluble	43.24
1:0.25	Insoluble	26.29
1:0.1	45:55	15.86
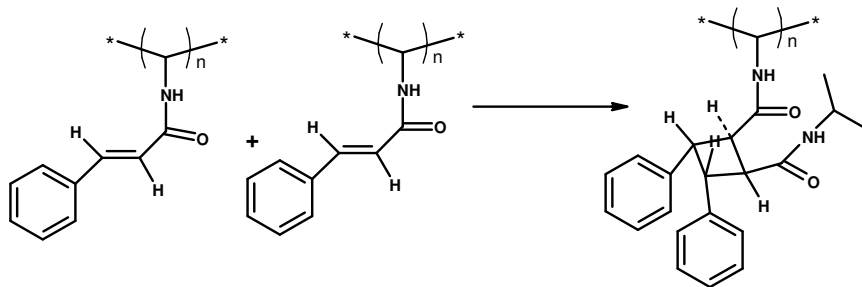
Figure 5.8 A simplified sketch of photodimerization of cinnamoylated poly(methylene amine).

Figure 5.9 represents the change in absorbtion of cinnamoylated poly(methylene amine)(stochiometry 1:0.1) on exposure to UV irradiation centered at 254 nm. The transition of a photoactive molecule to its photo inactive counterpart was easily tracked by a change in UV absorption. This is the case with cinnammoyl derivatives where the photoactive host polymer loses its absorbtion due to [2+2] cycloaddition

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yielding cyclobutane derivatives (Figure5.8). Loss of absorbtion is proportional to time of exposure to irradiation as well as the wavelength of irradiation beam. As evident from the Figure 5.9, the absorbance decreased with increase in the time of exposure due to loss of conjugation.
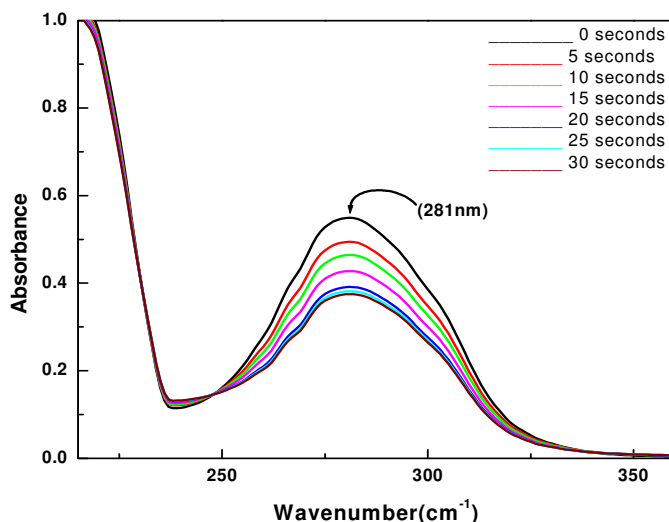
Figure 5.9 Change in the UV Spectrum of PMA-cinnamide (1:01 molar ratio) in solution exposed to 254 nm light in the interval ranging from 0 – 30 seconds.

5.9 Cyclization of poly(methylene amine), Attempts to synthesize poly(4,5-imidazole)

Imidazole functionality is of paramount importance in many natural products and processes. Amino acid histidine[12] contains an imidazole ring as does its derivative histamine,[13] which plays a role in allergic responses. The imidazole of histidine acts as a ligand to facilitate metal binding, e.g. iron binding in non-heme metal proteins. The basicity of imidazole gives it an important role as an enzyme catalyst e.g. alpha chymotrypsin. In this project we seek to prepare synthetic imidazole materials, which exploit some of these properties.

5.9.1 Poly(4,5-Imidazole)

At present imidazoles have been incorporated into materials for various purposes. Oligomeric imidazole ligands have been synthesized as models of multi histidine sites in metalloproteins. Poly(N-vinylimidazole),[14-16] once quarternized; has been used as an anion exchange polymeric stationary phase while N-vinylimidazole copolymers or imidazole functionalized polymer beads have been tested as metal binding agents which could find application in analytical chemistry or waste water management. Recently polybenzimidazoles are emerging as promising candidates for use as fuel cell membrane materials. Most of these examples have the imidazole attached to a polymer backbone and contain relatively low density of imidazole groups. We therefore turned to the investigation of synthesizing polymers containing imidazole as the repeat unit. The main target of the project was poly(4,5-imidazole). As well as being a novel conjugated polymer this material could also show several interesting properties.The close proximity of imidazole groups could lead to high proton conductivity along the polymer chain (Figure 5.10).

The polymer should show polyelectrolyte properties with protonation causing the chain conformation to straighten out due to repulsion between cationic imidazole units. Quarternization of the imidazole rings converts the material from an electron rich polymer to an electron poor cation. As depicted in Figure 5.10, Poly(2-vinylimidazole) has flexible imidazole units hanging from the main backbone as pendants. As a result, proton conduction which is believed to be direction oriented is presumably hindered. On the other hand, the targeted polymer poly(4,5-imidazole) would posses a stiff preoriented conformation thereby facilitating proton conduction.
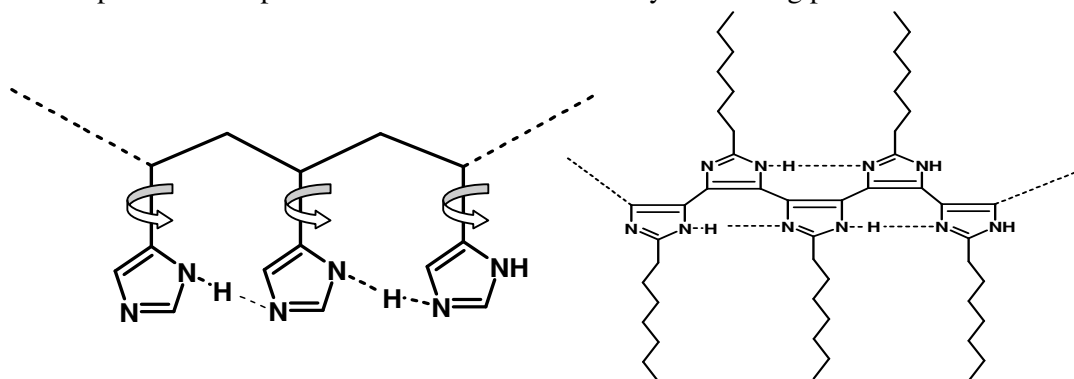
Figure 5.10 Stiff reorientations; facilitation of proton conduction and poly(2-vinylimidazole)

Looking at the molecular structure of the targeted polymer, poly(methylene amine) was considered a potential precursor. It could be considered as an extended chain with linearly placed vicinal diamines. Thus, cyclization of these vicinal diamines could lead to five membered imidazole moieties as shown in Figure 5.11.
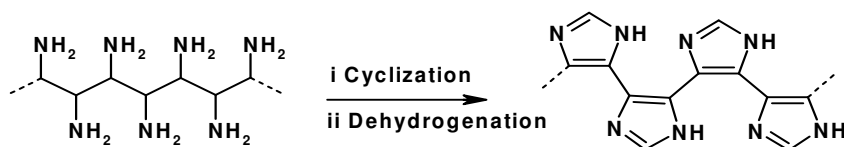
Figure 5.11 Schematic representation of cyclization of poly(methylene amine) to poly (4,5-imidazole).

Incidentally, there is literature precedence for cyclization of aliphatic vicinal diaminechlorides[17] with orthoformates to their imidazole analogue. A similar
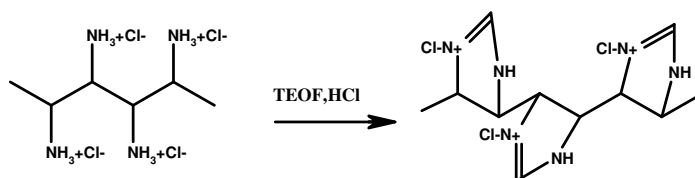
Scheme 5.3 Schematic representation of poly(methylene amine) to poly(4,5-imidazole) with triethylorthoformate

synthetic methodology was adopted on poly(methylene amine)hydrochloride as depicted in scheme 5.3. The cyclization process involved heating poly(methylene amine)hydrochloride in excess of triethylorthoformate (TEOF) in presence of catalytic amount of HCl. The mechanism follows initial protonation of ethoxy group on TEOF followed by nucleophillic attack by amino group and eventually elimination of one of the ethoxy groups as ethanol. The process repeats, however, with attack of another amine group located on the adjacent carbon resulting in a ring. The elimination of a third ethoxy group as ethanol incorporates a double bond in the ring. The cyclizized product was characterized by conventional ^{1}H NMR and ^{13}CNMR. ^{1}HNMR of cyclizized product showed three signals at 8.2 ppm (broad), 3.5 ppm

(broad) and 1.49 ppm (broad). The signal at 8.2 ppm can be assigned to –C<u>H</u> of imidazoline,[17] and the signal at δ3.5 ppm to –CH group on the polymer backbone. The signal at δ1.49 ppm is probably due to -C<u>H</u> group on the backbone arising from a different conformation. In addition, signals from ^{13}C NMR spectrum confirmed the above assignments. There were two signals at δ152.8 ppm(broad) and δ55 ppm (broad). The signal at 152.8 ppm was attributed to C 2 of imidazoline moiety and 50-57 ppm was attributed to –CH on the polymer backbone.The assignment of the peaks was based on Chem Draw simulation and previously reported literature.[17] The Chem. Draw simulations of the plausible imidazoline structures are given in Figure 5.13. Besides, assignment of NMR signals; there was a critical problem that remained unanswered.The problem was related to the mechanism of cyclisation. Because, the cyclisation process could take place in different ways, there by yielding different end products. Consequently, if the cyclisation involved locking of two adjacent amine groups, it would lead to a five membered ring (path I in Figure 5.12). On the contrary, if the process locked amine groups on alternate carbons it would result in the formation of a six membered ring (path II in Figure 5.12)
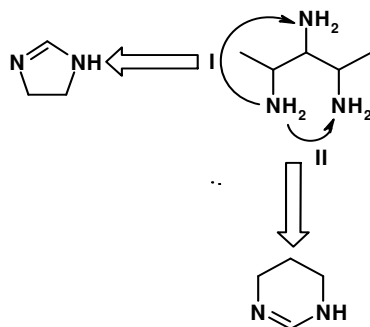
Figure 5.12 Schematic representation of cyclization of poly(methylene amine)

The revelations from ChemDraw simulation were not sufficient enough for differentiating between the sizes of the ring, which would result from different paths to cyclisation. The paths I and II resulted in structures I and II in Chem Draw simulation (Figure 5.13). There was an evident discrepancy over the size of the resulting ring and hence the structures. Thus, all possible structures from cyclisation were drawn and analysed (Figure 5.13).The formation of structure III was nearly impossible. A closer look at the governing mechanism of cyclisation showed that incorporation of the double bond in the ring required elimination of a third molecule

of ethoxy group. If it would be so, then there would be formation of a double bond on bridge head nitrogen. Conversely, if the third molecule of ethoxy group did not eliminate and stayed intact, then the signals from ethoxy group would show up in ^{1}H and ^{13}C NMR. The spectral findings did not support either of the two arguments in favour of the structure III. Furthermore, as it is clearly seen, signals from both the structures I and II on ^{1}H NMR and ^{13}C NMR appeared at same chemical shift values. This made it difficult to freeze the resulting structure arising from cyclisation.

Therefore, at this stage, in order to avoid discrepancies over formation of ring arising from cyclisation of poly(methylene amine), another route to poly(4,5-imidazole) was adopted. This route employed an intermediate, (poly(4,5-1,3-dihydroimidazole-2-one)(**23**) in the synthetic route to poly(methylene amine); as precursor as shown in scheme 5.4.
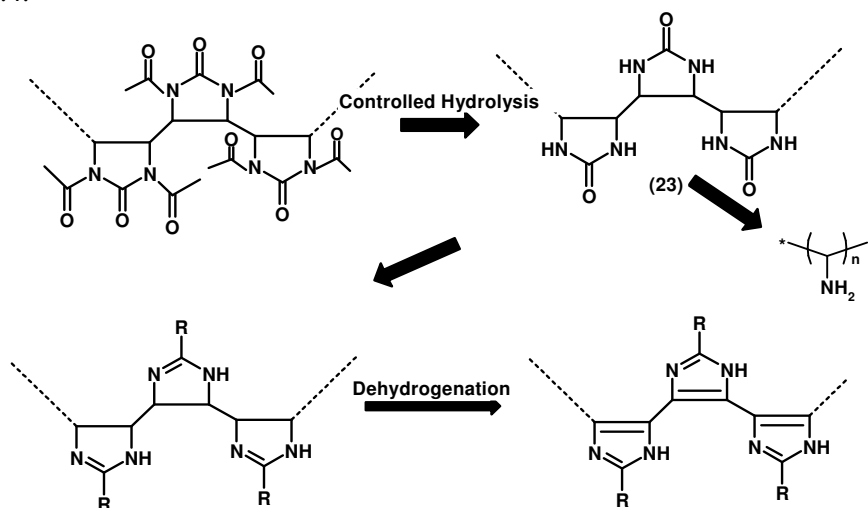
Scheme 5.4 Scheme for synthesis of poly(4,5-1,3-dihydro-2-imidazoline)

Before embarking on polymer analogous reaction, few model reactions[18] were carried on imidazolidone with propanoic acid and pentanoic acid respectively as shown in scheme 5.5. The product **20** was obtained by heating 1,3-dihydroimidazolidine-2-one with pentanoic acid at elevated temperature (240 -270 °C) and under reduced pressure < 0 mbar for 70 hours as already reported else where.[18] Adopting a similar procedure product **21** was obtained by heating ethylene urea with propanoic acid at 240°C for 40 hours under reduced pressure. Both the products were isolated in low yield. Product

20 was isolated at a yield of 10% and **21** at 6%. The isolation of these products involved tedious procedure.

PROTON NMR

I

II

III

^{13}C
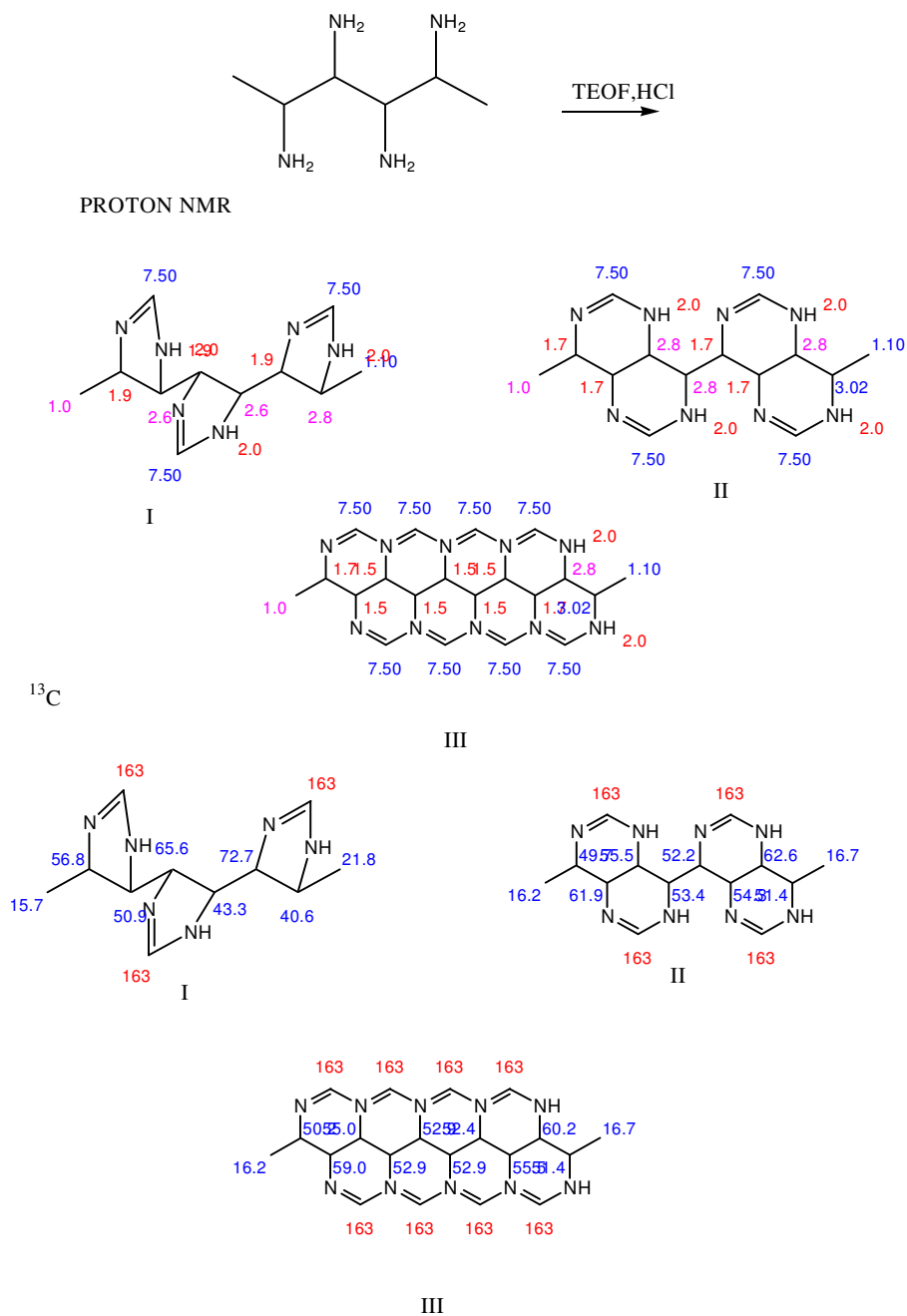
I

II

III

Figure 5.13 Chem Draw simulations of cyclizized structures of poly(methylene amine)hydrochloride

Thus, having established the feasibility of the reaction on model compounds, the precursor poly(1,3-dihydroimidazol-2-one) was then synthesized. The polymer poly (1,3-dihydroimidazol-2-one) was easily prepared by controlled hydrolysis of poly(1,3-diacetylimidazole-2-one) in presence of K_2CO_3 and ethanol as shown in scheme 5.4. The resulting polymer was characterized by solid state NMR and IR. The complete disappearance of the CO stretching in IR spectrum established the completeness in the removal of lateral acetyl groups on the imidazolidone moieties on the polymer backbone as shown in Figure 5.14. Following the exact procedure adopted for model reactions, poly(1,3-dihydroimidazol-2-one) was heated to 230°C.
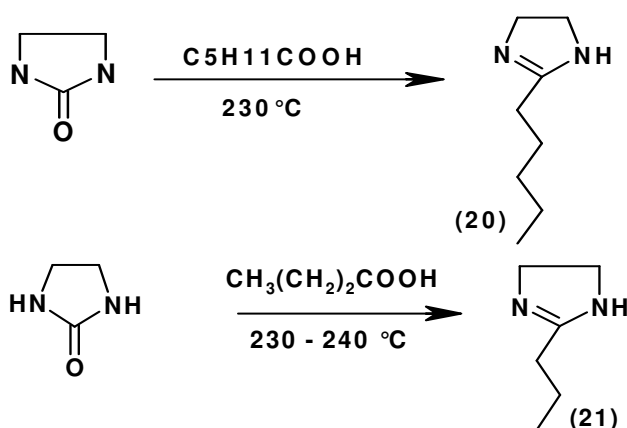
Scheme 5.5 Synthesis of 2-pentyl-2-imidazoline**(20)** and 2-propyl-imidazoline**(21)**

At this temperature, equivalent amount of stearic acid was introduced into the system.
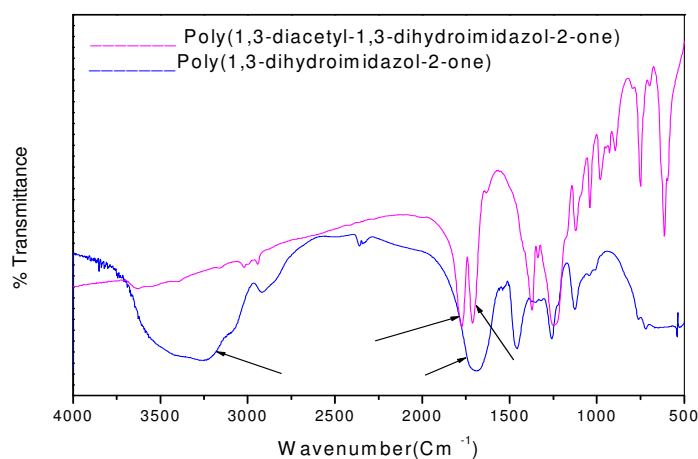
Figure 5.14 IR spectra of poly(1,3-diacetyl-1,3-dihydroimidazole-2-one)**(6)** and poly (1,3-dihydroimidazol-2-one)**(23)**

The ash colored substance was washed several times with boiling methanol and dried. It was insoluble in common organic solvents including DMF. The product was characterized by IR. The IR spectrum did not show any change. The peak arising from carbonyl stretching of imidazolidone moiety remained intact at 1687 cm^{-1}. Apparently; there was no transformation of carbonyl functionality to its alkene analogue. The reason for failure of the reaction was attributed to poor solubility of the intermediate polymer, poly(1,3-dihydroimidazol-2-one) due to strong intra and intermolecular hydrogen bonding. In addition, it was believed that lowering of the molecular weight of the parent polymer would probably facilitate the reaction. Because, in this case the polymer would posses less number of imidazolidone moieties on the backbone. Thus, a starting polymer with nearly half the molecular weight of the previous polymer was tried. The hydrolysed polymer resulting from controlled hydrolysis of this polymer (M_n=13,900 g/mol and M_w= 23,200 g/mol with PDI 1.66) was tried. However, the reaction with stearic acid did not bring about any change in the spectrum of the modified polymer. Therefore, at this stage the method was dropped and new route to the target polymer was explored.

Transformation of Poly(1,3-dihydroimidazole-2-one) to its sulphur analogue[19] wasconsidered promising due to high nucleophilicity of sulphur atom.

(23)
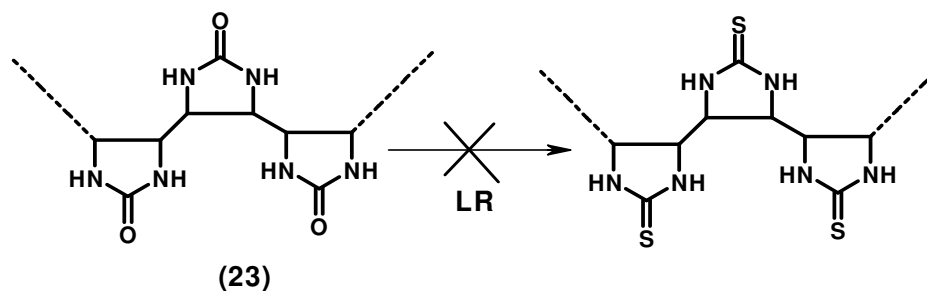
Scheme5.6 Transformation of poly(1,3-dihydroimidazole-2-one)**(23)** with Lawesson´s Reagent(LR)

Based on literature precedents, Lawesson´s reagent[20] was found suitable for the above polymer transformation. However, insolubility of the intermediate, poly (1,3-dihydroimidazol-2-one) prevented the polymer analogous reaction. In order to get rid of the inherent problem of solubility associated with poly(1,3-dihydroimidazol-2-one)**,** it was decided to incorporate the sulphur atom into the imidazolidone ring at monomer stage. Thus, 1,3-diacetylimidazol-2-one was attempted to be transformed

into its sulphur analogue with the help of Lawesson's reagent. However, the resulting product had its lateral carbonyls replaced with sulphur. The carbonyl of the ring remained unaffected. Further, reaction of 1,3-diacetyl-1,3-dihydroimidazole-2-one with Lawesson´s reagent yielded its sulphur analogue of diacetyl groups instead of integral carbonyl of imidazolidone ring (Scheme 5.7).
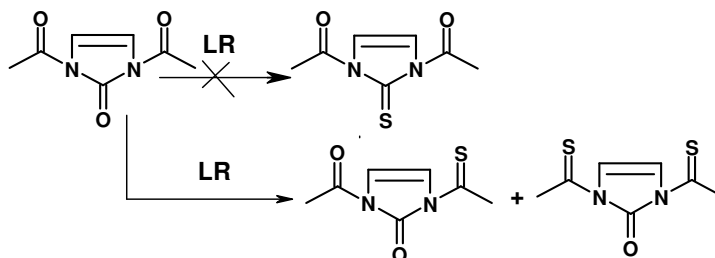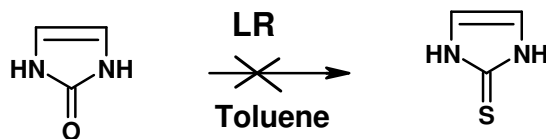

Scheme 5.7 Reaction of 1,3-diacetyl-1,3-dihydroimidazol-2-one with Lawesson´s reagent.

Further, transformation of 1,3-dihydroimidazolinone into its sulphur analogue with Lawesson´s reagent did not work (scheme 5.9). This prompted us to adopt a new synthetic route to core 1,3-dihydroimidazole-2-thione (scheme 5.8) and subsequently explore the possibility of achieving the target polymer, poly(1,3-dihydroimidazole-2-thione).[21] **22** was synthesized from Alpha amino acetaldehyde diethyl acetal which was then acetylated[22] to obtain the monomer 1,3-diacetyl-1,3-dihydroimidazole-2-thione**(23)**. The polymerisation of the monomer **23** in bulk gave low molecular weight polymer (M_n = 7,800 g/mol and M_w = 15,700 g/mol and PDI= 2.00). Further, the yield was low (17%). The low yield of polymer **24** could be due to unreactivity of the
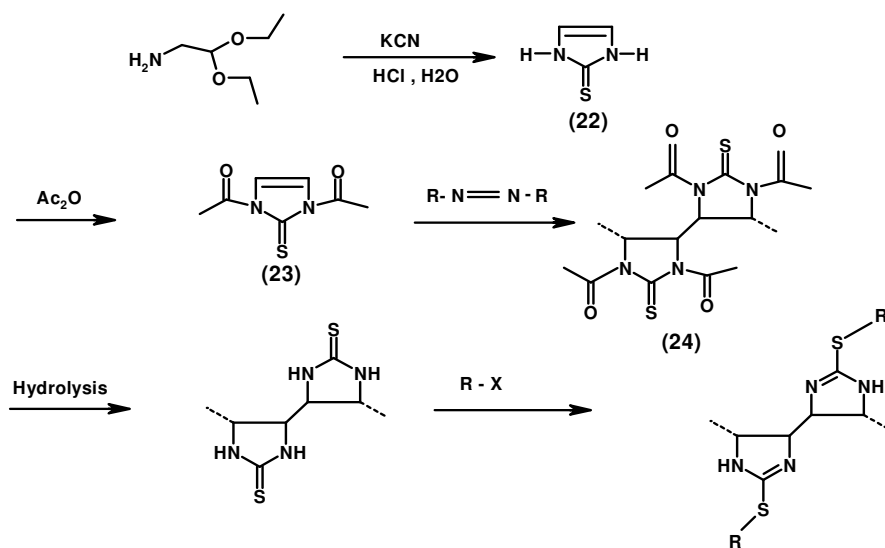
Scheme 5.8 Synthetic scheme for poly(2-alkylthioimidazoline).

monomer or chain transfer reactions, since sulphur containing monomers are more prone to chain transfer. Further, the peak at δ 4.5 ppm, which is attributed to –CH- proton of the ring showed a doublet. This could be attributed to stereochemistry of the carbon carbon single bond of imidazolidone ring on the polymer backbone.
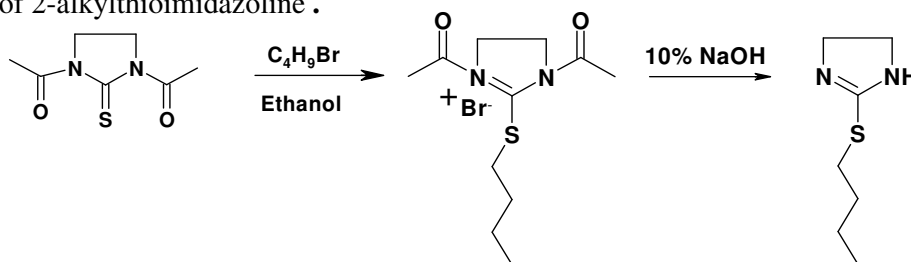

Scheme5.9 Transformation of 1,3-dihydroimidazole-2-one with Lawesson´s Reagent(LR)

Synthesis of poly(1,3-diacetyl-1,3-dihydro-imidazole –2-thione**(24)** has two major draw backs i.e. low molecular weight of the polymer and very low yield (17%). Furthermore, removal of acetyl groups via hydrolysis might result in an insoluble polymer like its oxygen analogue (poly (1,3-dihydro-imidazole –2-one) due to strong intermolecular hydrogen bonding. Therefore, the possibility of polymer transformation without knocking out the acetyl groups was considered. A model reaction with 1,3–diacetyl-1,3-dihydroimidazole-2-thione was initially done to test the feasibility.

5.9.1.1 Synthesis of 2-butyl-1,3-diacetyl-1, 3-dihydro imidazole-2-thione (A model reaction)

The purpose of carrying out the above model reaction[22] was to investigate if alkylation of 1,3-diacetyl-1,3-dihydroimidazole-2-thione can lead to its 2-alkyl imidazoline analogue. However, after working it up with 10% NaOH in order to liberate the free base, it was observed that the acetyl groups got hydrolyzed (the peak at δ2.78 ppm due to methyl groups disappears) keeping the alkyl chain intact. Further, there was appearance of broad peak at δ5.8 ppm that can be attributed to NH protons of 2-alkylthioimidazoline .

Scheme 5.10 Synthesis of 2-butyl-1,3-diacetyl-1, 3-dihydro imidazole-2-thione

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Polymer Transformation.
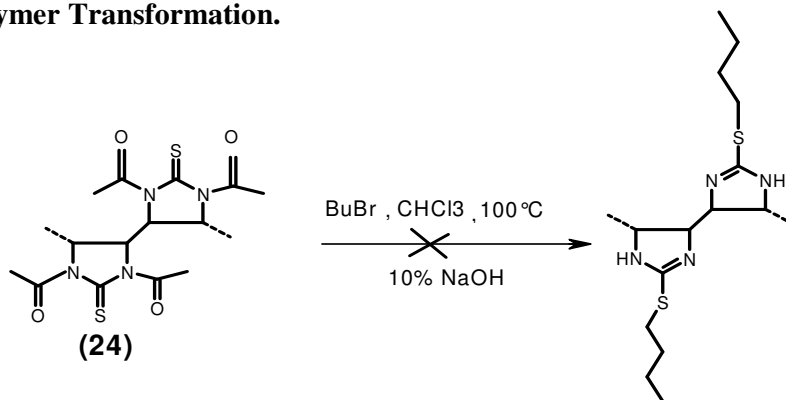
Scheme 5.11 Transformation of **24** with Butylbromide.

Since the polymer **24** was insoluble in ethanol, the reaction with butyl bromide was carried out in chloroform under reflux conditions overnight. Removal of solvent under vacuum gave the starting polymer. In another attempt, the transformation of polymer **24** with butyl bromide was tried in THF under reflux. Removal of the solvent under vacuum gave again the unreacted starting polymer**.** In order to study the effect of solvent on the reactions of thione, few model reactions of 1,3-dihydro-1,3-diacetylimidazolidine-2-thione with butyl bromide in different solvents was looked into.

Transformation of 1,3-diacetyl-1,3-dihydroimidazolidin-2-thione to 2-butyl thio imidazoline in chloroform and THF respectively.
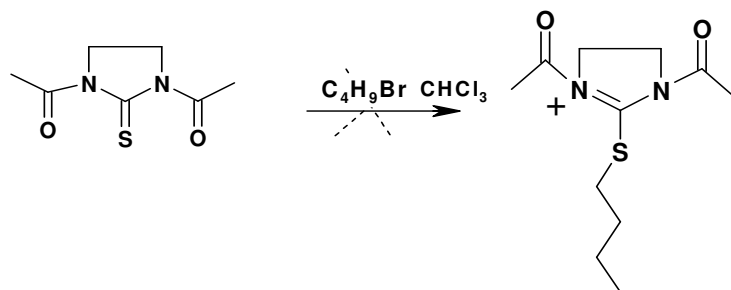
Scheme 5.12 Transformation of 1,3-diacetylimidazolidin-2-thione with Butylbromide in CHCl$_3$.

1,3-diacetyl-1,3-dihydroimidazolidin-2-thione was heated with a slight excess of butyl bromide in chloroform at reflux temperature overnight. Evaporation of solvent under vacuum resulted in starting material i.e. 1,3-diacetyl-1,3-dihydro imidazolidin-2-thione. In another attempt, 1,3-diacetyl-1,3-dihydroimidazolidin-2-thione was refluxed with butyl bromide in THF overnight. Removal of the solvent under vacuum gave only the starting material, 1.3-diacetyl-1,3-dihydroimidazolidin-2-thione. Incidentally, it was found in the literature that alcohol solvents are usually used for S-alkylation of ethylene thiourea.[22] It has been reported earlier in the literature that alkyl derivatives, like ethylene thiourea itself, are slowly decomposed by prolonged heating with acid or alkali, to yield at least in part the corresponding mercaptan.[22] Further, it was observed that the monomer 1,3-Diacetyl-1,3-dihydroimidazole-2-thione undergoes rearrangement on standing. A year later, Baer *etal*. reported the synthesis of 2-alkylmercapto-2-imidazolines; Foster[23] and Bianco *etal*[24] reported variation in melting point of benzyl derivatives. On re-determination of melting point it was observed that the samples had undergone rearrangement to their isomers which showed a melting point of 172°C against 147°C. This discrepancy in melting points, presumably; arising from isomerisation was explained by Donleavy[25] in terms of polymorphism, which he noted for S-benzyl derivatives. This phenomenon was believed to hold good for 2-benzylmercaptoimidazoline hydrochlorides as well. The proton NMR measured in $CDCl_3$ showed the appearance of a broad signal at $\delta 10.7$ ppm which could be attributed to –NH proton. In addition to above facts, it was observed that a sample of the monomer after sublimation and drying showed a similar trend.

Therefore, at this stage a new possible route to transform the existing polymer Poly (1,3-diacetyl-1,3-dihydroimidazole-2-one) was reconsidered. This polymer, however carried an inherent problem of poor solubility. Improper solubility was a forbidden barrier in polymer analogous reactions. Furthermore, the presence of unprotected nitrogen in the imidazolidone ring was essential for the transformation of imidazolidone moiety to 2-alkyl or alkoxy imidazoline.
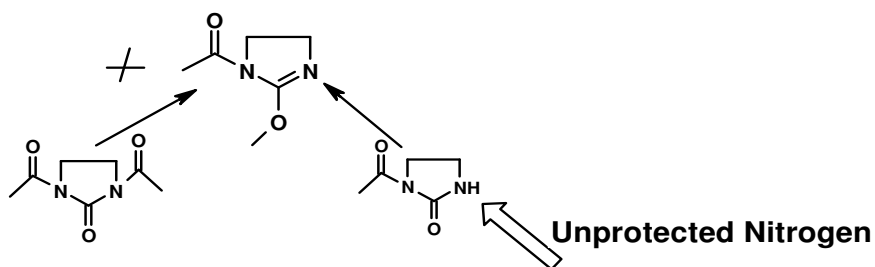
Figure 5.15 Unprotected nitrogen on imidazolidone skeleton.

This prompted us to design a molecule, which could take care of the above problems. Therefore, we turned to synthesize monoacetylimidazoline-2-one**(25)**. It was believed that the presence of acetyl protecting group will provide improved solubility and the unprotected nitrogen will help incorporate the double bond leading to imidazoline.
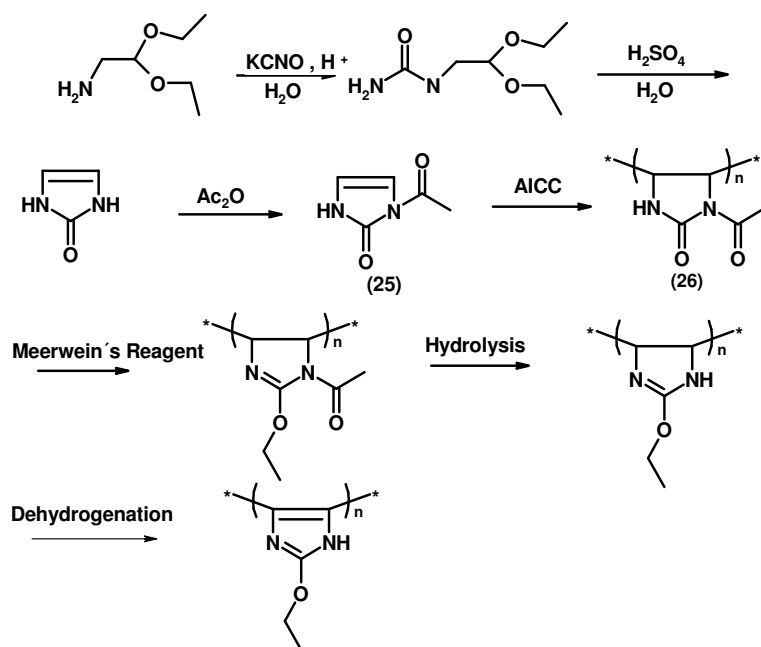
Scheme 5.13 Synthetic scheme for poly(2-alkoxyimidazole)

The monomer **25** was easily prepared by acetylation of 1,3-dihydroimidazolinone. **25** was polymerized in presence of AICC(1,1`-Azobis(cyclohexanecarbonitrile) at very high temperature (160 °C) and at a monomer to initiator molar ratio of (1:500). Higher concentration of the initiator was chosen in order to offset its loss due to sublimation at elevated temperature. The attempts were made in bulk as well as in very less amount of solvent (DMF). The isolated yield was only 6% when precipitated

from methanol water mixture. Further, with increase in quantity of monomer (with the same molar ratio) no polymer was recovered. The reason was attributed to unprotected nitrogen contributing towards chain transfer and considerable degree of ene-amine tautomerism which makes the double bond delocalized for radical polymerization.
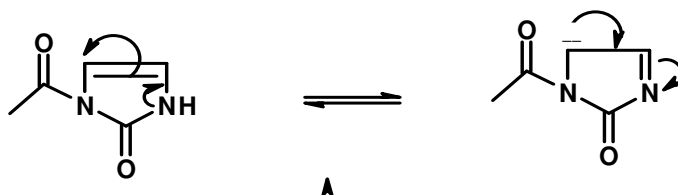

Figure 5.16 Ene-amine tautomerism in 1-acetyl-3-hydroimidazole-2-one.

The carbonyl functionality of imidazolidone is highly unreactive. The fact is further supported by unsuccessful attempts made while trying to transform the imidazolidone to its imidazoline analogue by electrophiles. In addition, the possibility of polymerizing an imidazoline entity protected at one nitrogen, by radical polymerization, does not lead to high molecular weight polymer with good yield, due to chain transfer reactions stemming from free –NH. Furthermore, imidazolidone`s proclivity for its thermodynamically stable keto form throws a major challenge at electrophillic reactions on carbonyl functionality. Apparently, the enol form once generated is highly nucleophillic and possibly facilitates the reaction of an electrophile.[26-28] Thus high reactivity of enol form prompted us to look for a strong electrophile, preferably an alkyloxonium salt,[28] that can transform the imidazolidone moiety to its imidazoline analogue via enol intermediate. Triethyloxonium tetrafluoroborate is known to be efficient at transforming amides to imidate esters in high yield, barring restricted solubility.[29]
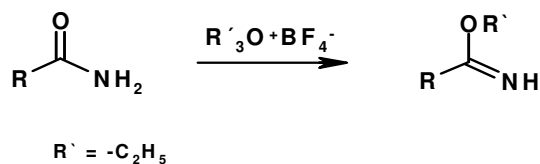
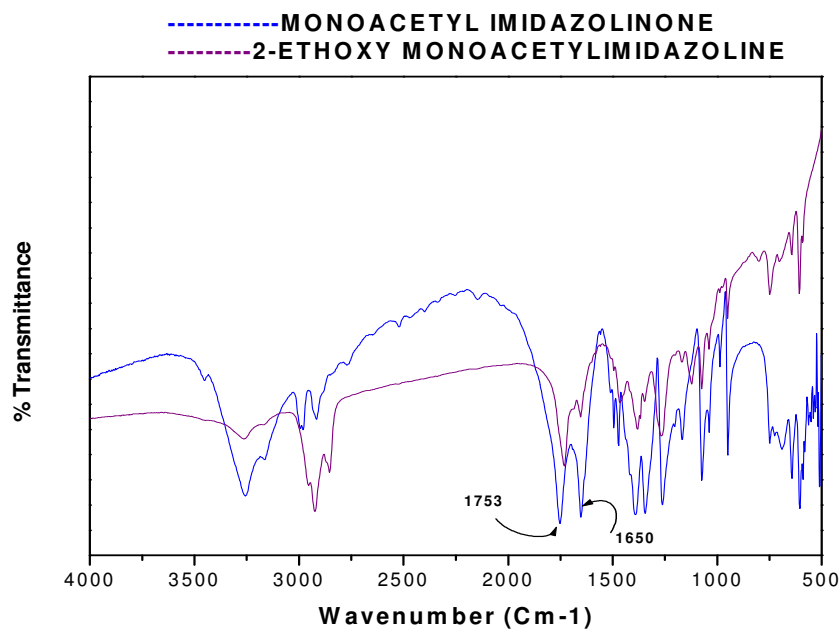**Scheme 5.14** Transformation of amides with Meerwein´s Reagent.

Figure 5.17 Changes in infrared spectrum of monoacetyl imidazolidone before and after reaction with triethyloxonium tetrafluoroborate.

Furthermore, mono acetyl imidazolidone has been successfully transformed to monoacetyl-2-alkoxy imidazoline by trimethyloxonium tetrafluroborate.[30] A model reaction made on the mono acetyl imidazolidone showed disappearance of the carbonyl stretching band from imidazolidone at 1650 cm^{-1} (Figure 5.17). However, **26** was insoluble in most of the common organic solvents including chloroform. Its solubility was limited to DMSO and DMF. Unfortunately, the Meerwein´s reagent does not work in these solvents. Due to problem of insolubility, the reaction with Meerwein´s reagent was tried with parent polymer poly(1,3-diacetylimidazoline-2-one), in dichloromethane. The IR spectrum does not show any change i.e. both the carbonyl groups were intact. The reason could be due to electron withdrawing nature of carbonyl groups of imidazoline that hindered formation of double bond.
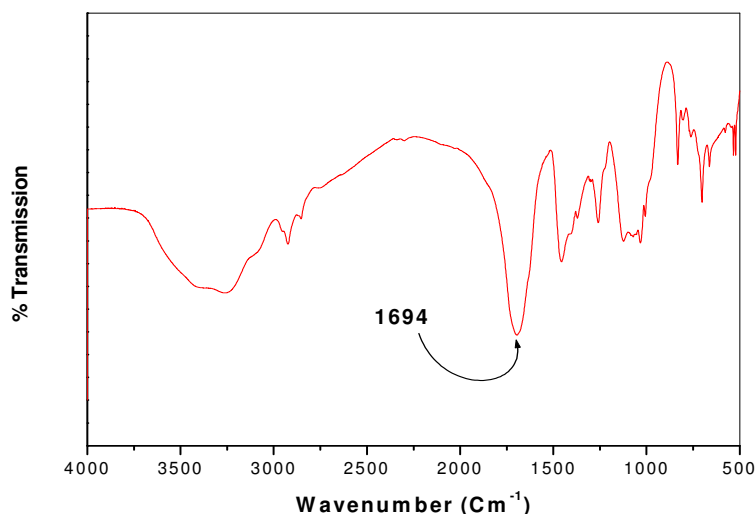
Figure 5.18 Poly(1,3-dihydroimidazole-2-one) after reaction with triethyloxonium tetra fluroborate.

In another attempt poly(1,3-dihydroimidazole-2-one) was reacted with triethyloxonium tetrafluoroborate in dichloromethane in suspension. The IR spectrum did not show any change in the carbonyl stretching frequency at 1694 cm^{-1}(Figure 5.18). Thus, the reagent did not work in suspension. Although, triethyl oxonium tetra fluoro borate is a strong electrophile yet it failed to work in suspension. In addition, electron-withdrawing groups attached to the imidazolone moiety restrict the reaction with triethyl oxonium tetrafluroborate. Therefore, we set out to synthesize a monomer **28** that has two different protecting groups on the nitrogen of imidazole ring (scheme 5.15). One is stable to alkali and other is not. Furthermore, the group, ethoxy methyl; being less electronegative would probably help in the reaction of triethyl oxonium tetra fluoroborate.
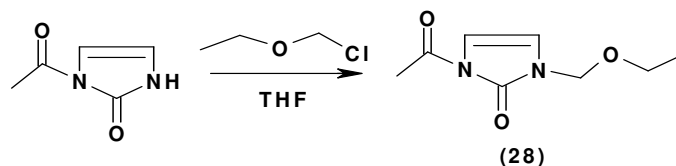
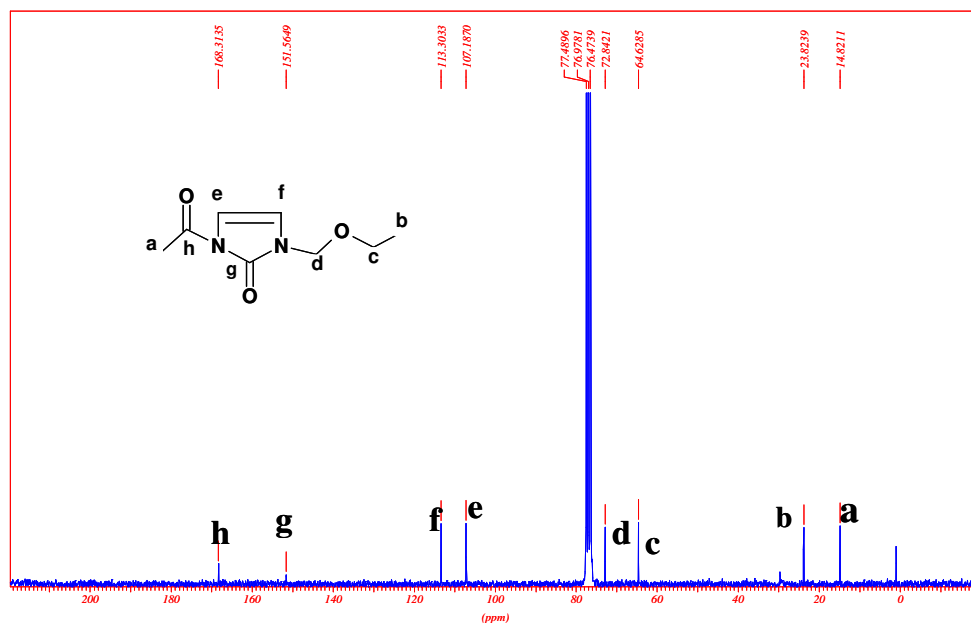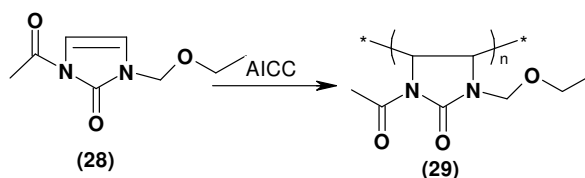**Scheme 5.15** Synthesis of 1-acetyl-3-ethoxymethyl imidazole-2-one**(28)**

Figure 5.19 ^{13}C NMR of 1-acetyl-3-ethoxymethylimidazoline-2-one**(28)**

Thus the use of Meerwein's reagent as a strong electrophile for the modification of imidazolidone was limited by its poor solubility. Furthermore, the necessity for a free nitrogen site or an electron donating substituent on the imidazolidone ring at 1 or 3 positions, presumably, is essential for incorporation of a double bond in the ring. Since, a monomer with free nitrogen site on the ring did not yield a polymer with high molecular weight owing to hydrogen bonding and possibly, ene-amine tautomerism and the resulting low molecular weight polymer is insoluble in common organic solvents, the transformation of the polymer with Meerwein's reagent was not feasible. This led to synthesis of **28.** The monomer was isolated in 35% yield.

Scheme 5.16 Synthesis of poly(1-acetyl-3-ethoxymethyl imidazole-2-one)**(29)**

It was polymerized by radical polymerization at 115^0C in presence of AICC. A low molecular weight polymer **29** was precipitated from water.(M_n = 6000g/mol, M_w =15,000 g/mol). The proton NMR of the polymer is shown as under (Figure 5.20).
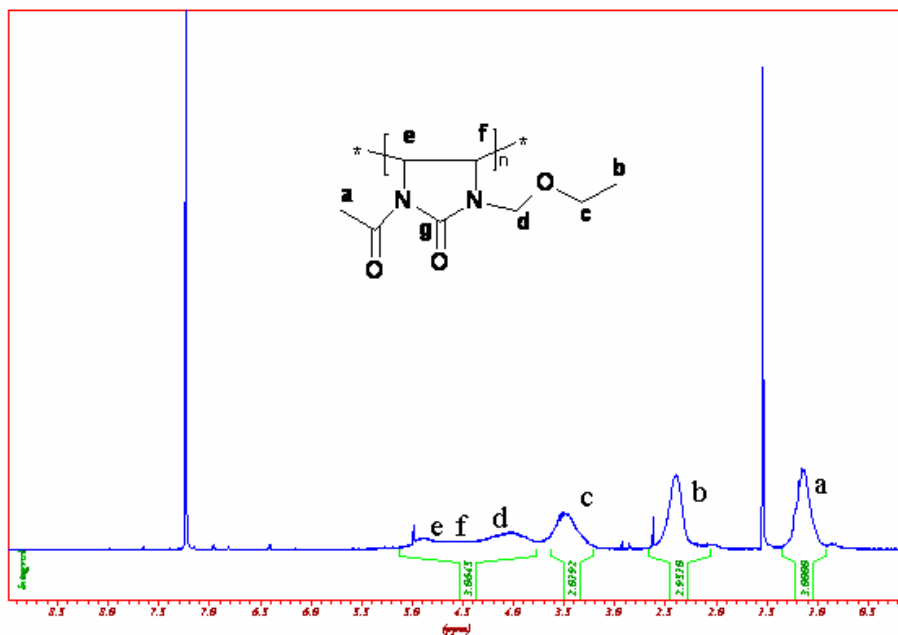

Figure 5.20 ^{1}H-NMR of poly(1-acetyl-3-ethoxymethyl) imidazole-2-one**(29)**

The polymer, Poly(1-acetyl-3-ethoxymethyl imidazol-2-one) (300mg, 0.0035mol) in 25 ml of dichloromethane was treated with triethyloxoniumtetrafluoroborate (0.759g, 0.004 mol) intermittently. The mixture was allowed to reflux for two days under argon. The color of the mixture changed to straw yellow. Solvent was evaporated off under high vacuum at low temperature. A brown colored substance was obtained. The substance was insoluble in water and soluble in DMSO.
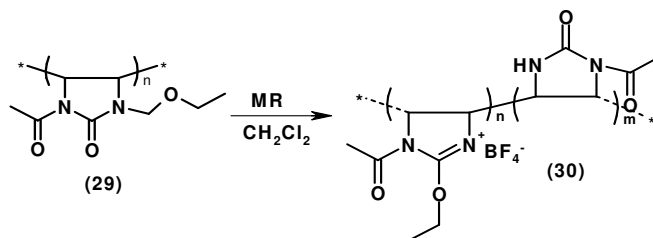
Scheme 5.17 Transformation **29** with Meerwein´s Reagent(MR)

The gross disappearance of imidazolidone carbonyl stretching frequency at 1700 cm^{-1} with carbonyl of acetyl group (1760 cm^{-1}) intact showed the transformation of imidazolone unit to imidazoline (Figure 5.21). The spectral analysis such as liquid state proton NMR could not be implemented due to lack of solubility of the isolated product. The product was even insoluble in trifluoroacetic acid. The solid state NMR of the product demonstrated transformation of imidazolidone carbonyl into its –ene analogue. The appearance of a signal at 165 ppm flanked by two carbonyl signals at 158 ppm (carbonyl of imidazolidone) and 178 ppm (carbonyl of lateral acetyl) accounted for C 2 of imidazoline as shown in Figure 5.22.
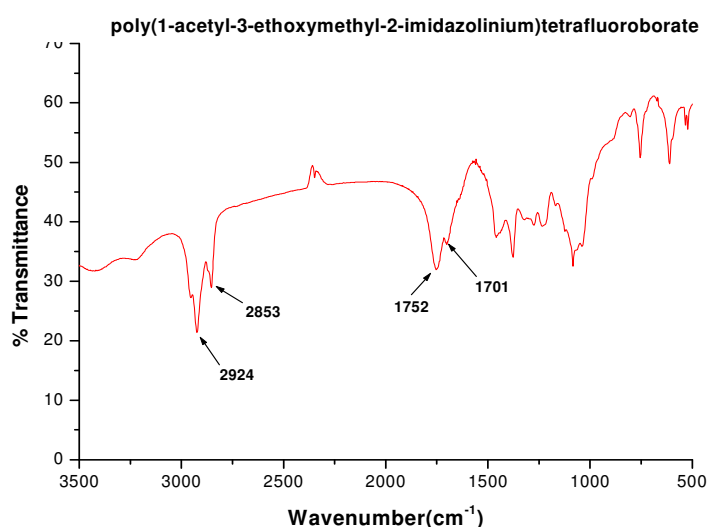

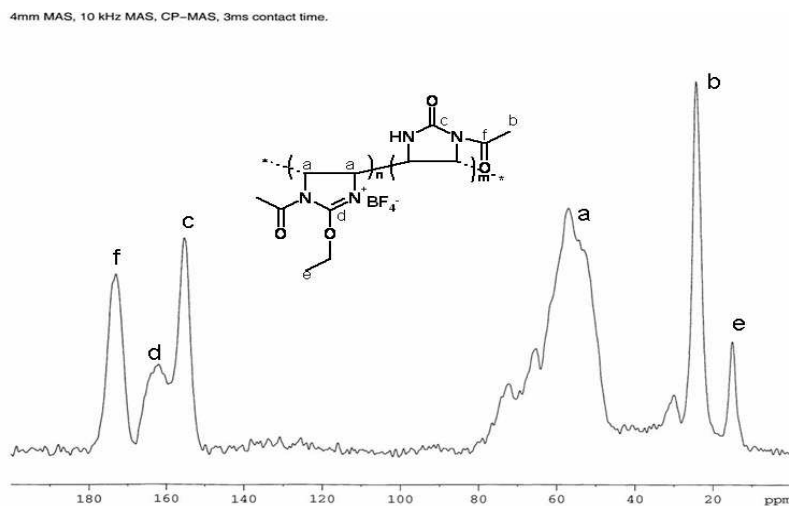**Figure 5.21** IR spectrum poly(1-acteyl-3-ethoxymethylimidazolium)tetrafluoroborate

Figure 5.22 Solid state ^{13}C NMR of poly(1-acetyl-3-ethoxymethylimidazolium) tetrafluoroborate(**30**)

5.10 Conclusions

The polymers poly(methylene amine) and polyvinylamine were reacted with electrophiles under similar conditions in order to investigate the influence of maximizing reactive sites on the degree of substitution. It was observed that under similar conditions the degree of substitution of an electrophile onto the polymer backbone was maximum in PVAm in comparison with poly(methylene amine). Methylation of poly(methylene amine) at a molar ratio of (1:10:: poly (methylene amine): Methyl iodide) resulted in 40% conversion where as under similar conditions PVAm demonstrated 75% degree of substitution. In another set of experiments with 1,3-propanesulfone, poly(methylene amine) showed 54% substitution at molar ratio of (1:10:: poly(methylene amine): propane sulfone) whereas under similar condition PVAm resulted in 75% conversion. These results can be interpreted as followes.While mono substitution of amino group increases nucleophilicity, it also imposes steric hindrance. Consequently, the degree of substitution is governed by two parameters viz.nucleophilicty and steric hindrance. The higher degree of substitution of polyvinylamine against poly(methylene amine) shows that steric hindrance outweighs nucleophilicity in deciding degree of substitution of amino groups with electrifies.

Furthermore, several attempts were made to synthesize poly(4,5-imidazole). The cyclization of poly(methylene amine) was foremost among all the attempts made. Due to the presence of amine groups on every carbon atom, the polymer was considered a promising substrate which could embed, after cyclizations; a battery of imidazoles connected at 4,5-positions. However, the mechanism of cyclization created discrepancy over the size of the ring, i.e. five or six membered, which would result from different paths of cyclization. The transformation of poly (4,5-1,3-dihydroimidazol-2-one) into its imidazole analogue remained unsuccessful due to poor solubility of the precursor polymer i.e. poly(4,5-1,3-dihydroimidazole-2-one)**(23)**. Transformation of poly(1-acetyl-3-hydroimidazol-2-one)**(26)** with Meerwein´s reagent was not successful due to poor solubility of the reagent in the solvent system in which the precursor polymer was soluble. Thus the most promising method was transformation of poly(1-acetyl-3-ethoxymethylimidazol-2-one)**(29)** into its imidazoline analogue. This polymer was soluble in common organic solvents including chloroform and methylenechloride thus facilitating the transformation reaction with the aid of Meerwein´s reagent. The transformation of this polymer into

its imidazoline analogue **30** resulted in an insoluble product. This insoluble product was characterized by solid state NMR. The ^{13}C spectrum demonstrated mixture of transformed product consisting of imidazoline units as well as unreacted monomer units. The integration showed approximate conversion of 30 %.

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6.1 Introduction

Polymer brushes are systems in which chains of polymer molecules are attached through an anchor group to a surface, to an interface or to the back bone of another polymer in such a way so that the graft density of the polymer is high enough to stretch the attached chains away from the main back bone resembling a brush like conformation as shown in Figure 6.1. [1]Stretching of the chains is triggered by their overlapping with chains in the vicinity and the effect becomes pronounced with increase in graft density.[2]

a   **b**
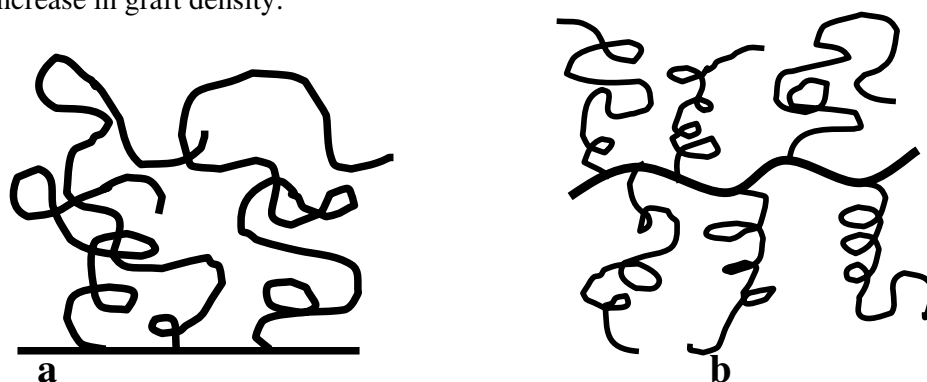
Figure 6.1 Schematic representation of brush regimes: (a) at a solid surface (b) chains attached to the backbone of another polymer

These brushes at solid surfaces are formed either by adsorption of charged block copolymers from the solution or by anchoring amphiphillic, charged block copolymers at their air water interface, compression and subsequent transfer of the layer to solid substrate. A third yet the most important one that is widely used these days is attachment of polymer chains to the surface of the substrate via chemical linkage. Generally, attachment of polymer chains chemically onto surface is carried out in two ways, viz. (1) linking of reactive end groups of the attachable polymer to the appropriate reactive site on the surface of anchor, the method is called "grafting to" procedure; (2) formation of a monolayer of surface attached-initiator on the surface of anchor as shown in Figure 6.1. This initiator layer is subsequently used for polymerization of monomers. The polymers, formed are projected out like bristles. The process is termed as "grafting from "or surface initiated polymerization. In normal practice the anchoring surface is mica, glass or gold substrates. These surfaces

are coated with a layer of immobized-initiator that subsequently initiates the process of polymerization emanating from the surface. The surface initiated polymerization method scores over "grafting to" method in eliminating diffusion barrier which strongly limits film growth.[3-5]
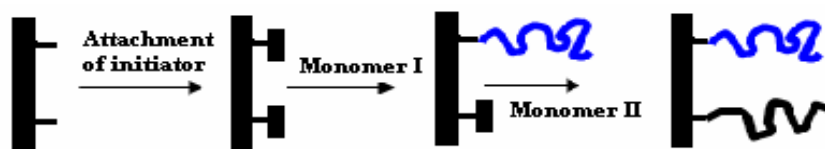
Grafting to procedure

Grafting from procedure

Figure 6.2 Schematic representations of "*grafting to*" and "*grafting from*" approaches for synthesis of binary polymer brushes.

Following a similar path, the synthesis of a mixed brush polymer is realized. Usually, neutral homopolymer brushes are synthesized by grafting to or grafting from method and the second homo polymer is then grafted in the next step. Finally, the mixed polymer brush is prepared from the mixed neutral brush with an appropriate polymer.[6-8] On going study, employs poly(methylene amine) as well as polyvinylamine as anchors to brush polymers via "grafting from" approach. Amines are widely known to be used as initiators for ring opening polymerization of N-carboxyanhydride leading to non-linear polypeptides. Since, the NCA (N-carboxyanhydride) ring opening polymerization does not provide enough control over chain length distribution and monomer sequence, the process does not yield linear polypeptides that can fold to well-defined 3D structures. Precedents in the literature include non-linear polypeptides synthesized via NCA polymerization with a wide range of topologies viz, star like, dendronised, dendritic graft, etc. On the other hand, macromolecular brushes or bottlebrush polymers are well known materials exhibiting
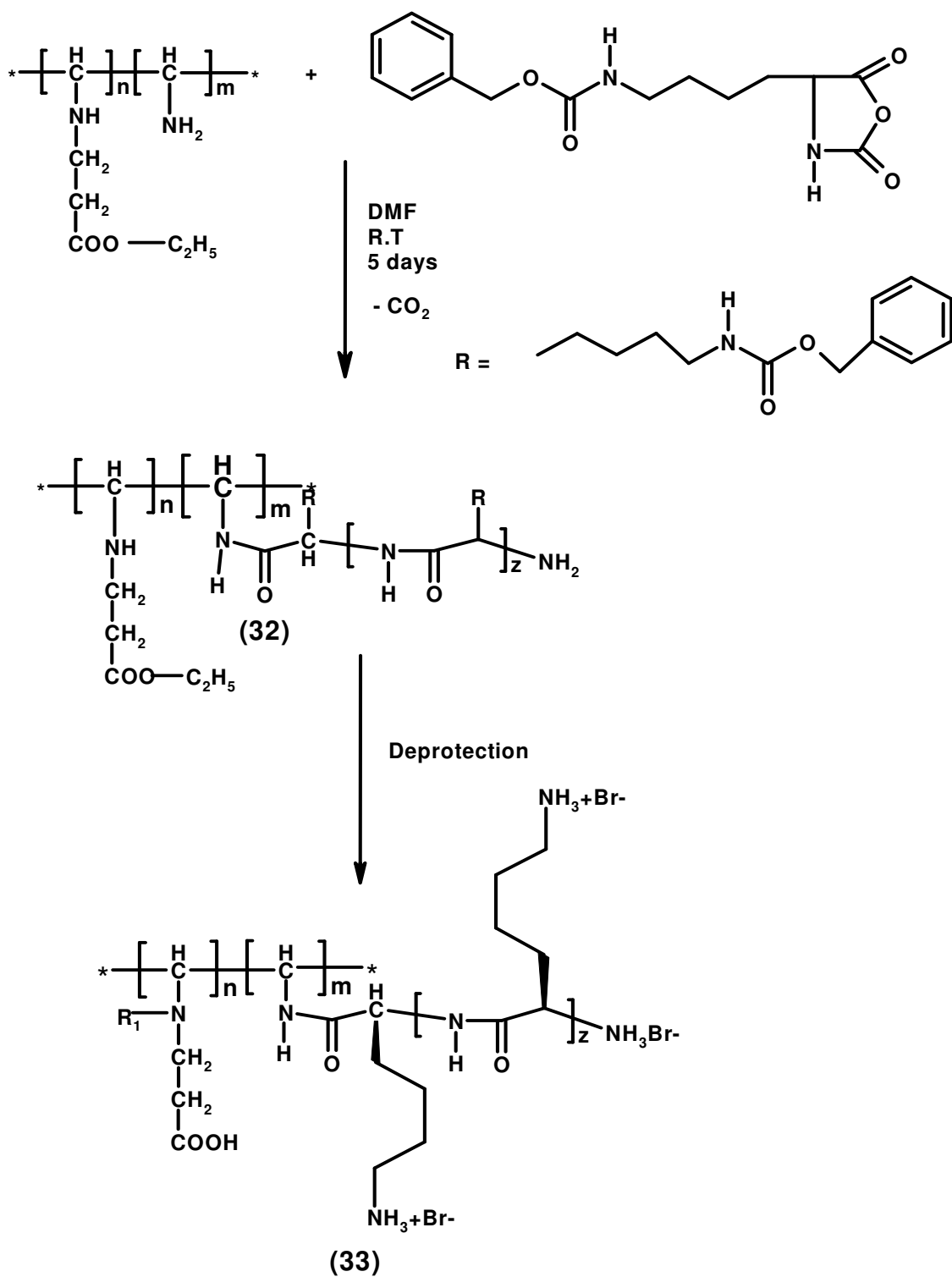
Scheme 6.1 Synthetic scheme of poly(methylene amine) grafted ethylacrylate initiated polymerisation of benzyloxy carbonyl protected –N-carboxy anhydride

interesting bulk properties. This class of polymers has been synthesized primarily through ATRP. Densely crowded with pendants on either side of the backbone, brush polymers adopt peculiar conformations and demonstrate interesting mechanical behavior. In the present study, poly(methylene amine), and polyvinylamine have been used as novel macroinitaiators for synthesizing grafted polypeptide via ring opening polymerization of NCA. Furthermore, the deprotection of benzyloxy carbonyl protecting group would liberate the amine groups leading to an architecture resembling hetero grafted brush copolymers with hydrophilic and hydrophobic units.

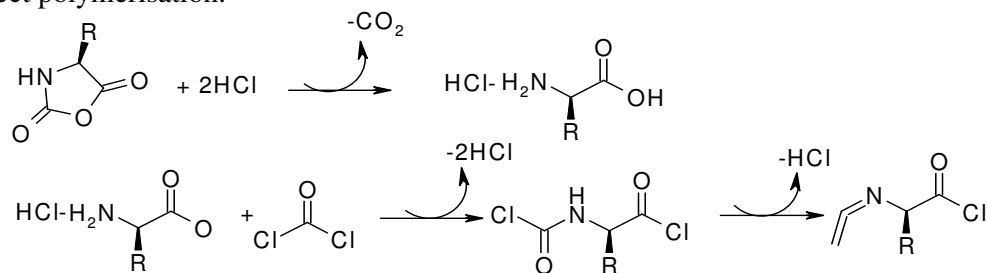## 6.2 Synthesis of alpha amino acid N-carboxyanhydride

The first synthesis of alpha amino acid N-carboxyanhydride dates back to 1906, when Hermann Leuchs tried to purify N-ethoxy carbonyl and N-methoxy carbonyl amino acid chlorides via distillation.[9] It was in the 1920's,[10,11] when the systematic investigation on the synthesis, polymerisation and evaluation of properties of NCAs were established by Wesley *etal.* Since then, alpha amino acid N-carboxyanhydride has been widely used as a versatile class of monomers for the synthesis of polypeptides. Although Leuchs method for the preparation of alpha amino acid N – carboxyanhydrides involved one pot synthesis yet it carried a serious draw back of decomposition of NCA at elevated temperature.[12,13] The second route for the preparation of NCA involves direct phosgenation of free alpha amino acids. This strategy, which is currently the most widely used procedure to prepare NCAs, is referred to as Fuchs–Farthing method.[14-17] The proposed mechanism for the reaction is shown in Scheme 6.2. The gaseous phosgene has been replaced with diphosgene and triphosgene.
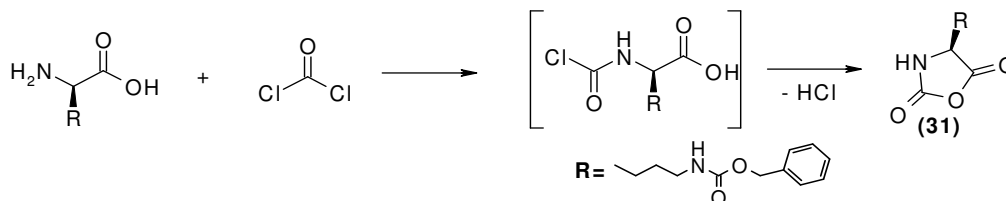
Scheme 6.2 The phosgenation of free alpha amino acid.

Diphosgene[18] and triphosgene[19,20] are liquid and solid, respectively, which makes them easy to handle and allows them to be used in stoichiometric quantities. The

choice of the solvent plays an important role in the Fuchs-Farthings synthesis. In principle, each low boiling organic solvent can be used. Solvents that have been used include; tetrahydrofuran (THF), 1,4-dioxan, toluene and ethylacetate. Kircheldorf has proposed use of 1:1 mixture of THF or dioxane with CH_2Cl_2, because of the reduced solubility of HCl in the mixtures compared with pure ethers.[21]A low concentration of HCl during NCA synthesis is important, since NCA can lead to ring cleavage and the formation of unwanted alpha isocyanate acid chlorides scheme 6.3. Impurities found in NCA´s prepared by Fuch Farthing method include e.g. N-chloroformylaminoacid chlorides and alpha isocyanato-acid chlorides. Also here purification of the monomer is important since these impurities have an acidic or nucleophilic character and can affect polymerisation.

Scheme 6.3 Ring cleavage and the formation of alpha isocyanate acid chlorides.

6.3 Mechanism of polymerisation of alpha amino acid N-carboxyanhydride

Alpha amino acid N – carboxyanhydrides (NCAs) are characterized by four reactive sites, two electrophillic sites (C-2, C-5) and two nucleophillic sites (after deprotonation of the NH and CH groups) (Figure 6.3). Due to this multiple reactivity,
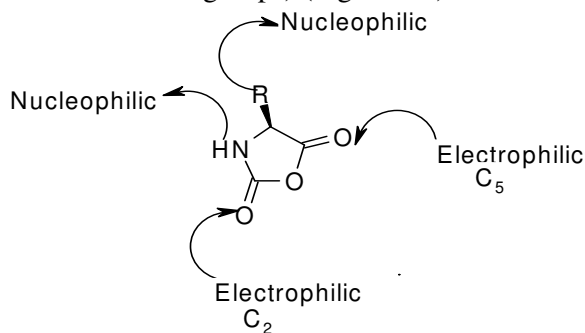

Figure 6.3 Four reactive sites of alpha amino acid N-carboxyanhydride (NCAs)

NCAs can be polymerized via several concurrent mechanisms, which make it difficult to prepare polypeptides that are well defined in terms of chain length and polydispersity. Traditionally, two major mechanisms are distinguished for the polymerization of NCAs, the amine mechanism and activated monomer mechanism.[21-23] Polymerizations via the amine mechanism, which is also called the protic mechanism, can be initiated by protic nucleophiles e.g. primary amines, and was first reported by Wessely and by Watson *et.al*. The primary amine attacks at the C-5 of the NCA monomer. After ring opening, carbon dioxide is eliminated and a molecule with a new primary end group is formed for further reaction. The amine initiator is incorporated in the growing chain. Primary amines, such as, n-butylamine and n-hexylamine are highly nucleophilic compared to the reactive amine chain ends. Therefore, initiation is much faster than propagation and the reaction has in principle a living character. Unfortunately, termination reactions such as cyclization of chain ends cause formation of relatively low molecular weight material. (DP < 150-200)
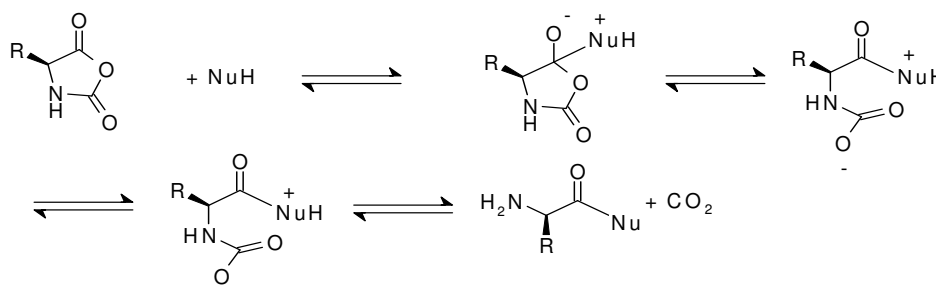

Scheme 6.4 Polymerization via the amine mechanism

6.3.1 Mechanism for synthesis of brush polymers with poly(methylene amine) backbone(32).

The brush polymers with poly(methylene amine) backbone were synthesized by using ethyl acrylate derived poly(methylene amine) as initiator. These initiators were prepared via Michael addition of ethyl acrylate with poly(methylene amine) as already described elsewhere (Chapter 5). The initiators were characterized by ^{1}H NMR, IR and ^{13}CNMR. The percentage conversion was determined from elemental analysis. The elemental analysis data showed 80% degree of substitution, which implied availability of unreacted amino groups on the polymer backbone. Apparently,

these amino groups, which are randomly distributed along the polymer backbone, are initiating sites for ring opening polymerization of benzyloxy carbonyl protected N-carboxyanhydride. Thus, polymerization of Benzyloxy protected–NCA, initiated by ethylacrylate derived PMA proceeds through amine mechanism (scheme 6.5).
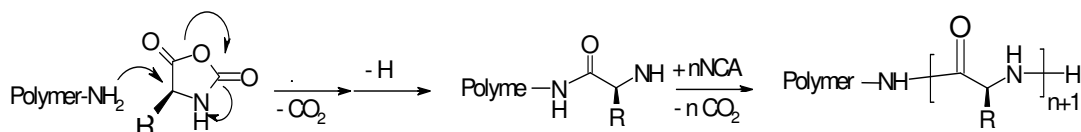
Scheme 6.5 polymerization of benzyloxy protected –NCA, initiated by ethylacrylate derived poly(methylene amine)

The polymerization of z-L-Lys-NCA using PMA-co-EA as the initiator at different ratios in DMF at 40^0C yielded PMA-co-EA–Poly(z-LLysine) (samples. **BPMA-S1** & **BPMA-S2**) with different molecular weights and polydispersities as shown in Table 6.1. The molecular weights of the samples were determined by GPC with PS standard in DMF as eluent.

Table 6.1 Feed composition and characteristics of (co)polypeptide obtained by ethylacrylate modified poly(methylene amine) as initiator

Entry	stoichiometry (Initiator: N-carboxyanhydride)	M_n (G/mol)	M_w (G/mol)	M_w/M_n	z
BPMA-S1	1:1	33,600	38,900	1.15	10
BPMA-S2	1:2	53,300	65,500	1.22	18

z =Average number of z-L-lysine repeating units (calculated from NMR) M_w = weight average molecular weight, M_n=Number average molecular weight M_w/M_n = polydispersity index.
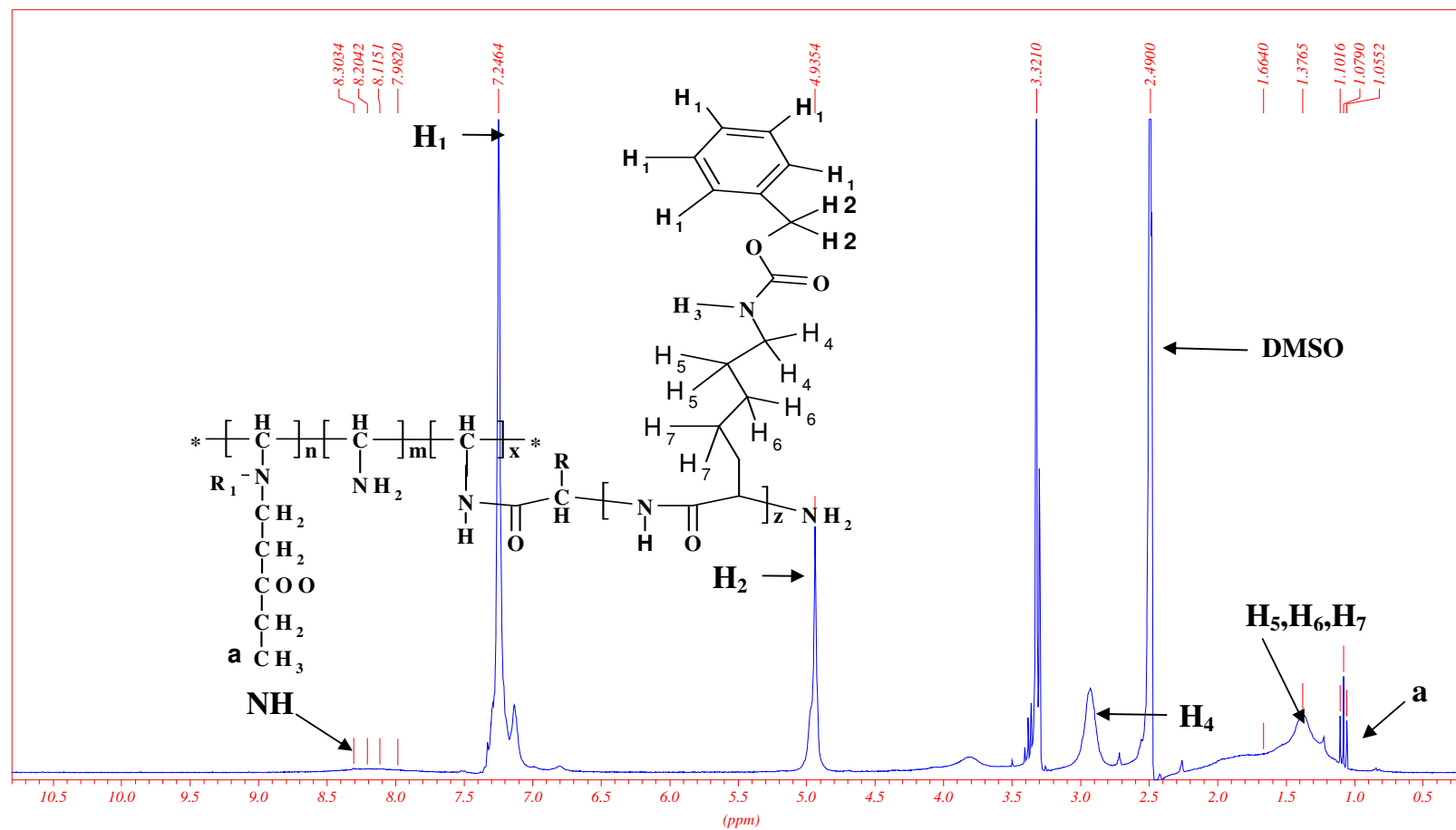
Figure 6.4 ^{1}H NMR of polybenzyloxy carbonyl protected N-carboxyanhydride -co-ethylacrylate BPMA-S1

6.4 Thermal Properties of brush polymers with PMA backbone.

DSC thermogram of the polymer, poly(z-L-lysine) grafted PMA-co-ethylacrylate was investigated at heating rate 10 K/min. There appeared one clear glass transition temperature at 27 °C that belonged to z-L-lysine segment. TGA of the polymer showed two degradation steps. The first step was at 118 °C and the second step was at 350 °C. The sample for AFM image was prepared up on evaporation of a drop of polymer solutions (0.3 wt %) in DMF/THF (v: v = 1:1) on mica surface. Then the sample was put in the vacuum oven set at 140°C for 2 hours and 70 °C for two days. After thermal treatment, the sample was quenched to low temperature. It is expected that the z-L-lysine chain hanging from the main polymer backbone of PMA would exhibit strong intra as well as inter molecular hydrogen bonding between amide groups of adjacent z-L-Lysine resulting in regular structures. The AFM image of the polymer reveals vesicle like structures organized in a regular fashion yet randomly distributed over the substrate. The observation is well in agreement with theoretical anticipation.
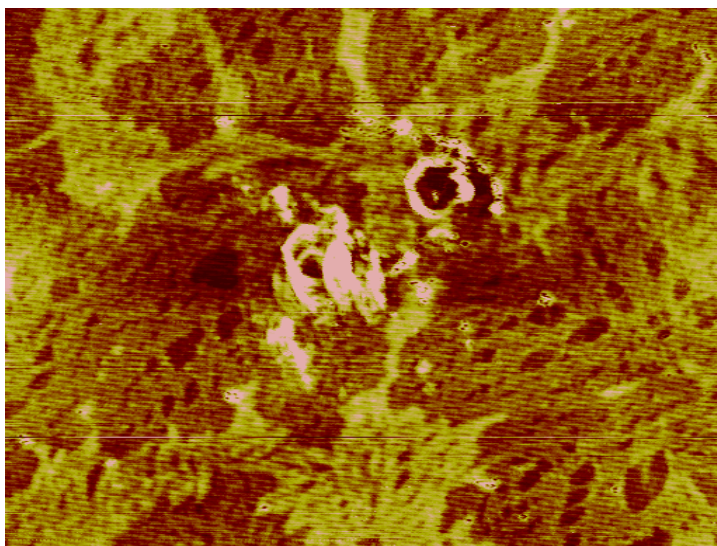

Figure 6.5 Tapping-mode AFM phase image of the supra molecular self-organization formed poly(z-L-lysine) grafted from ethylacrylate modified poly(methylene amine), scale bar indicates 2 micron.
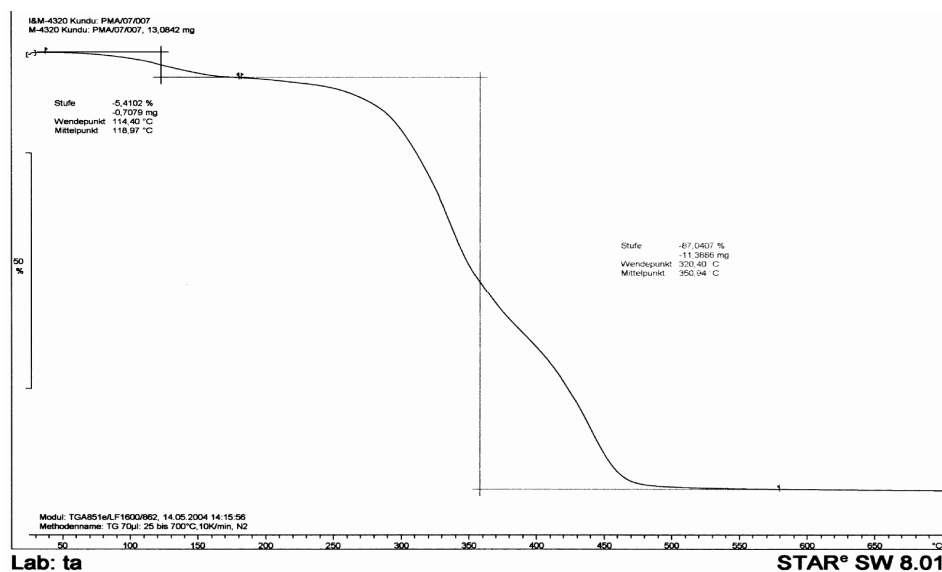
Figure 6.6 TGA curve of poly(z-L-lysine) grafted from ethylacrylate modified poly(methylene amine).

The synthesized brush polymer with poly(methylene amine) backbone has interesting architecture. It was anticipated that the removal of benzyloxy carbonyl protecting group on polypeptide units would liberate amine groups and hydrolysis of ester linkage would liberate acid groups thereby making the polymer an ampholyte. Therfore, the brush polymer **BPMA-S2** was deprotected and it´s polyampholytic behavior was studied by viscometry.

6.5 Deprotection of the brush polymer with poly(methylene amine) backbone(BPMA-S2)

The hydrolysis of protecting groups on the brush polymer made it a polyampholyte. The resulting polymer **33** with amine and acid functionalities statistically distributed along poly(methylene amine) backbone, manifested typical anionic and cationic polyelectrolyte behavior in acid and basic pH regimes respectively.

A four fold molar excess of HBr (33% in acetic acid) was added to the solution of the side chain protected polypeptide in trifluoroacetic acid. The reaction mixture was

stirred for 1h at room temperature. Diethyl ether was added, and the precipitated polymer was washed extensively with Diethyl ether. After drying in vacuum the deprotected polymers were obtained in quantitative yields.
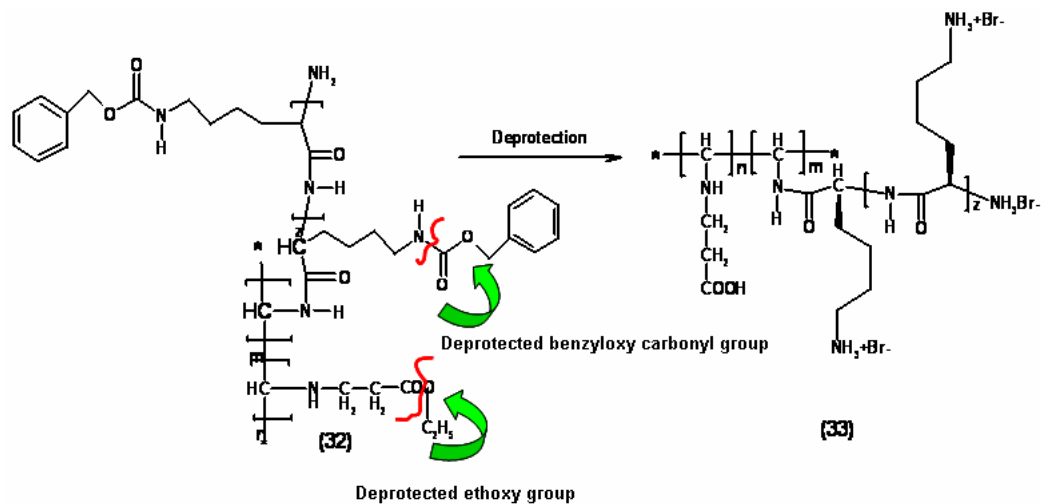

Figure 6.7 Schematic representation of deprotection of benzyloxy carbonyl and ethoxy groups on the brush poly(methylene amine)

Figure 6.4 shows the ^{1}HNMR of the polymer of benzyloxy carbonyl protected N-carboxyanhydride derived from Lysine. The signal from the phenyl protons of benzyloxy carbonyl group appeared at 7.24 ppm. The hydrolysis of the polymer was tracked by disappearance of the signal at 7.24 ppm. The brush shaped polyamine thus obtained was isolated in the form of its hydrobromide. The hydrolyzed polymer **33** displayed an interesting architecture comprised of acid and basic ionizable groups that are randomly distributed along the polymer backbone. High concentration of amine groups would make it a cationic polyelectrolyte like the parent PMA and acid groups would make it an anionic polyelectrolyte. Hence, the solution properties of this brush shaped polyamine were investigated by viscosimetry in aqueous solution.

6.5.1 Solution properties of brush polyampholyte obtained from hydrolysis of brush polymer based on PMA (BPMA-S2)

Figure 6.8 represents the plot of reduced viscosity (η_{red}) of brush polyamine hydrobromide(BPMA-S2.HBr) as a function of solution concentration. The reduced viscosity rises gradually from the region of higher concentrations (3.5–0.5 g/L) towards the region of lower concentrations. This behaviour is ascribed to a change in the conformation of the polymer chain with dilution. At higher concentrations the apparent shielding of positively charged species on the backbone by the counter ions result in weak electrostatic repulsion. Thus the polymer chains remained in the form of globular networks with minimum electrostatic repulsion. However, dilution liberated the positively charged species from the shield of counter ions. Consequently, the strong electrostatic force of repulsion operating between neighbouring positive charges resulted in straightening of the polymer backbone. The long straightened conformation of the polymer chain arising from electrostatic repulsion led to rise in reduced viscosity of the polyelectrolyte in solution. The increase in reduced viscosity with decrease in concentration demonstrated a typical polyelectrolyte behavior.[1,2] Figure 6.9, shows the profile of reduced viscosity of brush polyampholyte hydrobromide(BPMA-S2.HBr) as a function of pH which is rather complex. At low pH range the polymer behaved like a cationic polyelectrolyte, since the amine groups are protonated. As the pH increased, a viscosity minimum is obtained which should correspond to the isoelectric point (IEP) of the polymer; at this point the number of ionized amine groups and acid groups are equal. With further increase in pH the number of ionized acid groups greatly exceeded the number of amine groups and this rendered the polyampholyte brush anionic polyelectrolyte effect.
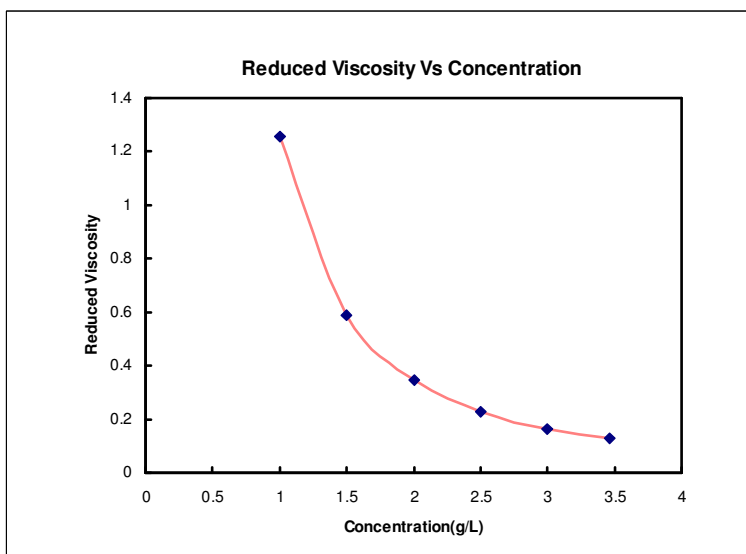
Figure 6.8 Reduced viscosity of BPMA-S2.HBr as a function of solution concentration.
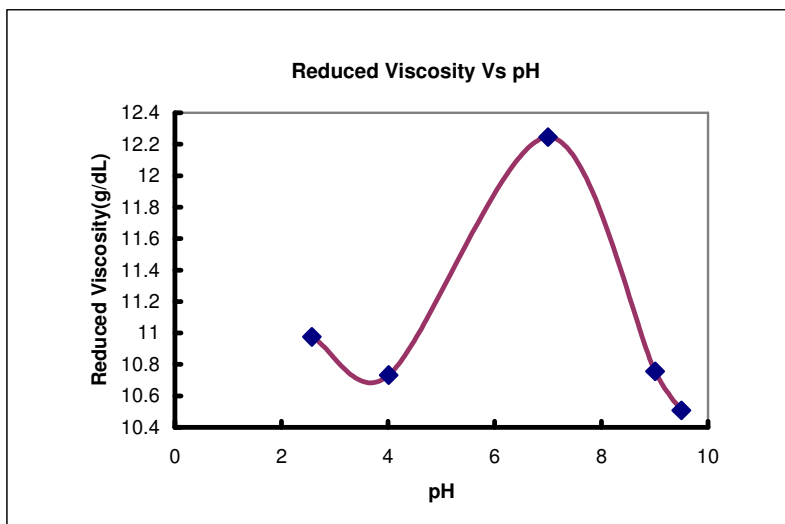

Figure 6.9 Reduced viscosities of BPMA-S2.HBr as a function of pH in deionised water (Cp (concentration of polymer in solution) = 0.1 g/dL).

In order to compare brush polymers with poly(methylene amine) backbone against brush polymers with polyvinylamine backbone, polyvinylamine was synthesized and modified with ethylacrylate like its counterpart poly(methylene amine) as described under.

6.6 Synthesis of brush polymers with PVAm backbone

6.6.1 Synthesis of polyvinylamine

PVAm was synthesized via alkaline hydrolysis of poly-N-vinylformamide. PVAm was isolated as PVAm hydrochloride.
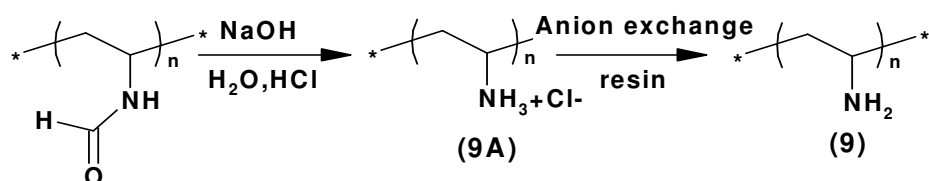
Scheme 6.6 Synthesis of polyvinylamine.

PVAm was obtained from PVAm hydrochloride after eluting it through anion exchange resin Amberlite (IRA – 400Cl⁻). Figure 6.10 shows the ^{13}C NMR of PVAm hydrochloride.
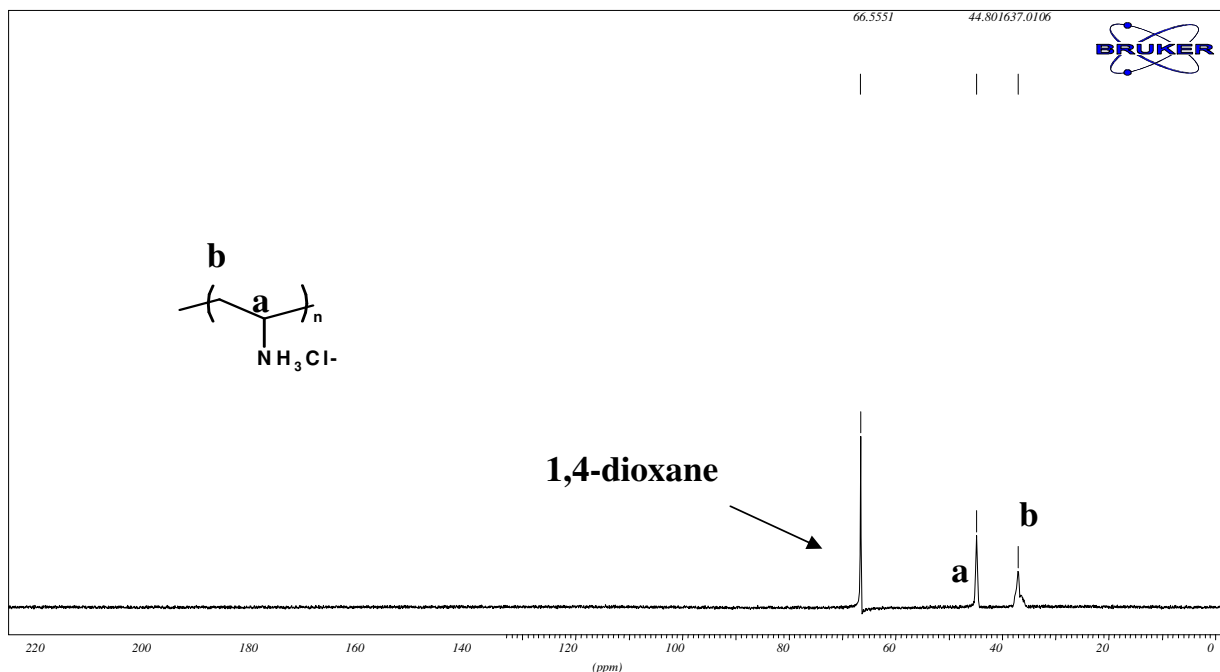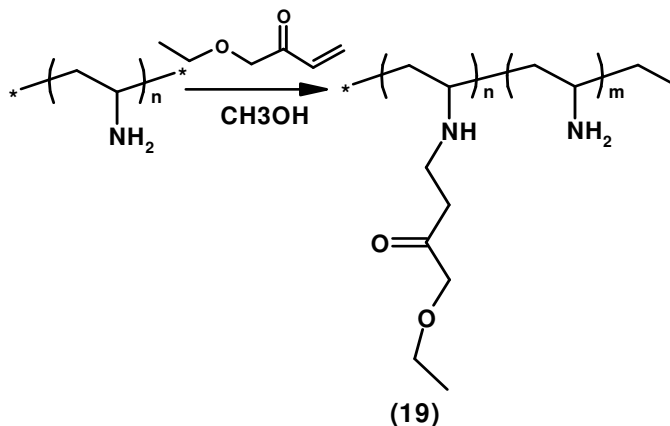

Figure 6.10 ^{13}C NMR of PVAm hydrochloride in D_2O

6.6.2 Synthesis of ethylacrylate modified PVAm (Initiator)

(19)

Scheme 6.7 Synthesis of ethylacrylate-modified PVAm

PVAm was modified with ethylacrylate following a procedure reported in literature. The modified polymer was characterized by NMR, IR and elemental analysis. Further, the polymer was used as an initiator for ring opening polymerisation of benzyloxyprotected N-carboxyanhydride by using a procedure similar to PMA brush polymer.

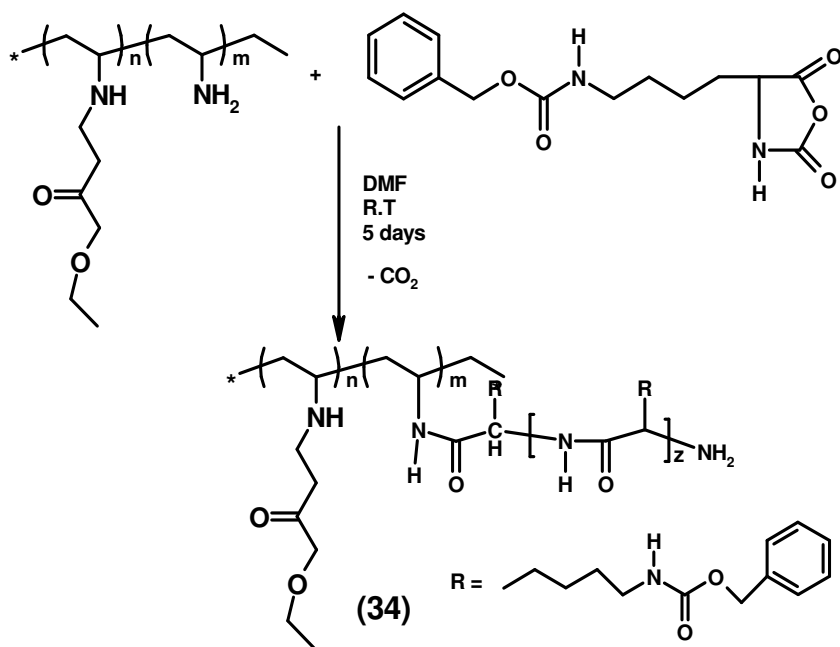**6.6.3 Synthesis of poly(z-L-lysine) grafted ethylacrylate modified PVAm(34).**

The polymers were synthesized via ring opening polymerisation of benzyloxy protected N-carboxyanhydride following a procedure as described earlier for poly(methylene amine) modified with ethylacrylate as initiator. The synthetic scheme is shown in scheme 6.8. The molecular weights obtained are listed in Table 6.2.

Table 6.2 Feed composition and characteristics of (co)polypeptide obtained by ethylacrylate modified polyvinylamine as initiator.

Entry	stoichiometry (Initiator: N-carboxyanhydride)	M_n	M_w	M_w/M_n	z
PVAm-S1	1:1	45,800	84,200	1.84	38
PVAm-S2	1:2	107,000	311,600	2.91	71

z =Average number of z-L-lysine repeating units (cal from NMR) M_w= Weight average molecular weight, M_n = Number average molecular weight M_w/M_n = polydispersity index obtained from GPC,PS standard.

Scheme 6.8 Synthetic Scheme of polyvinylamine grafted ethylacrylate initiated polymerisation of benzyloxy carbonyl protected –N-carboxyanhydride

6.7 Thermal properties and AFM images of poly(z-L-lysine) grafted from ethylacrylate modified PVAm.

DSC thermograms of the polymer, poly (z-L-lysine) grafted PVAm-co-ethylacrylate were investigated at heating rate 10K/min. There appeared one clear glass transition temperature at 25 °C that belonged to z-L-lysine segment.

The sample for AFM image was prepared up on evaporation of a drop of 0.3-wt % polymer solutions in DMF/THF (v: v = 1:1) on mica surface. One set of the sample was put in the vacuum oven set at 140 ° C for 2 hours quenching to low temperature followed by thermal treatment at 70 °C for two days and other was imaged without heat treatment. It was expected that the z-L-lysine chain hanging from the main polymer backbone of PVAm would exhibit strong intra as well as inter molecular hydrogen bonding between amide groups of adjacent z-L-Lysine resulting in regular structures. The AFM image of the polymer reveals organized structures distributed in random patches all over the surface (Figure 6.11).
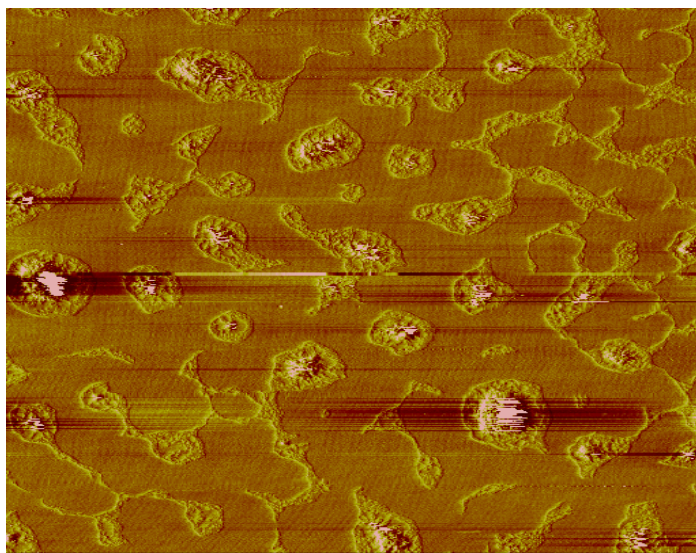

Figure 6.11 Tapping–mode AFM phase image of the supramolecular self organization formed by poly(z-L-lysine) grafted from ethylacrylate-modified PVAm with heat treatment, scale bar indicates 10 micron

It is interesting to note that the aforementioned polymer samples without heat treatment displayed vesicle like swollen structures randomly distributed on the surface (Figure 6.12).
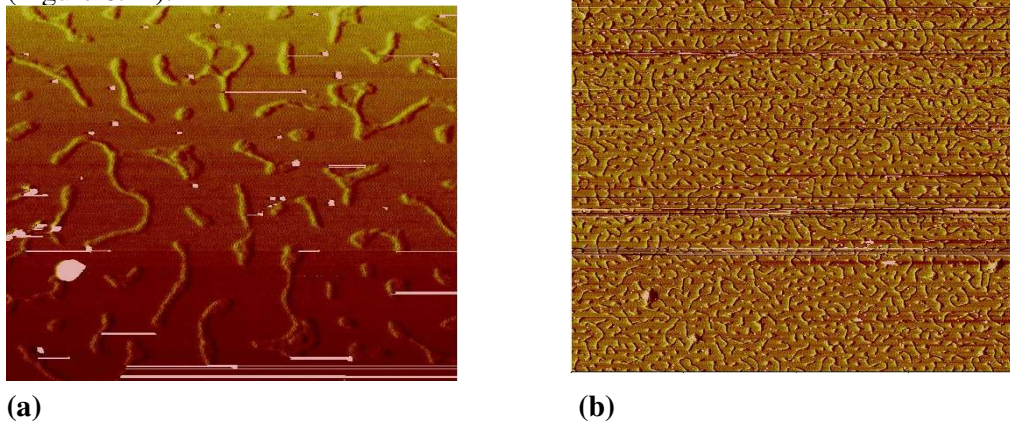

(a)   **(b)**

Figure 6.12 Tapping–mode AFM phase image of poly(z-L-lysine) grafted from ethylacrylate modified PVAm without heat treatment; scale bar indicates (a) 2 micron (b) 10 micron

6.8 Solid state morphologies of poly (z-L-lysine) grafted from ethylacrylate modified PVAm.

The solid-state morphologies of the modified polymers were investigated by wide-angle x-ray scattering(2D-WAXS). The investigation was aimed at analysis of the hybrid block copolymer with respect to polymer architecture and the secondary structure of polypeptide. The architecture of the hybrid block copolymer essentially depends on the initiating sites. If the initiating site forms the end group of a linear polymer, then the resulting polypeptide block copolymer would be a linear one. However, if the same is multifunctional and originating from a common point exhibiting a star like geometry, then the resulting polypeptide hybrid copolymer would take the shape of a bottle brush. Since, PVAm demonstrates a linear architecture; the resulting hybrid polymer is expected to display a comb-like architecture with segments of polylysine hanging onto the PVAm backbone. On the other hand, the secondary structure of the polypeptide segments primarily rests on the number of peptide repeating units. Thus, the helical conformation of polypeptide segment is a function of number of repeating polypeptide units in a segment and is

independent of total number of peptide units. Consequently, two types of conformation result from the number of peptide repeating units in a linear polypeptide segment, (1) when the segments are too short and hence in non helical conformation, the brush polymers form stiff cylinders.
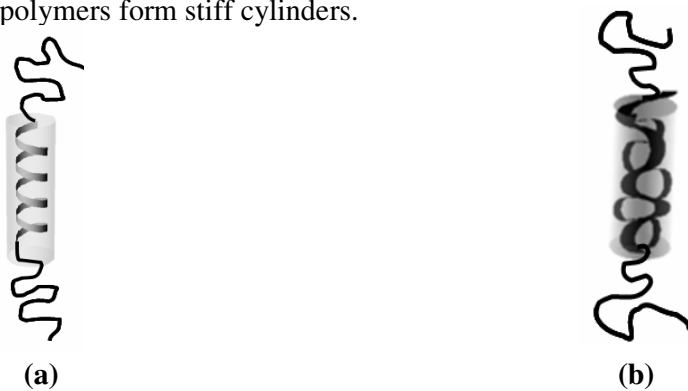

(a)   **(b)**

Figure 6.13 Schematic representation of the plausible structures arising from different architectures of poly(z-L-lysine) grafted PVAm-co-ethylacrylate (a) linear co polymers (b) star or bottle brush shaped copolymers.

These cylinders have larger diameter than the cylinders with helical peptide segments (**Fig.6.13 (b).**) (2) when the segments are long enough (at least 10 repeating units) to form alpha helical conformation, the peptide segments also form cylinders. In addition, these polymers might at all show characteristic Bragg peaks of a hexagonal packing of alpha helices in x-ray diffractogram (Figure 6.16). In order to study the arrangements of polypeptide segments, the samples were extruded above and below glass transition temperature of the polymer as shown in Figure.6.15.

As the polymers, polyvinylamine and poly(methylene amine) were modified with ethylacrylate to render solubility, prior to their reaction with z-L-lysine anhydride; the architecture of the resulting polypeptide grafted polymer became indecipherable. Thus, the conformation of polypeptide segment as it would usually adopt on reaction with initiators of defined architecture, became unpredictable. However, based on the structure of the backbone polymer, PVAm, it could be said that the polypeptide grafted polymer acquires comb-like conformation with ethyl acrylate and polypeptide segments emanating from the backbone. In addition to that, individual conformation of polypeptide segments which largely depends on the number of peptide units in the polypeptide segment was difficult to quantify. The reason for this discrepancy was

attributed to poorly defined architecture of the initiator (ethylacrylate modified PVAm), in which ethylacrylate units are statistically distributed along the polymer backbone.
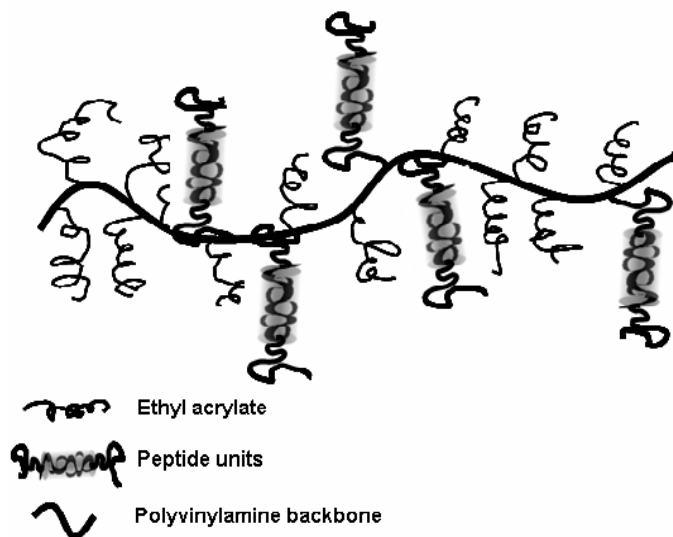

Figure 6.14 Schematic representation of brush polymer of polypeptide derived ethylacrylate modified PVAm(PVAm-S1)

Besides, assigning a comb-like architecture to the peptide derived polymer (Figure. 6.14), there was not much that could be said about the conformation of polypeptide segments. However, investigation of solid state morphologies of these polymers by two-dimensional wide-angle X-ray Scattering (2D-WAXS) revealed some valuable information about polypeptide segments. The extruded samples below and above Tg showed slightly different 2D patterns, whereby differences in the sharpness and intensity of the equatorial reflections were evident. The pattern of the sample extruded below T_g demonstrated better alignment in comparison to the sample extruded above T_g. Furthermore, it is known from the literature that polypeptide segments with less than 10 repeating units occupies non-helical conformation, and can form themselves quite stiff cylinders. These cylinders tend to posses a diameter that is much larger than the alpha helix. The characteristic Braggs peak of hexagonal packing of alpha helices shows a d_H (spacing between helices) value of approximately 1.4 nm.

The polymer sample under investigation showed a spacing of $d_H = 1.75$ nm, which is larger than it would otherwise be expected in case of a helix. As a result the polypeptide segments in these polymer samples acquired a hexagonal morphology of

peptide segments without formation of alpha helices. Hence, the peptide segments in the comblike architecture of ethylacrylate modified polyvinylamine are shorter than 10 repeating units and take the shape of stiff cylinders. The higher order equatorial reflections were characteristics for pronounced long-range order, whereby the cylindrical structures were oriented in both cases along the shearing directions applied during mechanical extrusion. In general, higher shear forces which lead to a better alignment, are attained when the processed material shows a lower viscosity.

In the presented case, the viscosity of the polymer was lower above the glass transition temperature resulting in decreased macroscopic orientation in comparison to the sample extruded below the phase transition. The structural investigation in the small-angle range did not indicate any scattering intensities and thus no super structure. This is in agreement with the expectation of an amorphous/disorder polymer chain, whereby only the peptide segments arrange in an ordered array.
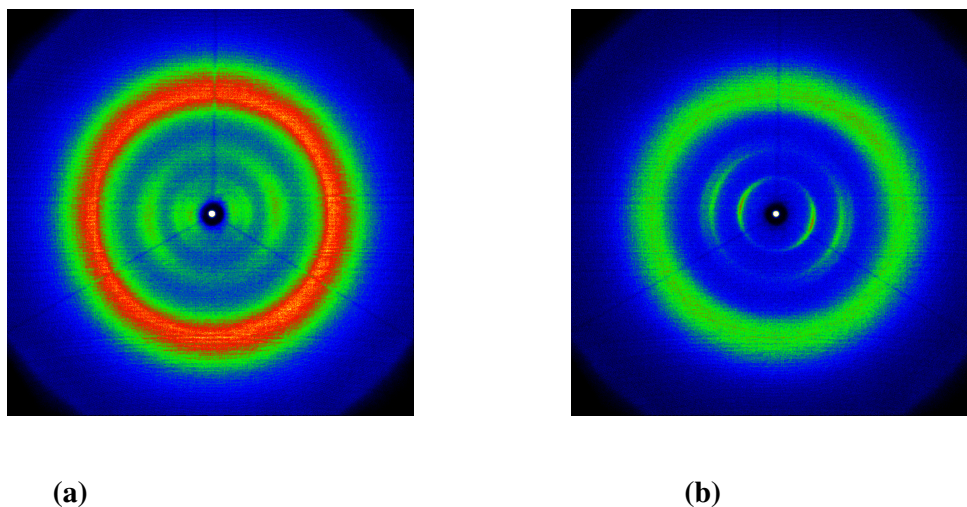

(a)   **(b)**

Figure 6.15 2D WAXS diffractograms of the polymer (a) Extruded above T_g (b) Extruded below T_g
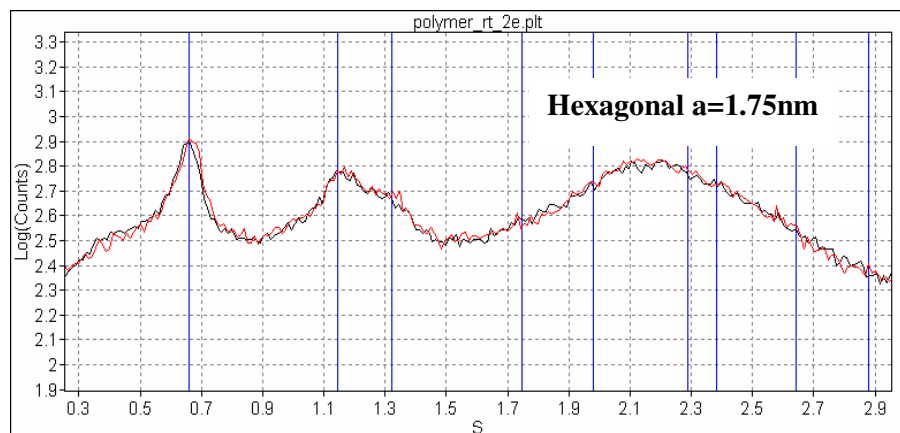
Figure 6.16 Equatorial scattering intensity as a function of scattering vectors.

6.9 Conclusions

Ethylacrylate derived poly(methylene amine) and polyvinylamine were used as initiators for ring opening polymerization of benzyloxy protected N-carboxyanhydride of Lysine. The polymers were characterized by GPC and NMR. The surface morphologies of both the polymers were investigated by AFM and SAXS. The morphology of these polymers was largely governed by the morphology of respective initiators. The initiators demonstrated comb-like architectures, where initiating sites, the pendant amine groups, are randomly distributed along the polymer backbone. The polypeptide units hanging from the back-bone try to self organize under suitable experimental conditions. The self organization behavior of polypeptide units were investigated by AFM and WAXS. The AFM images of brush polymers on PMA backbone at 0.3 wt% polymer concentration in the solvent mixture THF: DMF (v:v =1:1) displayed vesicle structures randomly distributed. Furthermore, the samples subjected to heat treatment showed stacking of these worms like vesicles presumably due to intra and inter molecular hydrogen bonding. Further, studies on the self organization of polypeptide units attached to the polymer backbone were investigated by SAXS. The small angle x-ray scattering of polymers **(PVAm-S1)** revealed hexagonal arrangement of polypeptide segments fitted into stiff cylinders. The spacing between helices packed in these cylinders was determined to be 1.75 nm. This rather larger d value in comparison to helices showed that peptide segments are short enough for helical arrangement. In addition to this, hydrolysis of benzyloxy carbonyl

protecting groups and ester linkage of ethylacrylate units on the polymer **BPMA-S2** liberated amine as well as acid groups. This, led to a novel architecture called polyampholyte brushes. The solution properties of these hydrolyzed polymers were investigated by viscosimetry. The polymer **(BPMA-S2)** demonstrated polyelectrolyte behavior at acid as well as basic pH regimes. The hydrochlorides of these polymers demonstrated an increase in viscosity with decrease in polymer concentration, a typical polyelectrolyte behavior. A clear transition from cationic to anionic polyelectrolyte behavior was noticed while measuring the viscosity of these polymers as a function of pH. Thus, at a concentration (1g/L) the plots of the hydrolyzed polymer, **BPMA-S1** vs. pH showed isoelectric point (IEP) at pH = 4.2, a typical characteristic of polyampholytes.

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7.1 Characterization Methods

7.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was used to examine the structure of the polymers and to monitor the process of hydrolysis of poly(1,3-diacetylimidazol-2-one)**(6)**. Spectra were obtained with a Nicolet Impact 400 FT-IR spectrometer.

7.1.2 Elemental Analysis

Elemental analyses were performed on a Perkin Elmer Model 2400 CHN analyzer.

7.1.3 UV

UV-Vis absorption spectra were recorded at room temperature on a Perkin Elmer Lambda 900 with 60 mm integrating sphere, deuterium source (UV) and Tungsten – halogen source (VIS)

7.1.4 Mass spectroscopy

FD and EI mass spectra were recorded on a VG instrument ZAB 2 SE FPD spectrofield, Bruker Reflex I (MALDI-TOF) and Bruker Reflex II (MALDI-TOF) mass spectrometers.

7.1.5 Nuclear Magnetic Resonance (NMR) spectroscopy

Proton NMR and ^{13}C NMR spectra were recorded using a Bruker AMX 250 Hz, Bruker AC 300 Hz and Bruker AMX 700 Hz NMR spectrometers in CDCl$_3$, CD$_2$Cl$_2$ or DMSO–d_6. or D$_2$O. Depending on the solubility of the material being analyzed. ^{1}H and ^{13}C –NMR spectra were referred to tetramethylsilane (TMS) at 0 ppm. NMR spectra were used to determine purity and chemical composition.

7.1.6 Melting point of monomers by capillary methods

The melting points of purified compounds were determined on a Buchi melting point apparatus at a heating rate of no greater than 1 °C/min. Samples were ground before measuring.

7.1.7 Viscometry

Viscosity measurements were performed at 25 °C in DMF and water. Depending on the solubility of the tested polymer using a Cannon – Ubbelhode viscometer. The intrinsic viscosity value was obtained by measuring specific viscosity and reduced viscosity at different concentrations and plotting reduced viscosity vs concentration and extrapolating to zero concentration.

7.1.8 Gel Permeation chromatography

GPC measurements were used to determine molecular weight and molecular weight distribution information. Chromatographs were on a waters 150 CALC/GPC instrument equipped with a differential index detector and a Viscotek Model 100 viscosity detector connected in parallel.

7.1.9 Differential Scanning Calorimetry

DSC was used to determine glass transition temperatures of polymers. DSC was conducted on a Perkin Elmer DSC 7 instrument. Scans were run in nitrogen at a heating rate of 10 °C /min. T_g values were identified as the mid point of the change in endothermic baseline from the second heat after a quench cool from the first run.

7.1.10 Thermo gravimetric analysis

Dynamic TGA was performed to access the relative thermal stability of the polymers Thermograms were obtained using a Perkin Elmer TGA 7 thermo gravimetric analyzer. Thin film or powder samples of ~ 10mg were placed in platinum pan connected to an electric microbalance. The samples were heated at a rate of 10°C/min in air or nitrogen, weight loss of the sample was measured as a function of temperature.

7.1.11 AFM Measurements

The samples were scanned with a Dimension 3100 model (Veeco, Santa Barbara, CA) at room temperature under ambient conditions. Single beam silicone cantilevers (Olympus OMCLAC160TS-W2 Tapping mode) with spring constants ~ 45 N/m and resonance frequency of ~300 kHz were used. All topography were recorded in tapping mode. The resulting images have been flattened and plane fitted some have been median and low pass filtered

7.1.12 Contact angle goniometry

The measurement were carried out on DSA 10–MK2 model (Kruess GmBh, Hamburg, Germany) contact angle measuring system with full computer control and automated image analysis system. Drops of liquid of known volume were applied from micro syringe to the surface of the test material. The reported values are the average of at least 8 drops placed and measured on different parts of the sample surface.The precision of measurements was below $\pm$ 10.

7.1.13 Degassing (Freeze Thaw cycles)

In order to remove oxygen and other gases from a liquid mixture, a simple procedure of degassing was employed. The flask containing the liquid mixture was connected to the vacuum line through a port. The mixture was frozen under liquid nitrogen and then gasses and oxygen in the frozen system were pumped out on application of vacuum. The system was allowed to stay at that condition for 3-5 minuets followed by thawing of the liquid. The freeze thaw cycle was repeated two to three times. In this way during every cycle a new equilibrium was attained between the gases dissolved in the liquid and the part of the flask above the liquid. The gases occupying the free space were driven out of the liquid into vacuum line while the liquid was maintained in the solid state.

7.1.14 Laser Light Scattering

Preparation of Samples

The procedure for preparation of samples involved two steps

Step I: Cleaning of Cubets

Cubets were cleaned extensively, first in VE wasser followed by acetone fountain. Having cleaned in acetone fountain, they were covered with aluminimum foil and placed carefully in the oven at 60°C, so as to avoid sticking of dust and foreign particles to the exterior surface of the cubets. The Teflon caps were cleaned in acetone fountains and dried in the oven in the same way as cubets.

Step II: Preparation of solutions

The solution of poly(methylene amine)**(8)** at varying concentrations viz. 0.5g/L, 1g/L, 3g/L and 5g/L were made in Milli Q water and mixed well with the help of shaker. However, the solution of poly(1,3-diacetylimidazol-2-one)**(6)** at varying concentrations were prepared in dry THF (sure sealed, stored under molecular sieve, ACROS). The solutions were filtered through a membrane filter (Micropore, 0.22μ pore size) into the cubets. The pH of the solution of poly (methylene amine) was maintained by careful addition of conc. HCL (37%). The entire procedure from cleaning of cubets to mounting sample cells before measurement was followed diligently in order to avoid trapping of dust particles.

7.1.15 MALDI-TOF Mass spectrometry

MALDI TOF Mass spectrometry was measured in Bruker Time of flight MS Reflex III, Samples of poly(methylene amine) polylysine-NCA were prepared in Dithrinol matrix.

**7.1.16 Refractive Index Increment (dn/dc)**

Refractive Index Increments were measured by Michelson scanning interferometer dn/dc of the samples were measured in THF and water for poly(1,3-diacetylimidazol-2-one) and poly(methylene amine), respectively.

7.1.17 GPC-MALLS

The instrument DAWN EOS WYATT was used to measure absolute Molecular weight M_w and distribution $<Rg^2>$. THF was used as solvent and polystyrene column.

7.2. Syntheses

7.2.1 Synthesis of N,N'-dicarbethoxy-1,2-diaminoethene(1)

[1]
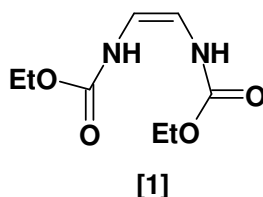
Imidazole (1.25g, 0.018mol) was dissolved in 35ml of water and 15ml of 30% NaOH. Ethylchloroformate (11ml, 0.116 mol) was added drop by drop into the system at $0\,^0C$ under constant stirring overnight. White precipitate formed was allowed to stand overnight and filtered under suction. It was dried and washed repeatedly with dilute sodium hydroxide and water. It was dissolved in 50 ml methanol. On dilution white needle like crystals formed was filtered and dried under vacuum (Yield = 40%)

M.p.: 136 -137 ^{0}C **^{1}H-NMR** (DMSO-d$_6$, 250MHz, 298 K): δ = 5.67 (2H, s), 4.03 (4H, q), 1.18(6H, t) **^{13}C-NMR** (DMSO-d$_6$, 65MHz, 298K) δ = (153.18, 105.15, 60.8, 14.38) **MS-FD** (70ev, CDCl$_3$): m/z (%) = 202 (100%, M$^+$) (calculated for $C_8H_{14}N_2O_4$ = 202.21) **Elemental Analysis**: calculated for $C_8H_{14}N_2O_4$ (%); C 47.52 H 6.98 N 13.85, Found C 47.39 H 6.88 N 14.02

7.2.2 Synthesis of 1,3-2H-4-imidazolin-2-one(2)

[2]
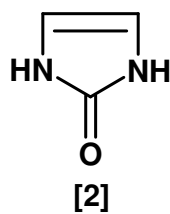
In a flask with reflux condenser and thermometer were added, α-ureidoacetaldehydacetal (96.5g, 0.55 mol) and a mixture of 75 ml sulphuric acid 0.1 N and (15.25) ml distilled water was added.. The mixture of the reaction was heated at 55°C. At 24-30°C were added 15.25 ml sulphuric acid 1N and after that the other 49.95 ml sulphuric acid 1N.The pH of the reaction mixture was 1.6. The solution is transparent at a temperature higher than 40°C. Water vacuum was introduced to distil the resulted ethanol. The first crystal appeared in 2 ½ hr. After another one hour, 23g of product in the form of crystals were isolated followed by further 6.25 g after sometime. (Yield =63.3 %.)

M.p: 242-244°C **IR:**(KBr, cm^{-1}): 146, 3000, 1653, 1575, 1475, 1400, 1250, 1087, 1072, 898, 836, 746, 697, 505. **^{1}H-NMR** (DMSO-d_6, 250MHz, 298 K): δ = 6.2 (2H, s), δ 9.75 (2H, s), **^{13}C-NMR** (DMSO-d_6, 65MHz, 298 K): δ = 155, 108

Elemental Analysis: calculated C 42.86% H 4.80 N 33.32 Found C 42.48% H 4.74 N 33.58

### 7.2.3   Synthesis of 1,3-diacetyl-4-imidazolin-2-one(3)

[3]
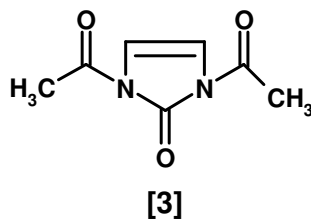
4-imidazolin-2-one (31.7g, 1.27 mols), 3 times more acetic anhydride and (1.5 g) dimethylpiperidine as catalyst were charged into a flask.The reaction was refluxed first at 106 °C, then at 116 °C and at the end at 124 °C for 5 h. The compound was crystallised from ethylacetate/cyclohexane; (Yield = 80 %.)

M.p.: 102 ^{0}C **^{1}H-NMR** (CDCl$_3$, 250 MHz): δ= 7.0(2H, s), 2.1 (6H, s), **^{13}C-NMR** (CDCl$_3$, 300MHz, 298 K): δ = 167.6, 149, 109, 23.79 **MS-FD** (70ev, CDCl$_3$): m/z (%) = 168 (100%, M$^+$) (calculated for C$_8$H$_{14}$N$_2$O$_4$ = 168.15), **Elemental Analysis**: calculated for (C$_7$H$_8$N$_2$O$_3$) C 50.0 H 4.80 N16.66 Found C 49.95 H 4.94 N 18.43 **IR** (KBr, cm^{-1}): 3476, 3420, 3218, 3130 (CH- stretching vibration of CH=CH),1760

(C=O stretching vibrations of acetyl groups), 1713 (C=O stretching vibration of the ring),1602,1520,1384,1240,1126,1037,986,927,780,766,714,634.

### 7.2.4 Synthesis of 1, 3-diformylimidazole-2-one(4)
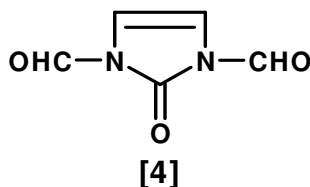
Dry N,N-dimethylformamide (DMF) (27ml) was introduced, under anhydrous conditions, in a 250 mL three-necked flask equipped with a reflux condenser and magnetic stirrer. The flask was cooled to 0°C with an ice-water bath and POCl$_3$ (27 ml) was added drop wise, under stirring, during 15 mins, followed by addition of 1,2-dichlorethane (24ml). The ice-water bath was taken off and the temperature was allowed to reach room temperature. The flask was kept at room temperature for 10 mins, it was cooled again to 0°C and compound, 1,3-dihydroimidazol-2-one (9g, 0.107 mol) was added. The ice-water bath was taken off after 10 min and the flask was heated at 80°C, for 25 mins. The reaction mixture was cooled to room temperature and poured, under stirring; onto ice (270g). The resulting white precipitate was immediately filtered and washed several times with ethanol. The compound was dried under vacuum and it was further purified by sublimation, under vacuum, at 150°C (Yield = 43%).

M.p: 119-120°C**. IR**(KBr, cm^{-1}): 3604, 3205, 3160, 2980, 1770, 1743, 1600, 1390, 1235, 760**. ^{1}H-NMR** (DMSO-d$_6$, 250 MHz): δ = 7.2 (2H, s), 9.05 (2H, s). **^{13}C-NMR** (DMSO-d$_6$, 300 MHz, ppm): δ = 157, 150, 109.5

Elemental Analysis: C$_5$H$_4$N$_2$O$_3$ (140 g mol^{-1}) Calcd (%) C 42.85, H 2.85, N 20.00 Found (%) C 42.04, H 2.55, N 20.05.

7.2.5 Synthesis of 1,3-dicarbethoxyimidazole-2-one(5)

[5]
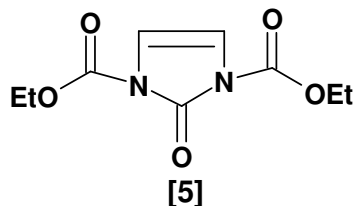
N, N`- Dicarbethoxy-1,2-diaminoethene(**1**), (1g, 5 mmol), was dissolved in 100 mL freshly distilled THF(100 ml) under inert atmosphere. Phenyl lithium (6ml) was added drop wise into the system under stirring at -78 °C. The mixture was allowed to stir for an hour. The colour changed to light yellow. (5ml) of phosgene in toluene was added slowly into the system at –78 °C. The reaction mixture was then stirred for 24 hours after which the reaction was quenched with water followed by dichloromethane extraction of the product. The extract was dried over MgSO$_4$, dichloromethane was evaporated and the product mixture was chromatographed with 20% acetone in high boiling. petroleum ether as eluent over a column of silica gel to yield a white floppy mass after recrystallization from ethyl acetate. (Yield 22%)

.

M.p.:100-102 °C **^{1}H NMR** (250 MHz, CDCl$_3$): δ = 6.72 (s , 2H, -CH=), 4.39 (q, 4H, -CH$_2$-, J= 7Hz), 1.38 (t, 6H, -CH$_3$, J= 7Hz), **MS-FD** (70ev, CDCl$_3$) (m/z, %) = 228 (100, M$^+$) (calculated for C$_9$H$_{12}$N$_2$O$_5$ = 228.21), **IR** (KBr, cm^{-1}): 2988 (CH stretching), 1811 (C=O stretching of carbethoxy), 1744 (C=O stretching from imidazolidone), **^{13}CNMR** (CDCl$_3$):δ = 14.03, 64.02,109.91, 145.92, 148.91 **Elemental Analysis** calculated for (C$_9$H$_{12}$N$_2$O$_5$) C 47.37 H 5.30 N 12.28 Found C 47.17 H 5.30 N 12.31

7.2.6 General procedure for the synthesis of poly (1, 3-diacetylimidazole-2-one)(6)

[6]
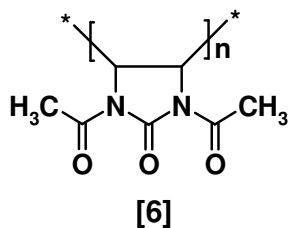
In a typical procedure (10 g, 0.060 mol) of monomer and (12 mg, 0.49×10^{-4} mol) of the initiator (1,1`-Azobiscyclohexanecarbonitrile or t-butylhydroperoxide (70% solution in toluene) were introduced into the flask. The mixture (monomer, solvent and initiator) was subjected to freeze –thaw (three cycles) in order to ensure complete removal of oxygen from the system. Further, the flask was kept under argon for nearly 15 minuets. The flask was fitted to a condenser with an argon inlet so as to run the reaction under inert atmosphere. The temperature was allowed to reach the set reaction temperature.

IR (KBr,cm^1)**:**3019, 2940, 1774, 1700, 1525, 1371, 1331, 1246, 1121, 1040, 980, 927, 896, 749, 697, 613 **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 3.7-4.6 (2H, b), 2.5-2.2 (6H, b) **^{13}C NMR** (CDCl$_3$, 500 MHz):δ = 168.3, 147, 54-49 (CH ring), 20.62 (CH$_3$, s) **Elemental Analysis**: Cal: C 50.0 H 4.80 N 16.66 Found C 48.52 H 4.87 N 16.51

TGA:
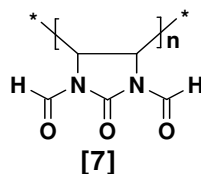
Polymer	$T^d_{\ 5}$	$T^d_{\ 10}$	$T^d_{\ 20}$	$T^d_{\ 50}$
Poly(1,3-diacetylimidazol-2-one)	372	382	393	408

T$_n$ = n % weight loss at the temperature in ^{0} C
DSC: T$_c$ = 220 ^{0}C, T$_g$ = 115 ^{0}C

7.2.7 General procedure for the synthesis of poly (1,3-diformyl-1,3-dihydroimidazole-2-one) (7)

[7]

In a typical procedure (10g, 0.071mol) of monomer and (12 mg, 0.49×10^{-4}mol) of the initiator (1,1`- Azobis(cyclohexanecarbonitrile)) were introduced into the flask. The mixture (monomer, solvent and initiator) was subjected to freeze–thaw (three cycles) in order to ensure complete removal of oxygen from the system. Further, the flask was kept under argon for 15 minuets. The flask was fitted to a condenser with an

argon inlet so as to run the reaction under inert atmosphere. The temperature was allowed to reach the set reaction temperature.

IR (KBr,cm^{-1}): 3421, 3140, 2920, 1782, 1709, 1414, 1376, 1217, 1107, 950, 749, 676
^{1}H NMR (250 MHz ,DMSO-d$_6$) δ = 9.0 (2H,b); 5.1-2.49 (2H,b) **^{13}C NMR** (DMSO-d$_6$, 300 MHz): δ = 58-52, 152, 163 **Elemental Analysis**: $C_5H_4N_2O_3$ (140 gmol^{-1}): Calcd (%): C 42.85, H 2.85, N 20.00. Found (%): C 42.04, H 2.55, N 20.05.

TGA:

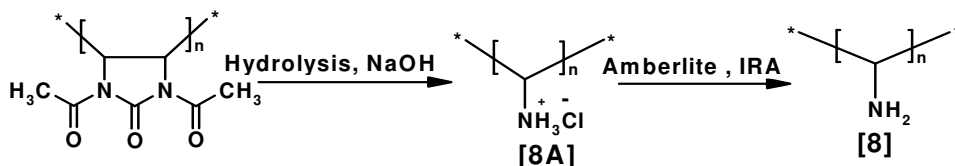| Polymer	T^d_5	T^d_{10}	T^d_{20}	T^d_{50}
Poly(1,3-diformylimidazol-2-one)	96	241	314	418

T$_n$ = n % weight loss at the temperature in ^{0}C
DSC: T$_c$ = (105 – 154 ^{0}C), T$_m$ = (154 – 235 ^{0}C), T$_g$ = No glass transition temperature was observed within the limits of measurement.

7.2.8 Hydrolysis of poly (1, 3-diacetylimidazole-2-one)

Sodium Hydroxide (6.5 gms), distilled water (4 ml), polymer **6** (2 gms), lithium chloride (0.8 gms) and ethylene glycol (7 ml) were added together into a two necked flask equipped with reflux condenser under inert atmosphere. Temperature was raised to 170 °C. The mixture was allowed to reflux under stirring for 12 hours.

Step: 2

The flask was cooled to room temperature. Poly (methylene amine) along with salts were extracted with (approx. 25ml) water followed by addition of conc. HCl (37%) to neutralize the system. Further an excess amount of HCl was added to convert polyamine into its hydrochloride, which is insoluble. Then it was stirred, filtered and dried.

<u>Step:3</u>

Ethanol (200 ml) was taken in a 500 ml flask and argon was bubbled through. (1.5 gm) of NaOH was added into the system in order to convert amine hydrochlorides to polyamine. Poly (aminehydrochloride) along with the salts were added in to the system and stirred for 12 hours under argon atmosphere.

<u>Step: 4</u>

The mixture was allowed to stand for some time. Then ethanol layer was decanted off. Excess of ethanol was distilled off and the mixture was concentrated to approximately 50ml. conc. hydrochloric acid (37%) was added to precipitate polyamine hydrochloride. Then it was filtered and dried under vacuum.

<u>Step: 5</u> (*DIALYSIS*)

The resulting amine hydrochloride was dissolved in water and subjected to dialysis for four days under argon atmosphere. Water was changed twice a day. A cellulose acetate membrane with a molecular weight cut off of 1000 gms/mol was used for dialysis.

The membrane was soaked in distill water for some time in order to remove residual sodium azide solution. A dialysis sack was made by puting knots at both the ends of the flat membrane. The solution was put in the sack and then dialysed in a three necked flask filled with distilled water under argon atmosphere for four days. At the end of fourth day aqueous solution of poly (methylene amine) was collected in a beaker. Then conc.hydrochloric acid was added to convert polyamine into hydrochloride. In case of haziness, the solution was filtered prior to its conversion into hydrochloride.
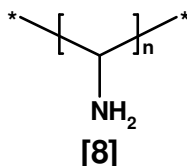
Poly(methylene amine) hydrochloride (8a)

[8A]
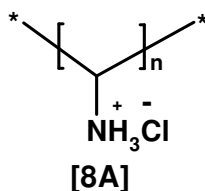
^{1}HNMR (250 MHz, D_2O, pH=2.5):δ=3.84(s, 1H, -CH) **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 56.0 (CH, broad), **IR** (KBr, cm^{-1}): 3415(NH), 2932(NH_3^+), 2500(NH_3^+), 2000(NH_3^+), 1615(NH_3^+), 1515, 1384, 1150,870 **Elemental Analysis**: Calc.C 18.46, H 6.15 N 21.54 Found C 22.60 H 7.16 N 24.20

7.2.9 Preparation of poly (methylene amine)(8)

[8]

(1g, 0.015mol) of poly(methyleneamine)hydrochloride**(8A)** was dissolved in water (25ml) and eluted through a short column filled with ion exchange resin (Amberlite IRA-400 Cl⁻). Poly (methylene amine) **(8)** was collected through lyophillization of its aqueous solution. Residual traces of water were removed under high vacuum.

¹H NMR (250 MHz, D_2O, pH=10.2): δ = 2.85 (bs, 1H, -CH) **¹³C NMR** (D_2O, 500 MHz, pH = 10.2, 1,4-dioxane as standard)**:**δ = 51.3(CH, broad), **IR** (KBr,cm⁻¹): 3372(NH), 2924(CH),1600(NH), 1550, 1485, 1383, 933, 667 **Elemental Analysis** Cal. C 41.36 H 10.41 N 48.23 Found C 36.27 H 9.49 N 35.62

7.2.10 Preparation of polyvinylamine hydrochloride (9A)
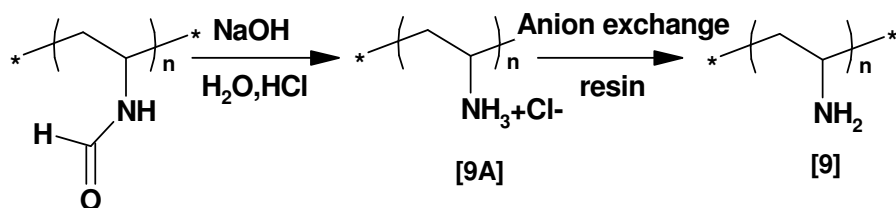
In a typical procedure 50g of partially hydrolysed PVA-co-NVF (Lupamin, BASF) was dissolved in a solution of 2N NaOH and kept at 100 ⁰C overnight. Then the solution was neutralized and dialysed for three days in 20 L of water in cellulose acetate tubing. Purified aqueous solution of polyvinylamine was transformed into its aminehydrochloride **(9A)** up on treatment with conc. HCl (37%).

^{1}H-NMR (D$_2$O, 300 MHz, ppm): δ = 2.27 (s, 2H, CH$_2$), 3.85(s, 1H, -CH-) **^{13}C-NMR** (D$_2$O, 1,4-dioxane, 75MHz): δ = 38.40 (CH$_2$), 45.96 (CH) **Elemental analysis**: (C$_2$H$_6$NCl): Calcd.(%): C 30.3, H 7.59, N 44.30. Found (%): C 23.48, H 6.98, N 13.62.

7.2.11 Preparation of polyvinylamine(9)

polyvinylamine hydrochloride (1g) was dissolved in water (25ml) and eluted through a short column filled with ion exchange resin (Amberlite IRA – 400 Cl$^-$). Polyvinylamine was collected through lyophilisation of its aqueous solution. Residual traces of water were removed under high vacuum.

IR (KBr, cm^{-1}): 3346, 2926, 1594, 1469, 1440, 1383, 1325, 1127, 938, 825, 719 **^{1}H-NMR** (D$_2$O, 250 MHz): δ = 1.41 (s, 2H, CH$_2$), 3.05 (s, 1H, CH); **^{13}C-NMR** (D$_2$O, 65MHz): 40.00 (CH, b), 44.65 (CH$_2$,b) **Elemental analysis**: C$_2$H$_5$N (43g mol^{-1}): Calcd. (%): C 55.81, H 11.62, N 32.55 Found (%): C 43.68, H 10.30, N 21.71.

7.2.12 General procedure for synthesis of Poly(N-methyl-ammonium-iodide-methyleneamine)(10) and poly(vinyl-N-methyliodide)(10B)

Poly (methylene amine) (0.1g, 3.44x10^{-3} mol) was dissolved in dry methanol (100 ml) and treated with methyliodide (4.8g, 10mmol for 1:10 molar ratio and 0.48g for 1:1 molar ratio) for 3h, at 30°C, under stirring. Methanol was distilled off and the resulting polymer was washed with acetone (3 x 30 ml) and dried under vacuum.

[10]
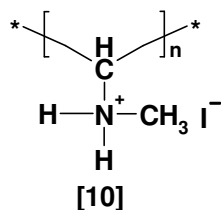
IR (KBr, cm^{-1}): 3420, 2980, 2945, 1600, 1470, 1380, 1243, 1080, 1024. **^{1}H NMR** (D$_2$O, 250MHz, ppm): δ = 2.85-2.5 (N-CH$_3$), 3.8-3.1 (CH-N$^+$ and CH$_3$-N$^+$). **^{13}C-NMR** (D$_2$O, 125 MHz): δ = 37-32 (N-CH$_3$), 57-47 (CH-N$^+$ and CH$_3$-N$^+$).
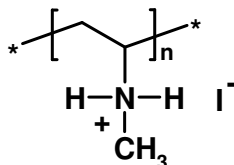
Elemental analysis: C$_2$H$_6$N (44 g mol^{-1}) Calcd (%) C 72.18, H 5.26, N 10.52.

Found (%) C 25.92, H 7.24, N 23.00 (for molar ratio 1:1); *(%) Conversion* = 32

C 23.42, H 6.55, N 19.47 (for molar ratio 1:10); *(%) Conversion* = 40

Polyvinylamine (0.1g, 2.3×10^{-3} mol) was dissolved in dry methanol (100 ml) and treated with methyl iodide (3.3g, 10mmol for 1:10 molar ratio,0.33g for 1:1 molar ratio) for 3h, at 30°C, under stirring. Methanol was distilled off and the resulting polymer was washed with acetone (3 x 30 ml) and dried under vacuum.

[10B]

^{1}H NMR (D$_2$O, 65MHz, ppm): δ = 1.83 (s-CH$_2$), 2.65 (s, CH$_3$-N) and 3.2-3.4(m,CH-N$^+$,-CH$_3$-N$^+$)

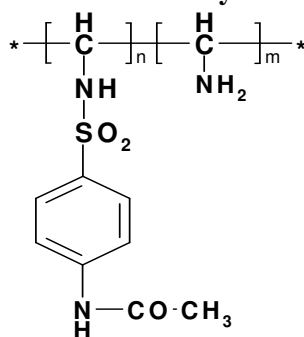**Elemental Analysis**: C$_3$H$_8$N (58 gmol^{-1}): Calcd.(%) C 62.06, H 13.79, N 24.13

Found (%) C 27.90, H 6.08, N 11.58 (for molar ratio 1:1); *(%) Conversion* = 34

C 23.49, H 5.47, N 9.35 (for molar ratio 1:2); *(%) Conversion* = 44

C 27.52, H 5.92, N 10.42 (for molar ratio 1:10); *(%) Conversion* = 56

**7.2.13 Synthesis of poly (4-acetamido-N-methylenebenzensulfonamide)(11)**

[11]

4-N-acetamido-benzenesulfonylchloride (0.69g, 2.95 mmol) was added to a solution of poly (methyleneamine) hydrochloride (0.5g, 7.69×10^{-3} mol), in water (7ml) and NaOH solution 8 N (0.7 ml), and stirred for 5 min. Tetrahydrofuran (THF) (3 ml) and 4-N-acetamido-benzenesulfonylchloride (0.69 g, 2.95 mmol) were added and the resulting solution was stirred for 15 min. The pH of the solution was adjusted to 10 by adding additional NaOH solution (8N). Finally, THF (3ml) and 4-N-acetamido-benzenesulfonylchloride (0.69 g, 2.95 mmol) were added again and the solution was stirred for 1h. The pH of the solution was adjusted again to 10 by adding NaOH

solution (8N). THF was distilled off from the reaction mixture and the polymer precipitated. It was filtered, washed several times with water and methanol and dried under vacuum.

IR (KBr, cm $^{-1}$): 3250, 1685, 1580, 1390, 1315, 1250, 1251, 1080, 1007, 830, 730, 630. **^{1}H-NMR** (D$_2$O / THF: 1/1, 250 MHz) δ = 8.5-7.1 (aromatic, broad), 2.2 (CH$_3$, s), CH-N peak was hidden under the THF peak.**^{13}C-NMR** (D$_2$O / THF: 1/1, 125 MHz): δ=60-50(CH, broad), 24(CH$_3$), 119 (aromatic), 129 (aromatic), 134 (aromatic), 143 (aromatic), 172 (C=O). **Elemental analysis:** (C$_9$H$_{10}$N$_2$SO$_3$) (226 g mol^{-1}) Cal.(%) C 47.78, H 4.42, N 12.38 Found (%): C 41.98, H 5.76, N 12.8

(%) Conversion = 67%

7.2.14 Synthesis of Poly(N-methylene-N-phenylurea)(12)

[12]
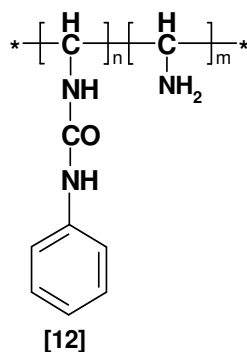
Phenylisocyanate (0.890g, 7.47 mmol) was added, under stirring, to a solution of poly (methylene amine) (0.14g, 4.83x10^{-3}mol) in methanol (25 ml). The reaction mixture was stirred for 3 h. The precipitated polymer was filtered, washed with methanol and dried under vacuum.

IR (KBr, cm $^{-1}$): 3350, 3052, 1940, 1870, 1670, 1600, 1530, 1500, 1440, 1320, 1240, 900, 720, 684. **^{1}H-NMR** (solid state, 700 MHz): δ = 7.0 (aromatic, broad), 3.8 (NH$_2$, s), CH-N peak was hidden under NH$_2$ peak. **^{13}C-NMR** (solid state, 175 MHz) 60-50 (CH, b), 24 (CH$_3$), 124 (aromatic), 130 (aromatic), 140 (aromatic), 160 (C=O), 80-50 (CH-N). **Elemental analysis**: C$_8$H$_8$N$_2$O (148 g mol^{-1}) Calcd (%) C 64.86, H 5.44, N 18.Found (%): C 57.17, H 6.65, N 18.51. **(%) Conversion:** 76%

7.2.15 General procedure for synthesis of poly (methylene amine)-acrylic acid derivatives(13 & 14)

R = H, CH₂ - CH₂ - CN   R₁ = H, CH₂ - CH₂ - COO - C₂H₅
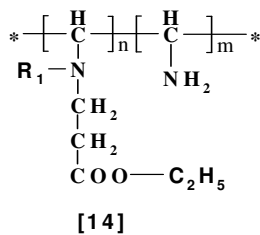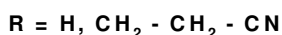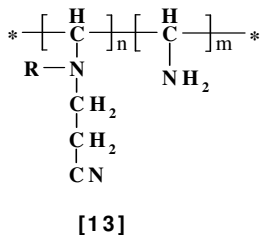
Freshly distilled acrylonitrile (22.4 ml, 0.34 mol) was added to a solution of poly(methylene amine) (0.1g, 3.44 x 10^{-3} mol) in methanol (15 ml) and refluxed for 24 h. The excess of acrylonitrile and solvent was distilled under vacuum at room temperature and the resulting polymer was washed with THF and dried under vacuum at 60°C.

Polymethyleneamine / acrylonitrile, **[13a]** and **[13b] IR** (KBr, cm^{-1}): 3445, 2935, 2932, 2853, 1734, 1652, 1457, 1376. ^{13}**C-NMR** (CDCl$_3$, 500 MHz): δ = 125.8 (C=O), 70-66 (N-CH$_2$, broad), 56-48 (CH, broad), 25 (CH$_2$-CN).

Elemental Analysis: C$_4$H$_6$N$_2$ (82 g mol^{-1}) Calcd. (%): C 58.53, H 7.31, N 34.1.

Found (%) **13a**: C 59.03 H 10.13, N 29.98; for molar ratio (1:2)

(%) Conversion = 64

Found (%) **13b**: C 58.58, H 10.14, N 31.16; for molar ratio (1:100)

(%) Conversion = 100

Polymethyleneamine / ethyl acrylate, **[14]**: **IR** (KBr, cm^{-1}): 3445, 2935, 2932, 2853, 1735, 1652, 1457, 1376. ^{1}**H-NMR** (DMF, 250 MHz): δ = 0.8 (CH$_3$), 2.5 (CH$_2$-CH$_2$-CO, broad), 3.6(O-CH$_2$), CH peak was hidden under other peaks. ^{13}**C-NMR** (DMF, 500 MHz): δ = 48-40, (CH and NH-CH$_2$), 34 (CH$_2$-CO, broad), 62-56 (O-CH$_2$), 13(CH$_3$). **Elemental analysis**: C$_6$H$_{11}$N$_1$O$_2$ (129 g mol^{-1}) Calcd (%): C 55.81, H 8.52, N 10.85.   Found (%): C 54.54, H 8.05, N 11.89; For molar ratio 1:5 (PMA: Ethylacrylate) *(%) Conversion =* 87

7.2.16 Synthesis of poly(N-methylene-N-propanesulfonicacid)(15)

[15]
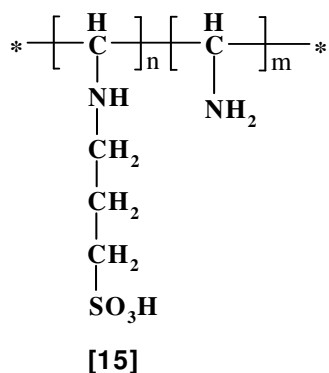
Poly(methylene amine) and 1,3-propanesulfone were reacted at varying molar ratios 1/1, 1/2 and 1/10 poly (methylene amine)/1,3-propanesulfone. 1,3-propenesulfone (0.420g, 3.344 mmol) in methanol (5ml) was added to a solution of poly(methylene amine) (0.1g, 3.44 x 10^{-3}mol) in methanol (25ml). The reaction mixture was refluxed for 24h and methanol was evaporated. The residue was dissolved in distil water (50 ml) and the resulting solution was dialyzed for two days using a cellulose acetate membrane (MW-cut-off 1000 g/mol) .The resulting polymer solution was freeze-dried and the obtained polymer was dried under high vacuum for 18 hours at 60°C.

IR (KBr, cm $^{-1}$): 3434, 2925, 1628, 1472, 1192, 1035 **^{1}H-NMR** (D$_2$O, 250 MHz, ppm): δ =1.8 (-CH$_2$-C$\underline{H}_2$-CH$_2$-, pent), 2.8 (-C$\underline{H}_2$-NH-, t), 2.7(-C$\underline{H}$-NH, b, merged with signals from –CH2-NH-); 3.43 (-C$\underline{H}_2$-SO$_3$H-, t); **^{13}CNMR** (D$_2$O, 125 MHz, 1,4-dioxan standard, ppm): δ = 57, 54-51, 47.9, 24

Elemental Analysis:

C$_4$H$_9$N$_1$O$_3$S$_1$(151) Calcd.(%): C 31.78, H 5.96, N 9.27, S 21.19

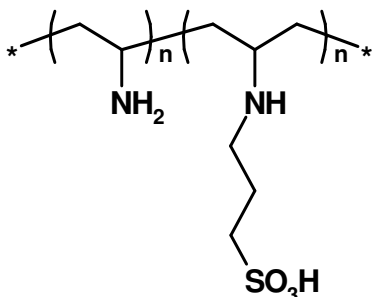Found (%): C 36.24, H 7.73, N 17.98, S 12.18 (for molar ratio 1:1)

(%) Conversion = 44

Found (%): C 35.64, H 7.81, N 17.84, S 13.32 (for molar ratio 1:2)

(%) Conversion = 48

Found (%): C 35.85, H 7.64, N 16.00, S 13.62 (for molar ratio 1:10)

(%) conversion = 54

7.2.17 Preparation of poly(vinylamine-co-vinyl-N-propanesulfonicacid)(16)

[16]

Polyvinylamine and 1,3-propanesulfone were reacted at varying molar ratios 1/1, ½ and 1/10 polyvinylamine/1,3-propanesulfone. 1,3-Propenesulfone (0.420g, 3.344 mmol) in methanol (5ml) was added to a solution of polyvinylamine (0.1g x 3.44×10^{-3} mol) in methanol (25 ml). The reaction mixture was refluxed for 24 h and methanol was evaporated. The residue was dissolved in distil water (50 ml) and the resulting solution was dialyzed for two days using a cellulose acetate membrane with a molecular weight cut-off 1000. The resulting polymer solution was freeze-dried and the obtained polymer was dried under high vacuum for several hours at 60° C.

IR (KBr, cm^{-1}):3434, 2925, 1628, 1472, 1192, 1035

^{1}HNMR (250 MHz**,** D$_2$O, 300K):

PVAmS-1 δ =1.9 (bs,-C$\underline{H}_2$-CH-N-), 1.99 (pent,-CH$_2$-C$\underline{H}_2$-CH$_2$-, 2H), 2.94 (t,-NH-C$\underline{H}_2$-CH$_2$-), 3.36 (bs, -SO$_3$H), 3.43-3.54 (bs, -C$\underline{H}$-NH-), 3.57 (t,-C$\underline{H}_2$-SO$_3$H)

PVAmS-2 δ = 2.01 (pent, -CH$_2$-C$\underline{H}_2$-CH$_2$-, 2H), 2.22 (bs, -C$\underline{H}_2$-CH-N-), 2.98 (t, NH-C$\underline{H}_2$-CH$_2$-), 3.36 (bs,-SO$_3$H), 3.58 (t, -C$\underline{H}_2$-SO$_3$H), 3.76 (bs, -C$\underline{H}$-NH-)

PVAmS-3 δ =1.94 (pent,-CH$_2$-C$\underline{H}_2$-CH$_2$-, 2H), 2.08 (bs,-C$\underline{H}_2$-CH-N-), 2.96 (t,-NH-C$\underline{H}_2$-CH$_2$-), 3.36 (bs,-SO$_3$H), 3.57 (t,-C$\underline{H}_2$-SO$_3$H), 3.60 (bs, -C$\underline{H}$-NH-)

Elemental Analysis: C$_4$H$_9$N$_1$O$_3$S$_1$ (151) Calcd. (%): C 31.78, H 5.96, N 9.27, S 21.19

Found (%): C 36.24, H 7.73, N 17.98, S 12.18 (for molar ratio 1 / 1)
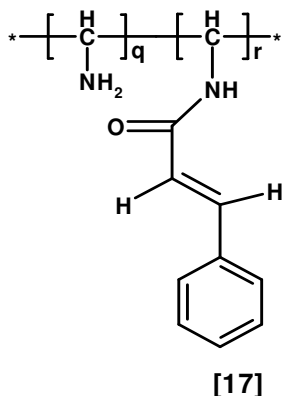
(%) conversion: 54

Found (%): C 35.64, H 7.81, N 17.84, S 13.32 (for molar ratio 1 / 2)

(%) conversion: 66

 Found (%): C 35.85, H 7.64, N 16.00, S 13.62 (for molar ratio 1/10)

(%) conversion: 75

7.2.18 Synthesis of cinnammoylated poly(methylene amine)(17).

[17]

In a typical procedure, a 3 wt % solution of poly(methylene amine)hydrochloride in water is neutralized to pH 9–10 by addition of 4M NaOH solution.THF is then added to the basic solution (16ml per gm of polymer). A solution of cinnammoyl chloride in THF (25 g.L^{-1}) was dropped from a funnel in small portions to avoid sudden depression of pH. Between successive additions, the necessary volume of 4M NaOH solution is introduced `for maintaining the solution pH in the range of 9-10. On completion of addition of desired amount of cinnammoyl chloride, the solution was acidified to pH = 2 by addition of 6M HCl and poured into a large volume of acetone under vigorous stirring. The cinnammoylated polymer, precipitated as white powder, was filtered and washed thoroughly with acetone. Transformation of the photosensitive polymers into their free bases was carried out by elution through an anion exchange resin (IRA - 400 CL$^-$). The neutral form of the photosensitive polymer is isolated as a white solid after freeze-drying. (Yield = 60%).

IR (KBr, cm^{-1}): 3421, 2923, 2853, 1655, 1623. **^{1}H-NMR** (250 MHz, ppm) δ =7.1-7.5 (aromatic, b), 4.18 (b, s, CH=CH -) **^{13}C-NMR** (solid state, 700 MHz, ppm) δ =52-57 (CH, b), 120(-CH=CH-), 128-129(aromatic), 136.20 (aromatic CH), 168.2 (-C=O)

Elemental analysis   Found (%): C 1.02, H 0.40 N 0.25 (for molar ratio 1:1)
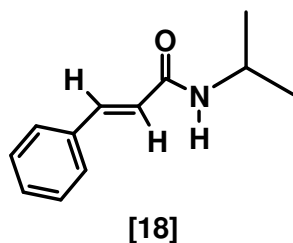
(%) conversion: 42

Found (%) C 39.26 H 8.06 N 16.27 (for molar ratio 1:0.25)

(%) conversion: 21

Found (%): C 1.18 H 8.04 N 18.51 (for molar ratio 1:0.1)

(%) conversion: 8

7.2.19 Synthesis of (E) N-iso-propylcinnamamide (18)

[18]

E-N-iso-propylcinnamamide was synthesized by reacting (*E*)-cinnamoyl chloride with 2-fold excess of freshly distilled isopropyl amine in anhydrous ether solution. After stirring for one hour at room temperature, the solution was concentrated by evaporation under vacuum. White solid was washed three times with water and recrystallized from ethanol. The pure (E) amide was isolated as white needles. (Yield = 40%)

IR (KBr, cm^{-1}): 3270, 3080, 2960, 1650, 1610, 1540, 1450, 1360, 1230, 980, 720 **^{1}H-NMR** (CDCl$_3$, 250MHz): δ = 1.20 (6H, d, J = 6.6Hz, -(CH$_3$)$_2$), 4.21 (1H, oct, *J* = 6.6Hz, -CH-), 6.08 (1H, bs, -NH), 6.40(1H, dd, J_1=14.13Hz, J_2=1.57Hz, Ph-CH=), 7.27 (3H, t, *J* = 3.14Hz, aromatic), 7.41(2H, q, *J* = 3.14Hz, Ph-aromatic), 7.55 (1H,d, *J*=15.38Hz, = CH-C=O) **^{13}CNMR** (CDCl$_3$, 65 MHz): δ = 21.8, 40.62, 120.3, 126.77, 127.8, 128.54, 130.40, 139.61, 164.25 **Elemental analysis**: Calculated for (C$_{12}$H$_{15}$NO) : C 76.16, H 7.99, N 7.40. Found (%): C 76.94, H 7.91, and N 7.43.

7.2.20 Synthesis of Ethyl acrylate modified polyvinylamine(19)

[19]
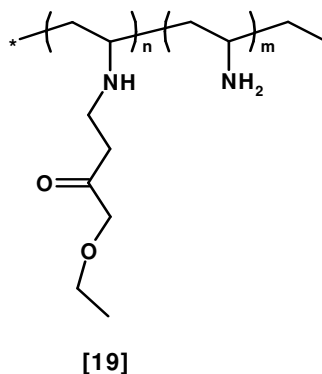
To methanolic solution of polyvinylamine (c = 0.25 mol/L) freshly distilled ethyl acrylate was added and refluxed overnight. The samples were isolated by evaporation of excess acrylate and methanol at room temperature.

IR (KBr, cm^{-1}): 3450, 3340, 2953, 2847, 1732, 1615, 1437, 1178 **^{1}H-NMR** (CDCl$_3$, 250 MHz): δ = 1.25 (m, CH$_3$), 1.35 (m), 1.60 (m, CH$_2$-CH-NH, CH$_2$-CH-N), 2.45 (m, CH$_2$-CO), 2.76 m (CH-N, CH$_2$-N), 4.10 (s, CH$_2$O) **Elemental analysis**: Found(%): C 52.26 H 8.09 N 9.10; *(%) Conversion* = 74%

**7.2.21 Synthesis of 2-pentyl-2-imidazoline(20)**
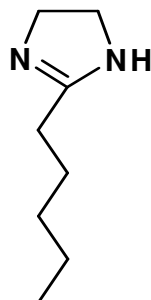
[20]

Hexanoic acid (11.6g, 0.1mol) was heated gradually to 240 °C together with (10g, 0.115 mol) of ethylene urea. Water formed during the reaction was allowed to escape through a condenser. The reaction mixture was heated for 69-70 hrs at 240-250 °C, the content of the flask with brownish black coloration was distilled at 116°C and under reduced pressure, < 0 mbar. **Yield** 9.5 %

^{1}H-NMR (250 MHz ,CDCl$_3$) δ = 0.73 (3H, t,-CH$_3$), 1.16 (4H, q, -CH2-), 1.43 (2H, sex, -CH$_2$-), 2.06 (2H;t,-CH-C=N-), **^{13}C-NMR** (65 MHz, CDCl$_3$): δ = 13.5, 22.01, 26.03, 29.08, 31.24, 49.43, 167.71 **EIMS** (70 ev, CDCl$_3$) m/z (%) =100%, M$^+$ = 140) (calculated for C$_8$H$_{16}$N$_2$ = 140.23)

7.2.22 Synthesis of 2-propyl-2-imidazoline(21)

**[21]**
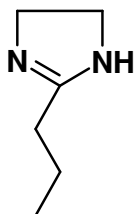
Butyric acid (0.8 g, 0.1 mol) was heated gradually to 240 °C together with (10g, 0.115 mol).Water formed during the reaction was allowed to escape through a condenser. The reaction mixture was heated gradually for 50 hrs to 240°C, the content of the flask with feeble yellowish coloration was distilled at 115 °C under very reduced pressure < 0 mbar. An oily liquid was obtained which solidifies at very low temperature in the refrigerator. **Yield:** 6 %

^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.88 (3H, t,-CH$_3$), 1.54 (2H, sex, -CH$_2$-), 2.13 (2H, t, -CH-C=N -) **^{13}C NMR** (65 MHz, CDCl$_3$): δ = 13.5, 19.6, 30.92, 49.23, 167.64 **EIMS** (70 ev, CDCl$_3$): **m/z (%) =** 112 (100%, M$^+$) (calculated for C$_6$H$_{12}$N$_2$ = 112.18)

**7.2.23 Synthesis of 1, 3-dihydroimidazoline-2-thione(22)**
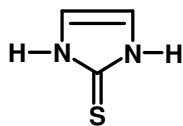
[22]

A flask with cooling condenser and thermometer was charged with α-amino acetaldehyde acetal (5g, 0.056 mol), was cooled at –5° C and HCl (5N) 45.6 ml was added while maintaining the temperature between 0-5 °C during 20 minuets. The flask was then cooled at – 40 °C followed immediately by the introduction of solution of potassium thiocyanate (8.21g, 0.084 mol) in 60 ml water during 15 minuets. The resulting solution was refluxed at 100 °C and was maintained at this temperature for 3h. It was cooled. On cooling fine yellow crystals settled down. It was filtered and then dried.

M.p.230-232 °C **^{1}H-NMR** (DMSO –d_6): δ = 6.80 **^{13}C-NMR** (DMSO-d$_6$): δ = 115.4, 160.43 **IR** (KBr, cm^{-1}): 3117, 2648, 2551, 2301, 2121, 1586, 1484, 1423, 1276, 1230, 1071, 912, 870, 832, 788, 729

7.2.24 Synthesis of 1, 3-diacetyl-1, 3-dihydroimidazole-2-thione(23)
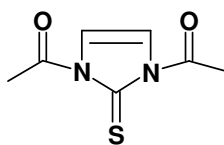

[23]

1,3-Dihydroimidazole-2-one (**2**) was dissolved in 3 ml. of acetic anhydride. The solution turned yellow almost at once and it was refluxed overnight. The mixture was evaporated to dryness under reduced pressure.

M.p.177-179 °C **^{1}HNMR** (CDCl$_3$, 250 MHz) δ = 2.97 (6H, s, -CH$_3$), 7.44(2H, s,-CH=) **^{13}CNMR (**65 MHz, CDCl$_3$): δ = 26.43, 113.72, 166.01, 168.51 **IR** (KBr, cm^{-1}): 3129, 2981, 2874, 1585, 1477, 1267, 1225, 1119, 1070, 911, 788, 735, 673.

### 7.2.25 Synthesis of poly (1,3-diacetyl-1, 3-dihydroimidazole-2-thione)(24)
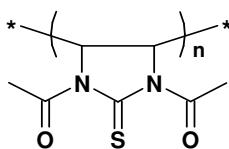
[24]

The monomer (0.5g, 2.72 x 10^{-3} mol) was polymerised with (2mg, 8.16x10^{-6}mol) of initiator (AICC) under above conditions at 130°C for an hour. The slightly viscous reaction mixture on cooling yielded an off-white brittle solid that stuck to the walls of the schlenk flask. It was dissolved in THF and precipitated from hexane. Off-white, precipitate formed was washed with water and dried.

^{1}HNMR (CDCl$_3$, 250 MHz): δ = 4.5 (b, d, 2H), 2.5 (b, 6H) **GPC:** (THF, PS) M$_n$= 8,800 g/mol and M$_w$ = 15,300 g /mol and **PDI** = 1.73

7.2.26 Synthesis of 1-acetyl-3-hydroimidazoline-2-one(25)
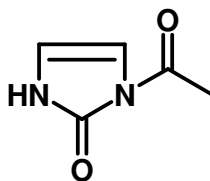
[25]

1,3-dihydroimidazole-2-one(**2**) (5.00 g, 0.059 mol) was heated with 80 ml of acetic anhydride at 95°C for 30 minuets until dissolution was complete. The resulting solution was cooled immediately. Then acetic anhydride was evaporated from the system under vacuum at 10^{-1} mbar and 45°C. After recrystallization from ethyl acetate, 3g (Yield -39%) of the compound were obtained, mp =145°C

¹HNMR (250 MHz, $C_2D_2Cl_2$): δ = 2.7 (s, 1H, -COCH$_3$), 6.39 (t, 1H,-N-CH-), 6.91 (t, 1H,-N-CH=CH-), 6.96 (b, NH-), **¹³C-NMR** (65MHz, $C_2D_2Cl_2$): δ = 24.0 (-CH$_3$-), 108.05, 111.60 (-CH=CH-), 168.61(-CO-), **IR** (KBr, cm^{-1}): 3148, 1704, 1599, 1553, 1369, 1293, 1240, 1197, 1128, 1086, 1039, 979, 879, 759, 701.

7.2.27 Synthesis of poly (1-acetyl-3-hydroimidazoline-2-one)(26)

[26]
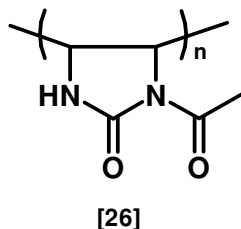
1-Acetyl-3*H*-imidazole-2-one (500mg**,** 0.00396mol) was heated to 160°C under inert atmosphere until it formed a melt. Azo-bis(cyclohexane carbonitrile) (1.5 mg, 6.12 x 10^{-6} mol) in 0.1ml of DMF was introduced into the system under stirring. The mixture was kept under stirring for one and half an hour at the reaction temperature. The viscous melt formed was cooled, diluted with 1 ml of DMF and precipitated from 5ml of methanol water mixture.

Yield (30 mg, 6%) **¹H-NMR** (250 MHz, DMSO- d$_6$): δ = 2.30 (b,-CH3-), 4.0– 4.5 (b,-CH-CH-), 8.14 –8.44 (b,-NH-), **GPC**(DMF, PS): M$_n$ = 62,800 g/mol, M$_w$ = 130,000 g/mol, **PDI** = 2.07 **IR**(KBr,cm^{-1}): 3513(b,-NHstretch), 1750(-CO-of acetyl), 1689(-CO of imidazolidone).

7.2.28 Synthesis of 2-propyl-2-thioimidazoline(27)

[27]
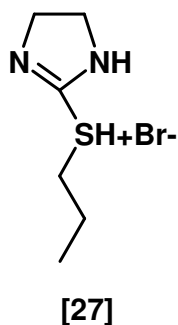
Ethylene thiourea (2g, 0.02 mol) and slight molar excess of the propyl bromide were refluxed in 20 ml of ethanol for 3 hours. Evaporation of the solvent under reduced pressure yielded either the crystalline salt or syrup that crystallized slowly in the cold. The salt was crystallized from alcohol acetone.

^{1}H-NMR (D_2O, 250MHz): δ = 0.98 (3H, t, -CH$_3$), 1.71 (2H, sex, -CH$_2$-), 3.07 (2H; q, -CH$_2$-S-), 3.90 (4H, s, -N-CH$_2$-CH$_2$-N-), **^{13}C-NMR** (D_2O, 65MHz):171.12, 45.52, 33.31, 22.36, 12.56

7.2.29 Synthesis of 1-acetyl-3-ethoxymethylimidazoline-2-one(28)

[28]
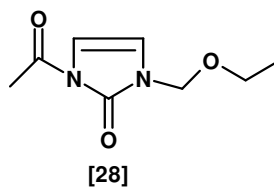
Monoacetyl imidazolinone (500 mg, 0.0039 mol) was dissolved in dry THF(30 ml) followed by addition of sodium hydride 60% dispersion, (0.2g, 0.005mol) under stirring for 45 minuets. Then it was cooled to 0-5°C followed by addition of chloromethyl ethyl ether (0.5 ml, 0.005 mol). The reaction mixture was kept under stirring over night. It was quenched with water. It was extracted with methylene chloride (2 x 25 ml), dried over MgSO$_4$ and filtered. Product was chromatographed with petroleum ether (bp.=. 45 –60 °C) and 20% acetone. Yield = 34%

^{1}HNMR (CDCl$_3$, 250 MHz): δ = 6.95 (d, -CH=CH, 1H), 6.41 (d,-CH = CH,1H), 4.98 (s, -OCH$_2$N, 2H), 3.52 (q ,2H; -CH$_2$-CH$_3$), 2.62 (s,-COCH$_3$, 3H), 1.18 (t, 4H, CH$_2$CH$_3$), **^{13}C NMR** (CDCl$_3$, 65 MHz): δ =168, 151, 113, 107, 64.62, 23.82, 14.82

**7.2.30 Synthesis of poly (1-acetyl-3-ethoxymethylimidazoline-2-one)(29).**

[29]
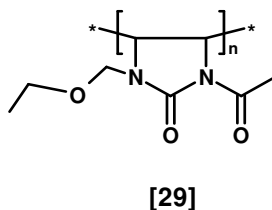
The monomer **28** was polymerized by radical polymerization at 115^0C A low molecular weight polymer was precipitated from water. Yield = 60 %

^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.37-0.88 (m, 3H,-O-CH$_2$-C<u>H$_3$</u>), 2.50-2.32 (m, 3H, -CO-C<u>H$_3$</u>), 3.74-3.24 (m, 2H, -O-C<u>H$_2$</u>-CH$_3$), 4.29-3.83 (m, 2H,-N-C<u>H$_2$</u>-O-), 5.07-4.78 (m, 2H, -NC<u>H</u>-C<u>H</u>N-) **GPC** (THF and PS standard)**:** M$_n$ = 6,000 g/mol, M$_w$ =15,000 g/mol)

7.2.31 Synthesis of poly (1-acetyl-3-ethoxymethylimidazoline-2-one)-co-poly(1-acetyl-3-ethoxymethyl-2-ethoxyimidazoline) tetrafluoroborate(30)
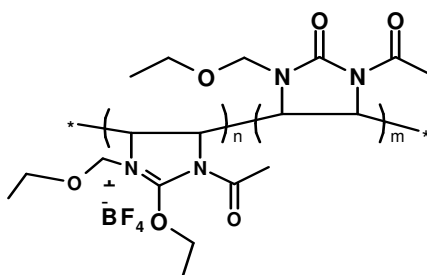
[30]

Polymer **(29)** (300 mg, 0.0035 mol) and tri (ethyloxonium) tetrafluoroborate (0.57ml, 0.004 mol) dissolved in 25ml of dichloromethane were refluxed overnight under argon, for 2 days. The color changed to straw yellow. Solvent was evaporated off under high vacuum at low temperature.

^{13}C-NMR (4mm MAS, 10 KHz MAS, CP-MAS, 3ms contact time): δ = 15, 25, 30, 50, 154, 162, 175 **IR** (KBr, cm^{-1}): 3434, 2925, 1743, 1434, 1383, 1233, 1083, 1037, 755, 610

7.2.32 Synthesis of N-carboxyanhydride derived from M-Lys (Z)-OH(31)
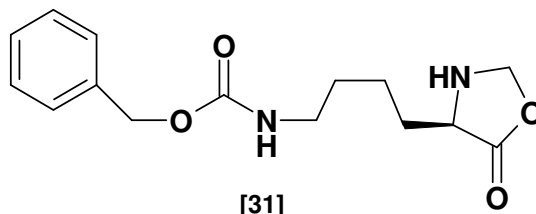
[31]

Ethyl acetate was distilled and kept under molecular seaves. In a three necked flask with reflux condenser, under inert atmosphere, was added M-Lys (Z)-OH (3g) and dry ethyl acetate (100 ml). After heating to reflux temperature, triphosgene (1.05 g) was added at once and the reaction allowed refluxing under argon for 5h. The reaction mixture was not clear and another small quantity of triphosgene (0.1g) was added and the reflux continued for the other 2h. The reaction mixture was not completely clear. It was allowed to cool to room temperature and then cooled in a stopper reaction vessel to $-5°C$. It was transferred to a separatory funnel and washed with water (35ml) chilled to $0°C$. The ethyl acetate layer was then washed with a solution 0.5% $NaHCO_3$ (35 ml) chilled to $0°C$. This wash was neutral. The ethyl acetate layer was treated with anhydrous $MgSO_4$ until no clumping was observed. The solution was gravity filtered and concentrated to about 1/3 rd its original volume on a rotary evaporator. The temperature of the water bath on the evaporator was kept below $30°C$ to minimize side reaction. An equal volume of hexane (30 ml) was added to induce crystallization of N-carboxyanhydride. After chilling to $-5°C$ the N-carboxyanhydride crystals were collected by filtration and dried under inert atmosphere. The N-carboxyanhydride is soluble in ethylacetate and dimethylsulfoxide.

^{1}H-NMR (250 MHz, DMSO-d_6, 300K): δ = 9.0(s,-NH,1H), 7.2 – 7.4 (m, ArH, 5H); 5.0 (s, Ar-CH_2-O-, 2H), 4.4 (t , -CH , 1H), 3.0 (m,-NH-CH_2-,2H), 1.1-1.5 (m,-CH_2-CH_2-,4H); 1.5-1.8 (m, CH-CH_2, 2H); **^{13}C-NMR** (65 MHz, DMSO-d_6, 300K): δ = 171.0, 135.5, 125.4, 63.3, 57.2, 40.0, 30.9, 28.1, 21.9 **Elemental Analysis**: Cal. C 61.63 H 6.90 N 9.58 Found C 59.90 H 7.44 N 9.68

7.2.33 Ring opening polymerisation of Benzyloxycarbonyl protected N-carboxyanhydride derived from M-Lys (Z)-OH initiated with ethylacrylate modified poly (methylene amine)
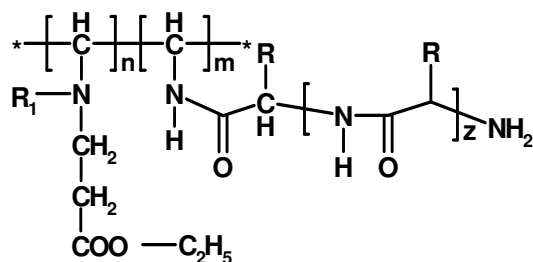

[32]

N-carboxyanhydride derived from M-Lys (Z)-OH (500 mg, 1.71×10^{-3} mol) and modified poly(methylene amine) with ethylacrylate (9 mg) were dissolved in dry DMF (5ml), under inert atmosphere and stirred for four days. After one day the reaction was very viscous and on the second day the solution became more viscous and stirring stopped. After 4 days the polymer was precipitated in distilled water, washed several times and dried under vacuum. Yield was quantitative.

^{1}H-NMR (250 MHz, DMSO - d_6): δ = 1.12 (t, $-CH_3-CH_2-$), 1.42 (b, m), 4.98 (b, s), 7.29 (b, m), **^{13}C-NMR** (DMSO, 65 MHz): 175.2, 155.9, 137.2, 128.1, 127.5, 65.09, 57.2, 39.6, 29.6, and 23.06

Entry	stoichiometry (Initiator: N-carboxyanhydride)	M_n (G/mol)	M_w (G/mol)	M_w/M_n	z
BPMA-S1	1:1	33,600	38,900	1.15	
BPMA-S2	1:2	53,300	65,500	1.22	18

z =Average number of Z-L-lysine repeating units (Calculated from NMR) M_w = Weight average molecular weight, M_n= Number average molecular weight, M_w/M_n = Polydispersity index, GPC measurements were performed with PS as standard and DMF as eluent.

7.2.34 Hydrolysis of polymer poly(methylene amine)-co-ethylacrylate-co-poly(z-L-lysine)(BPMA-S2)
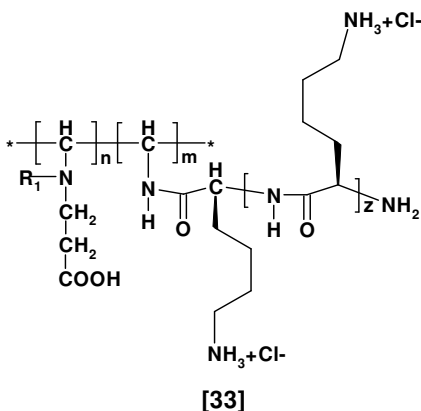
[33]

A four fold molar excess of HBr (33%in acetic acid) was added to the solution of the side chain protected polypeptide in trifluoroacetic acid. The reaction mixture was stirred for 1h at room temperature. The diethyl ether was added, and the precipitated polymer was washed extensively with diethyl ether. After drying in vacuum the deprotected polymers were obtained in quantitative yields.

^{1}H-NMR (D$_2$O, 250 MHz): δ = 1.10 (b, t), 1.43 (b, m), 1.70 (b, m), 3.50 (b, m), 4.28 (b, m), 8.38 **^{13}C NMR** (D$_2$O, 65MHz):173.20, 66.43, 66.57, 53.27, 39.20, 30.48, 26.15, 21.96, and 13.97

7.2.35 Ring opening polymerisation of Benzyloxycarbonyl protected N-carboxyanhydride derived from M-Lys (Z)-OH initiated ethylacrylate modified poly vinylamine.

[34]
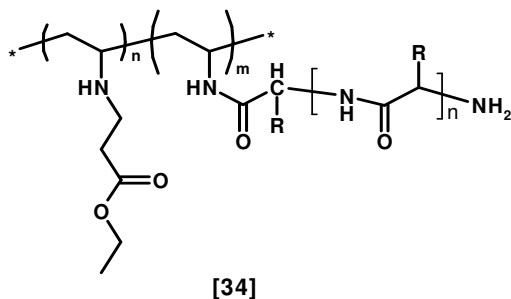
N-carboxyanhydride derived from M-Lys (Z)-OH (500 mg, 1.71×10^{-3} mol) and modified poly (vinylamine) with ethylacrylate (9mg) were dissolved in dry dimethylformamide (5ml), under inert atmosphere and stirred for four days. After one day the reaction was very viscous and in the second day the solution became more viscous and stirring stopped. After 4 days the polymer was precipitated in distilled water, washed several times and dried under vacuum.

PVAmBP-1 ^{1}H NMR (500 MHz, DMF): δ = 1.28-1.10 (t, 3H), 1.68-1.30 (m, 6H), 3.19-3.00 (m, 2H), 5.41- 4.69 (m, 1H), 7.63-6.66(m, 5H). **PVAmBP-2 ^{1}H-NMR** (500 MHz, DMF): δ = 0.91-0.77(m, 3H), 1.71-0.94 (m, 6H), 3.08-2.78 (m, 2H), 5.20-4.72 (m, 2H), 7.67-6.77 (m, 5H)

Elemental Analysis: Found (%) **PVAm BP-1** C 62.96, H 7.28, N 10.48

PVAm BP-2 C 63.32, H 7.47, N 10.55

Entry	Stochiometry (Initiator: N-carboxyanhydride)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	z
PVAm-S1	1:1	45,800	84,200	1.84	38
PVAm-S2	1:2	107,000	311,600	2.91	71

z =Average number of Z-L-lysine repeating units (Calculated from NMR) M_w = Weight average molecular weight, M_n= Number average molecular weight, M_w/M_n = Polydispersity index, GPC Measurements were performed with PS as standard and DMF as eluent.

A novel cationic polyelectrolyte, poly(methylene amine) was synthesized via two major steps viz.1.Synthesis of precursor polymers of poly(methylene amine) 2.Hydrolysis of the precursor polymer, to yield poly(methylene amine)(**8**). The isolated poly(methylene amine) was further modified with electrophiles leading to novel materials.

1. Synthesis of precursor polymers 6 &7

The precursor polymers of poly(methylene amine), poly(1,3-diacetylimidazole-2-one)(**6**) and poly(1,3-dihydroimidazole-2-one)(**7**) were synthesized via radical polymerization of 1,3-diacetylimdazole-2-one(**3**) and 1,3-diformylimidazole-2-one(**4**), respectively. The polymerization of both the monomers were investigated in bulk as well as in solution, in the presence of two different initiators viz t-butylhydroperoxide(70% solution in water) and 1,1`-Azobis(cyclohexanecarbonitrile). Polymerization in bulk yielded high molecular weight polymers in both the cases ($M_w$ = 1,15,000 g/mol with 50% t-butyl hydro peroxide solution and intiator to monomer molar ratio = 0.55 x $10^{-3}$/0.029); $M_w$ = 2,13,000 g/mol with 1,1`-Azobis(cyclohexanecarbonitrile) and initiator to monomer ratio = 0.9643/1000). However, the process involved high reaction isotherm and lower yield due to loss of monomer owing to sublimation. To circumvent the problem of higher reaction isotherm and loss of monomer due to sublimation, the polymerization was carried out in solution.

The solution polymerization of both the monomers **3** and **4** were tried in different solvents. To minimize the chain transfer to solvent the polymerization in solution was tried in high boiling polar aprotic solvents viz. DMF, NMP and THF. Maximum molecular weight of (M_w = 52,300 g/mol) in solution was obtained by polymerizing the monomer **3** in DMF. Nevertheless, the molecular weight obtained by polymerizing the monomer in DMF was much lower than those obtained through bulk polymerization. This unexpected lowering of molecular weight obtained through solution polymerization techniques was attributed to low reactivity of cyclic monomers and higher degree of chain transfer to solvent. Further, attempts to lower the rate of sublimation were done with implementation of an initiator with longer half life i.e. 1,1`-Azobis (cyclohexanecarbonitrile).

The maximum molecular weight of (M_n = 6.5 x 10^4 g/mol and M_w = 2.13 x 10^5 g/mol) GPC, PS and THF as standard) was obtained by polymerizing **3** in presence of 1,1´-Azobis(cyclohexanecarbonitrile) at 125 °C with intiator composition of 0.0964 mol % of monomer. Both the polymers demonstrated similar physical properties. However, the solubility of these polymers varied remarkably. While poly(1,3-diacetylimidazole-2-one) was well soluble in common organic solvents such as THF, chloroform, methylenechloride and DMF, poly(1,3-diformylimidazole-2-one) showed limited solubility in DMF and was insoluble in chloroform and methylene chloride. The poor solubility of poly(1,3-diformylimidazole-2-one)**(6)** was ascribed to tight packing of polymer chains due to presence of relatively small formyl lateral groups in comparison with poly(1,3-diacetylimidazole-2-one). In addition, hydrogen bonding between formyl and carbonyl of imidazolidone ring contributes substantially towards insolubility of the polymer. The rigid polymer backbone makes these polymers thermally very stable. Thermogravimetric analysis of poly(1,3-diacetylimidazole-2-one) displayed only one slump in the curve at 300 °C. The DSC curve did not show any transition within the range of measurement.

2. Hydrolysis of polymers preparation of poly(methylene amine)

The polymers were hydrolyzed under strong reaction conditions to yield poly(methylene amine). The attempt to hydrolyse the polymer under mild reaction condition in ethanol in presence of K_2CO_3 resulted in cleavage of lateral acetyl and formyl groups respectively. The partially hydrolyzed polymer was insoluble as well as infusible. Therefore, to hydrolyze this polymer, strong reaction conditions at elevated temperature were implemented. To maintain high reaction temperature a mixture of ethylene glycol(EG) and water in the ratio of 1:3 by weight was used. NaOH was used to a tune of 40% by weight of total reaction mixture. The temperature of the reaction mixture was kept at 170°C. Increase in reaction temperature led to degradation of the polymer indicated by smell of ammonia. Thus, to compensate with low concentration of base and temperature the duration of the hydrolytic process was prolonged. The use of LiCl facilitated

solubility of partially hydrolyzed polymer and hence allowed lowering of concentration of base and temperature. This eliminated any possibility of degradation of polymer backbone. Thus, the precursor polymers, poly(1,3-diacetylimidazole-2-one)**(6)** and poly (1,3-diformylimidazole-2-one)**(7)** were effectively converted into poly(methylene amine)**(8)** under basic reaction conditions, in presence of base (viz.NaOH or KOH) in a mixture of ethylene glycol(EG) and water to a tune of (1:2 by weight) in the presence of LiCl at elevated temperature. The temperature of the hydrolysis was in the range of 125-170°C and the concentration of the base was kept in the range of 30-40 %. The concentration of precursor polymer could be up to 20% and the concentration of LiCl up to 6%. The entire process of hydrolysis was monitored by IR spectroscopy. The hydrolyzed product was isolated in the form of its hydrochloride from the reaction mixture. It was further dialyzed in cellulose acetate tubing and in VE wasser to get rid of salts. The pure poly(methylene amine) was stored in the form of its hydrochloride. Poly(methylene amine)hydrochloride was converted into poly(methylene amine) by eluting its aqueous solution (4% by its weight) through a small column of anion exchange resin (IRA-400 Cl⁻). The solution of amine water was lyophilized to obtain poly(methylene amine) in 10-15% yield. Both the polymers were characterized by conventional characterization techniques. ^{1}H NMR of poly(methylene amine) hydrochloride showed a broad signals centered at 4.0 ppm.(CH) and in ^{13}C NMR spectrum of poly (methylene amine)hydrochloride(1,4-dioxane as standard) two broad peaks appeared very close to each other centered at 55.9 ppm. The division of a single broad peak was attributed to incomplete protonation of all the amine groups on the polymer backbone even at very low pH. IR spectrum of the polymer displayed characteristic absorption bands at 3415 cm⁻¹, 2932 cm⁻¹, 2500 cm⁻¹, 2000 cm⁻¹, 1615 cm⁻¹. On the other hand, ^{1}H NMR of poly (methylene amine) showed a broad signal at 2.7 ppm (-CH-) and in ^{13}C-NMR spectrum of poly(methylene amine) (1,4-dioxane standard) appeared a broad peak at 51.3 ppm. The shifting of signals was explained in terms of deshielding of protons caused by electronegative ammonium ions. Further, the shifting of signals was monitored with the help of ^{1}H NMR at varying pH.

The shift in the proton signals of poly(methylene amine) at varying pH was followed by ^{1}H NMR of the solution of poly(methylene amine)hydrochloride measured in D_2O. The pH of the solution was adjusted with NaOH. With fall in pH from 12 to 1.5, the signal due to CH proton of the back bone shifted from 3.84 ppm to 2.85 ppm for poly (methylene amine) at pH 12. The molecular weights of the precursor polymer of poly (methylene amine), poly(1,3-diacetylimidazol-2-one)**(6)** and poly(methylene amine)**(8)** were determined by static light scattering and GPC-MALLS. For parent polymer, poly (1,3-diacetylimidazol-2-one) a molecular weight ($M_w = 1.18 \times 10^5$ g/mol) was obtained from GPC in THF and PS as standard. The data was well in agreement with those obtained from GPC-MALLS in THF and PS as standard ($M_w = 2.82 \times 10^5$ g\mol). However, the corresponding hydrolyzed product, poly(methylene amine) showed a molecular weight of $M_w = 92,000$ g/mol in water determined by static light scattering. For another sample of poly(1,3-diacetylimidazol-2-one)**(6)** a molecular weight of ($M_w = 1.52 \times 10^5$ g/mol) was obtained by GPC in THF and PS as standard. Conversely, the corresponding poly(methylene amine) demonstrated a molecular weight of 21,300 g/mol determined by static light scattering in water.

3. Solution properties of poly(methylene amine) and its hydrochloride

The solution properties of the polymers, poly(methylene amine) and poly(methylene amine)hydrochloride were investigated by viscosimetry and light scattering. The reduced viscosity of poly(methylene amine) hydrochloride as a function of polymer concentration demonstrated a behavior typical of cationic polyelectrolytes. With decrease in concentration the reduced viscosity of poly(methylene amine)hydrochloride increased gradually and increasing sharply below the concentration 5g/L. This behavior was explained in terms of chain expansion due to electrostatic force of repulsion operating between closely spaced positively charged ammonium ions.

Polyelectrolyte behavior of the polymer in water was investigated by static and dynamic light scattering. Dynamic light scattering studies (DLS) of poly(methylene amine) was

investigated at different concentrations of polymer in water. The plot of decay time distribution at various concentrations in the absence of salt demonstrated two relaxation processes that resembled bimodal distribution. These modes were assigned as fast and slow modes respectively. The polyelectrolyte behavior was further investigated in presence of added salt (NaCl). On addition of salt, the slow mode started disappearing gradually. At a salt concentration of 1M, poly(methylene amine) solution of 1g/L, the slow mode disappeared completely. This was ascribed to collapse of counter ions thereby nullifying polyelctrolyte effect. Further, diffusion of the polymer in aqueous solution was studied at varying pH. The plot of diffusion coefficient as a function of pH demonstrated an interesting trajectory. The diffusion coefficient dropped off gradually along both sides of neutral regime. The decrease tendency of the diffusion coefficient along both sides of neutral region of pH was explained by shielding effect of counter ions.

3.Modification of poly(methylene amine)

The degree of substitution of poly (methylene amine) was investigated by reaction of the polymer with electrophiles. The extent of substitution was determined from elemental analysis. In case of methylation with MeI, 1:1 and 1:10 molar ratio of polymer to reactant gave 32% substitution and 40% substitution respectively. On the contrary, poly vinylamine under similar reaction conditions yielded 34% substitution at 1:1 reactant to polymer ratio and 56% conversion at 1:10 polymer to reactant ratio. The low degree of substitution on poly(methylene amine) in comparison to polyvinylamine was explained in terms of steric hindrance. In addition, attempts were made to cyclizize poly (methylene amine) to poly(4,5-imidazole); a promising material for proton conducting membrane. However, among all the attempts made transformation of poly(1-acetyl-3-ethoxymethyl-imidazol-2-one) to its imidazoline analogue remained partially successful. The resulting material showed a conversion of 30% and was an insoluble material. An extension of application of poly(methylene amine) was investigated through its use as an initiator for ring opening polymerization of benzyloxy carbonyl protected N-carboxyanhydride of z-L-lysine. The resulting hybrid polymer demonstrated brush like architecture. The solid

state morphologies of these brush polymers were investigated by 2D-WAXS (Two dimensional wide angle X-ray scattering) and AFM. X-ray diffractograms revealed, stiff hexagonal morphology of peptide segments without formation of alpha helices. Further, investigation on these polymers after hydrolysis resulted in a polyampholyte brush. The solution properties of these brush ampholytes demonstrated IEP (iso electric point).