# Studies on Synthesis, Characterization and Applications of Microencapsulation Process via Interfacial Polymerization

A Thesis submitted to Gujarat Technological University

for the Award of

Doctor of Philosophy

in

Chemical Engineering

by

Christian Ujvala Parsottamdas
Enrollment No. 129990905004

under supervision of

Dr. Shrikant J. Wagh


**GUJARAT TECHNOLOGICAL UNIVERSITY**

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June– 2021

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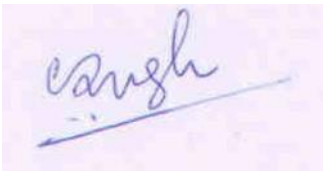

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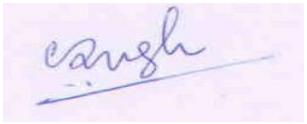

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*Dedicated to*

# My Parents

# ABSTRACT

Microencapsulation is the technology of packaging of micronized solid particles, liquid droplets, or gas bubbles in microcapsules by applying thin film of coating or shell material. Resulting microcapsules are particles with diameters between 1µm to 1000µm.They have a core/shell structure which contains polymeric material as a wall (shell) enclosing the core. Synthesis of microcapsules is considered as microencapsulation process which can be categorized into two groups: (i) chemical processes like In-situ polymerization, Interfacial polycondensation, Interfacial cross-linking etc. and (ii) physical processes like spray–drying, pan coating, centrifugal extrusion, air-suspension coating etc. In this work, the generic Interfacial polymerization process is considered as Interfacial polycondensation (IP) that is step-growth polymerization reactions taking place at the interface.

Interfacial polycondensation (IP), through several step-growth reactions, opens a wide window for synthesis of microcapsules (and membranes also) at ambient conditions without stringent conditions of monomer purity. IP is one of the important methods for synthesis of microcapsules. It offers advantages over other methods because it involves a chemical reaction between monomers dissolved in two different immiscible solvents. Variables such as nature of solvent, reactivity of monomers, types and concentration of surfactant, rate of chemical reaction, reaction conditions etc. play a vital role in deciding the characteristics of microcapsules produced. These give a great leverage over achieving the properties of microcapsules for certain pre decided applications, which may include encapsulation of pharmaceuticals, food additives, agrochemicals, solvents, adhesives, immobilization of living cells etc.

The research work presented includes study of various aspects of microencapsulation via IP to form polymer shell, and release behaviour of certain encapsulated agrochemicals as active ingredients through polymer shell. The experimentation includes systematic study on synthesis of polyurea microcapsules under specific preparative conditions controlling the kinetic and mass transfer regimes of reaction to produce polyurea microcapsules as a tailor made product. Synthesis experimentation is necessarily followed by characterization of the product formed. Various analytical tools like Fourier Transform Infrared (FTIR) Spectrophotometer, Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM), and X-ray Diffractometer XRD) are used to characterize polymeric shell of microcapsules.

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**Christian Ujvala P.**

**Date: 22-06-2021** **Place: Ahmedabad**

# Table of Contents

# List of Abbreviations

| | |
|---|---|
| IP | Interfacial Polycondensation |
| O/W | Oil-in-Water |
| W/O | Water-in-Oil |
| HMDA | Hexamethylene Diamine |
| HMDI | Hexamethylene Diisocyanate |
| PVA | Polyvinyl Alcohol |
| pH | Potential of Hydrogen |
| $T_g$ | Glass transition temperature |
| $T_{scp}$ | Cloud point temperatuure |
| PU | Polyurea |
| FTIR | Fourier Transforms Infrared Spectroscopy |
| DSC | Differential Scanning Calorimetry |
| TGA | Thermo Gravimetric Analysis |
| XRD | X-Ray Diffraction |
| PSD | Particle Size Distribution |
| SEM | Scanning Electron Microscopy |
| FE-SEM | Field-Emission Scanning Electron Microscopy |
| UV–Vis | Ultraviolet–Visible |
| EE | Encapsulation Efficiency |

# List of Figures

# List of Tables

# CHAPTER 1

# INTRODUCTION

## 1. MICROENCAPSULATION

### 1.1 Introduction to Microencapsulation

Microencapsulation is defined as the process of surrounding or enveloping one material or component within another material on a very small scale, capsules ranging in size from less than one micron to one millimetre.

Microencapsulation may be achieved by a myriad of techniques, with several purposes in mind. Substances may be microencapsulated with the intention that the core material is confined within capsule walls for a specific period of time. Alternatively, core materials may be encapsulated so that the core material will be released either gradually through the capsule walls, known as controlled release or diffusion, or when external conditions trigger the capsule walls to rupture, melt, or dissolve. The encapsulated substance is known as the core material, the active ingredient or agent, the fill, the payload, the nucleus, or the internal phase. The coating, membrane, shell, or wall material that surrounds the core is known as the encapsulating or wall material.

Another description of microencapsulation is the coating of small solid particles, liquid droplets, or gas bubbles with a thin film of coating or shell material, sealed capsules that can release their contents at controlled rates under specific conditions (Desai et al., 2005).

Microencapsulation technology provides a strategy for enhancing retention of sensitive and expensive active ingredient (AI) through protection from adverse conditions and allowing delivery to the target site at the designed time. Most researchers use the word microcapsule to designate tiny particles with diameters ranging from 1 to 1000 micrometres. (Thies et al., 2003).

Microencapsulation may be used to enhance a physical barrier between the core compound and the other components of the product (Gharsallaoui et al., 2003). More especially, in the food technology field, microencapsulation is a technique by which liquid droplets, solid particles or gas compounds are entrapped into thin films of a food-grade microencapsulating agent.

The core may be composed of just one or of several ingredients and the wall may be single or double-layered. The retention of these cores is governed by their chemical functionality, solubility, polarity and volatility (Zuidam et al., 2010).

Furthermore, a full understanding of the microencapsulation process and the potential contribution those microcapsules rests on knowledge of mass transport phenomena, properties of coating materials along with an understanding of processes by which small particles are produced. The shell of a microcapsule must control the diffusion of material either from a microcapsule or into a microcapsule since the primary purpose of microencapsulation is to control, in some manner, mass transport behaviour (Desai et. al., 2005 and Thies et al., 2003).

Microencapsulation is the method of enclosing the fine particles of one substance with the other substance to give small capsules called microcapsules. The microcapsules are spherical in shape and are covered by a uniform coating known as wall or shell. The material which is to be enclosed is called core material and the material which covers or surrounds the core material is called wall material or shell (Mali et al., 2013).

***Important characteristics of wall material***

1) Ability to seal and hold the active material or core material.
2) Non-reactivity of the coating material with the wall material.
3) Provide maximum protection to the coating material.
4) The wall material must be economical and it must be of the desired grade.

***Reasons for encapsulation***

1) Reduces the evaporation or transfer of the core material to the outside environment.
2) Enhances the overall quality of encapsulated products.
3) Superior handling of the active agent.
4) Provides the incorporation of vitamins and minerals.
5) Improved stability in the final product and during processing.
6) Control release of the active components.
7) Masks the aroma, flavour, and colour of some ingredient.

### 1.2 Processes for Microencapsulation

Microencapsulation processes can be classified as follows (Bansode et al., 2003).

#### 1.2.1. Chemical processes

i) Interfacial polymerization

ii) In situ polymerization

#### 1.2.2. Physico-chemical processes

i) Coacervation - phase separation

ii) Emulsion method

iii) Suspension method

iv) Pickering method

v) Micro-fluidic method

#### 1.2.3. Mechanical processes

i) Air suspension or fluidized bed coating

ii) Spray drying

iii) Spray congealing

Microencapsulation processes are usually categorized into two groupings: chemical processes and mechanical or physical processes. These labels can, however, be somewhat misleading, as some processes classified as mechanical might involve or even rely upon a chemical reaction, and some chemical techniques rely solely on physical events. A clearer indication as to which category an encapsulation method belongs is whether or not the capsules are produced in a tank or reactor containing liquid, as in chemical processes, as opposed to mechanical or physical processes, which employ a gas phase as part of the encapsulation and rely chiefly on commercially available devices and equipment to generate microcapsules.

#### 1.2.1 Chemical Processes

Capsules for carbonless paper and many other applications are produced by a chemical technique called complex coacervation. This method of encapsulation takes advantages of the reaction of aqueous solutions of cationic and anionic polymers such as gelatine and gum arabic. Polymers form a concentrated phase called the complex coacervate. The coacervate exists in equilibrium with a dilute supernatant phase. As water-immiscible core material is introduced into the system, thin films of the polymer coacervate coat the dispersed droplets of the core material. The thin films are then solidified to make the capsules harvestable.

### *1.2.1.1 Interfacial polymerization (IP)*

It is a chemical method of microencapsulation. This technique is characterized by wall formation via the rapid polymerization of monomers at the surface of the droplets or particles of the dispersed core material. A multifunctional monomer is dissolved in the core material, and this solution is dispersed in an aqueous phase. A reactant to the monomer is added to the aqueous phase, and polymerization quickly occurs at the surfaces of the core droplets, forming the capsule walls. IP can be used to prepare bigger microcapsules, but most commercial IP processes produce smaller capsules in the 20-30 micron diameter range for herbicides and pesticide uses, or even smaller 3-6 micron diameter range for carbonless paper ink. Polymer-polymer incompatibility, also called phase separation, is generally grouped with other chemical encapsulation techniques, although usually no actual chemical reaction is involved in the process. This method utilizes two polymers that are soluble in a common solvent, yet do not mix with one another in the solution. The polymers form two separate phases, one rich in the polymer intended to form the capsule walls, the other rich in the incompatible polymer meant to induce the separation of the two phases. The second polymer is not intended to be part of the finished microcapsule wall, although some may be caught inside the capsule shell and remain as an impurity. The process of interfacial polymerization is shown schematically in Fig. 1.1

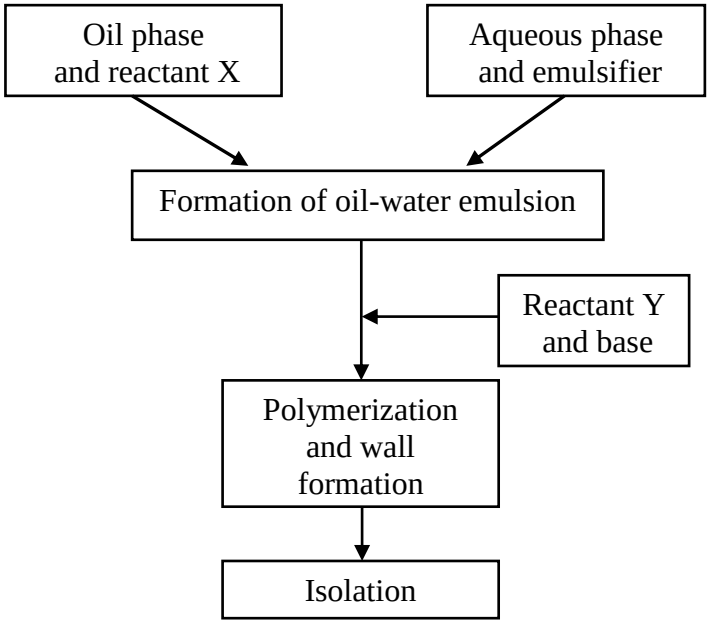



**Figure 1.1** Schematic diagram of interfacial polymerization (IP)

Ref. Encyclopedia of Polymer Science & Technology, vol.14, John Wiley & Sons (2005)

The interfacial polymerization has several advantages over other polymerization technique which are given below:

- This process is simple and requires ordinary equipment.
- Unlike bulk condensation polymerization, high molecular weights are obtained rapidly in interfacial polymerization because the monomer meets the growing polymer chain than the opposing monomer that leads to termination of the polymerization.
- Polymers which are unstable at the high temperatures can be easily synthesized by this method as it requires low temperature for synthesis.
- This polymerization process is effective in controlling the structure and composition of the resulting polymer chain as well as the copolymer, without the need for a conventional catalyst.
- It is a direct method of forming polymer solutions, dispersions, polymer coatings for encapsulates, fibrous particulates and films.

#### *1.2.1.2 In situ polymerization*

It is a chemical encapsulation technique very similar to interfacial polymerization. The absence of reactants in the core material is a distinctive feature of in situ polymerization. Unlike IP, where polymerization occurs on both sides of the contact between the continuous phase and the core material, all polymerization happens in the continuous phase. Urea formaldehyde (UF) and melamine formaldehyde (MF) are extensively used polymeric shell for microencapsulation by this method. (Dallas et. al, 2007)

In *in-situ* polymerization, the nanomaterials are first dispersed in liquid monomer by appropriate inorganic or organic initiators, by heat or radiation, or catalyst fixed: through cationic exchange inside the interlayer before swelling step by the monomer. This is much effective and easy technique to break down the particle agglomerates using a high shear device and also possible to achieve more uniform mixing of nanomaterials in the monomer, because of low viscosity of the monomer or prepolymer compared to polymer as in other techniques. Also, the low viscosity and high diffusivity result in a high rate of monomer or pre-polymer diffusion into the nanomaterials. This method is capable of producing well-exfoliated nanocomposites and has been applied to a wide range of polymer systems. The driving force of this technique is related to the secondary interactions of the monomers. In the swelling state due to the high surface energy, the nanomaterials attract the monomer molecules so that they diffuse between the layers or

tube structure of nanomaterials. After reaching the equilibrium the diffusion of the monomer is stopped and the nanomaterials are swelled. On starting of the polymerization, the polymer chains start to grow within the nanomaterials and ultimately result in the exfoliated structure (McNally et al, 2003). In-situ polymerization was the first reported method to prepare the polymer/clay nanocomposites (Vaia e al., 1996). A schematic diagram for the preparation of nanocomposites through in-situ polymerization technique is shown in Scheme Figure 2.

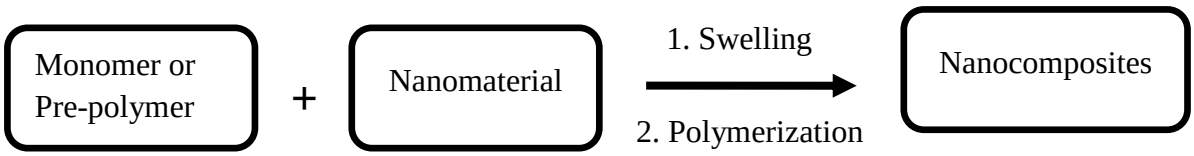



**Figure 1.2** Schematic diagram of *in-situ* polymerization technique

### 1.2.2 Physico-chemical processes

#### *1.2.2.1 Coacervation - phase separation*

The earliest known appearance of the word, phrase, was in 1812. An appropriate definition of the word for this chapter is 'a homogeneous, physically distinct, and mechanically separable portion of matter that is present in a non-homogeneous, physical-chemical system and that may be a single compound or a mixture, Phase separation is a broad term that may be applied to various processes such as the formation of a solid or liquid phase from a solution. Examples are the crystallization of salt or the precipitation of a polymer as the result of the removal of some solvent from the solution. The new phase is physically distinct and has different properties compared with its solution and can be separated by mechanical means.

The word coacervate was first noted in 1623. This word may be defined in the present context as 'an aggregate of colloidal droplets (as of two hydrophilic sols or a sol and ions of opposite charge) held together by electrostatic attractive forces. Coacervation is a term used to describe the formation of a coacervate related to phase separation and has been applied to the separation of a colloid from a solution into a phase rich in the colloid called the coacervate and the remaining phase which is poor in the colloid. The coacervate has certain properties that distinguish it from the original solution. The coacervate will form a separate liquid layer, but with stirring may form droplets suspended in the polymer-poor phase; furthermore, it is usually more viscous, more concentrated and often has the

property of binding or adsorbing onto, or engulfing a solid or liquid which may be added into the system.

The National Cash Register (NCR) Corporation and the patents of B.K. Green et al. are commonly credited with microencapsulation via coacervation phase separation. There are five steps in the procedure. (O'Donnell P B and McGinity (1997), Nairn et al., 1995).

A general description of coacervation-phase separation is outlined below.

**Step 1**

In order to produce a suitable product such as microcapsules or microspheres by this method it is necessary to select the polymer or macromolecule which will provide the appropriate coating or matrix characteristics desired in the final product, such as an enteric coating or a product to control the release of the drug. The polymer is dissolved in a suitable solvent so that it is usually fully solvated.

**Step 2**

If it is desired to encapsulate a core such as a drug or chemical, it may be added to the continually stirred polymer solution to form, preferably, a dispersion of the core in the polymer solution. The solvent for the polymer is selected, preferably so that it does not dissolve the core.

**Step 3**

One of many processes, such as the addition of a non-solvent for the polymer, is used to bring about the coacervation-phase separation of the polymer. This process promotes the formation of a new phase 'the coacervate' in a coacervation process. With stirring; coacervate droplets form which encapsulates the core to form microcapsules. It should be noted that most of the solvent used to dissolve the polymer is now the polymer-poor phase and forms the suspending medium in which the core and the coacervate droplets are stirred; this liquid is sometimes called the manufacturing phase. In the case of solvent removal, for example, by evaporation, the polymer phase is enriched in polymer and it will eventually deposit on the core.

**Step 4**

The polymer-rich droplets containing the drug are further desolvated by a process similar to that noted above, or a different process. The polymer may also be hardened by some methods such as thermal desolvation or crosslinking to form a product, microcapsules for example, which preferably does not aggregate.

**Step 5**

The microcapsules are then collected and may be rinsed with an appropriate liquid to remove unwanted solvents and excipients.

***1.2.2.2 Emulsion method:***

An emulsion may be defined as a biphasic system consisting of two immiscible liquids, one of which (the dispersed phase) is finely and uniformly dispersed as globules throughout the second phase (the continuous phase).

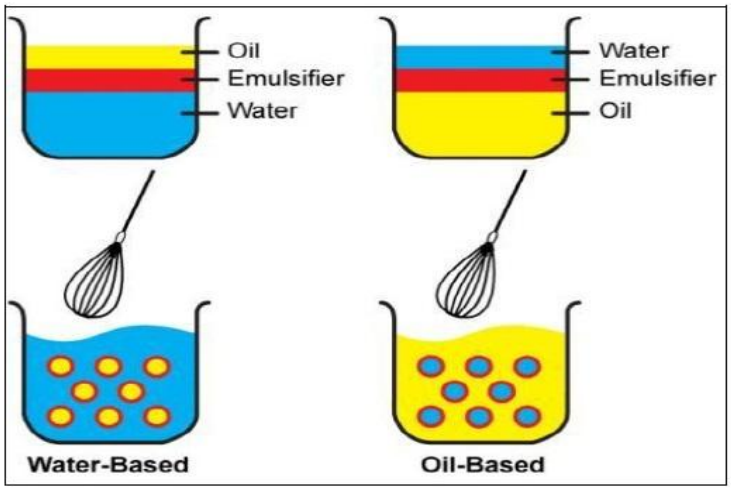



**Figure 1.3** Emulsion method

Since emulsions are a thermodynamically unstable system, a third agent, the emulsifier is added to stabilize the system. Emulsifier stabilizes the system by forming a thin film around the globules of the dispersed phase. Either the dispersed phase or the continuous phase may vary in consistency from that of a mobile liquid to semisolid (Alfred et al., 1993). Thus, pharmaceutical emulsions range from lotions (low viscosity) to creams (high viscosity). The particle size of the dispersed phase commonly ranges from 0.1 to 100 µm (Agarwal S P and Agarwal R K 2007). Types of emulsion Oil in water emulsion Pharmaceutical emulsions usually consist of mixtures of the aqueous phase with various oils and waxes.

**Oil in water emulsion:** If the oil droplets are dispersed throughout the aqueous phase, the emulsion is termed oil-in-water (O/W). Fats or oils for oral administration, either as medicaments in their own right or as vehicles for oil-soluble drugs, are always formulated as oil in water (O/W) emulsions. They are non-greasy and are easily removable from the skin surface and they are used externally to provide a cooling effect and internally to also

mask the bitter taste of the oil. Water-soluble drugs are more quickly released from O/W emulsion. O/W emulsion gives a positive conductivity test as water; the external phase is a good conductor of electricity.

**Water in oil emulsion:** A system in which the water is dispersed as globules in the oil continuous phase is termed water-in-oil emulsion (W/O). Water-in-oil emulsions will have an occlusive effect by hydrating the stratum corneum and inhibiting evaporation of echini secretions. It has an effect on the absorption of drugs from W/O emulsions. W/O emulsion is also useful for cleansing the skin of oil-soluble dirt, although its greasy texture is not always cosmetically acceptable. They are greasy and not water washable and are used externally to prevent evaporation of the moisture from the surface of skin e.g. cold cream. Oil-soluble drugs are more quickly released from W/O emulsion. They are preferred for formulation meant for external use like cream W/O emulsion is not given a positive conductivity test, because oil is the external phase which is a poor conductor of electricity (Aulton 1996).

### *1.2.2.3 Suspension Method:*

This procedure includes scattering of polymeric material contains core and dissolved in it and this combination will added in an organic solvent (suspension/ dispersion medium) in the form of little beads. The suspension medium contains a reasonable amount of stabilizer to provide stability to droplet/microcapsules.

These droplets/ beads are hardened by covalent crosslinking. The crosslinking handle is finished either thermally (at >500 °C) or by the use of a crosslinking agent (formaldehyde, terephthaloyl chloride, etc.). Suspension crosslinking could be a flexible strategy and can be received for microencapsulation of dissolvable, insoluble, fluid or strong materials, and for the generation of both smaller scale and nanocapsules.

### *1.2.2.4 Pickering Method:*

This method is widely applied to form polymer-inorganic hybrid shell based microcapsules. Pickering emulsion or suspension employed in this method is stabilized by adsorbed solid particles than regular emulsifier. These solid particles good protection against coalescence and thus induced a better stability compare to traditional surfactants.

Core material is protected by a hybrid layer which is formed on droplet surface, making the Pickering droplet to be a microcapsule. The structural characteristic of Pickering emulsion makes it a perfect template for microcapsule with polymer-inorganic hybrid shell.

#### *1.2.2.5 Microfluidic Method:*

In microfluidic methods, where reagents are flowed through micrometre-sized channels and mixed at a junction are, by contrast, capable of extremely precise control over both droplet size and dispersity. At the point of mixing, a high shear force is generated between the two immiscible fluids, resulting in droplet formation. The shear force can be adjusted by altering the relative flow rates of the two input streams, which, along with channel size, controls the size of the resultant droplet. Thus, it is possible to continuously produce monodisperse emulsions of a desired size. Examples of such droplet production methods have been used in the synthesis of multifunctional magneto responsive microcapsules, core-shell organ silicon capsules, and biopolymer hydrogels.

### 1.2.3 Mechanical processes

#### 1.2.3.1 *Fluid bed coating:*

It is a mechanical encapsulation method, restricted to the Solid core materials, including liquids absorbed into porous solids, is encapsulated. Pharmaceuticals are commonly encapsulated using this method. The encapsulated solid particles are suspended in material for liquid coatings. The capsules are then relocated to a location where the shells of the capsules are solidified using cooling or solvent vaporisation. The procedure of suspending, spraying, and cooling the capsule walls is repeated until the desired thickness is achieved. When the spray nozzle is at the bottom of the fluidized bed of particles, this is known as the Wurster process. The Wurster process and fluidized bed coating are also versions of the pan coating technology.

In pan coating, solid particles are mixed with a dry coating material and the temperature is raised so that the coating material melts and encloses the core particles, and then is solidified by cooling; or, the coating material can be gradually applied to core particles tumbling in a vessel rather than being wholly mixed with the core particles from the start of encapsulation. Centrifugal extrusion processes generally produce capsules of a larger size, from 250 microns up to a few millimetres in diameter. The core and the shell

materials, which should be immiscible with one another, are pushed through a spinning two-fluid nozzle. This movement forms an unbroken rope which naturally splits into round droplets directly after clearing the nozzle. The continuous walls of these droplets are solidified either by cooling or by a gelling bath, depending on the composition and properties of the coating material.

Another mechanical encapsulation process is rotational suspension separation or the spinning disc method is used. The internal phase is dispersed in the liquid wall material before being advanced into a turning disc. Droplets of pure shell material, as well as discrete particles of core material contained in a shell material skin, are ejected off the rim of the disc. The microcapsules are collected separately from the shell material particles after they have solidified by cooling. After having been solidified by cooling, the microcapsules are collected separately from the particles of shell material.

The particles of material will be supported by the drag forces and the bed is said to be "fluidized". The fluidized beds show the following liquid or fluid-like properties (Lachman et al., 1991).

- Lighter objects float on top of the bed
- The surface stays horizontal even in tilted beds,
- The solids can flow through an opening in the vessel just like a liquid,
- The beds have a “static” pressure head due to gravity.
- Levels between two similar fluidized beds equalize their static pressure heads.
- It has a zero angle of repose.
- Assumes the shape of the vessel that contains it.

A gas-fluidized bed may have the appearance of a boiling liquid. It has bubbles, which rise and appear to burst. The bubbles result in vigorous mixing and a generally horizontal free surface. The motion of the bed varies with the fluid flow rate. At high velocities, particles may become entrained and transported by the fluid.

### *1.2.3.2 Spray drying:*

It is a mechanical microencapsulation method developed in the 1930s. The core material, usually an oil or active ingredient that is immiscible with water, is dispersed into a concentrated solution of wall material until the desired size of oil droplets is achieved. Pumping the slurry through a rotating disc into the heated chamber of a spray drier

atomizes the emulsion into a spray of droplets. The water element of the emulsion is evaporated at this point, leaving dried capsules of various shapes with scattered drops of oil. The capsules are collected through continuous discharge from the spray drying chamber. This method can also be used to dry small microencapsulated materials from the aqueous slurry that are produced by chemical methods.

Among the preparation methods of microparticles, spray drying is extensively used in pharmaceutical, ceramic, polymer, chemical industries, biochemical fields, and in the food industry due to the potential for the large scale encapsulation of fragile drugs, use of mild conditions, large availability of types of equipment and easiness of industrialization to produce raw drug or excipients or as a microencapsulation process. Spray drying is a well-established technique that has been used for over a century but it remains an active field of innovation, driven by the ever-increasing demand for more sophisticated particles. In the pharmaceutical industry spray drying is used to manufacture particles that form the basis for dry dosage forms for parenteral, nasal, or pulmonary delivery, and are administered as suspensions, powders, or aerosols. Spray drying is an attractive microencapsulation method for oral, pulmonary and topical drug delivery. Unlike solvent-based microencapsulation methods, spray drying offers several advantages. It is also a mild ‘‘one-step’’ continuous processing operation to move from a liquid feed into a powder product that does not involve secondary drying of the produced particles. This method is highly reproducible and relatively easy to scale up (K. Masters, 1976). The spray drying process consists of four basic stages: the atomization of the liquid, mixing of the liquid with the drying gas, evaporation of the liquid, and separation of the dried particles from the gas (Sansone et. al., 2011). The atomization produces a fine spray from the feed and is a key factor in achieving economic production of top quality products, by creating optimum conditions for evaporation (Rizi et. al., 2011). One of the most important characteristics of spray-drying is that it can be applied to both heat resistant and heat sensitive, as well as water-soluble and water-insoluble, drugs mainly due to rapid solvent evaporation. This is important in the development of pharmaceutical carriers specifically designed for the delivery of hydrophobic drugs, which represents one of the major challenges in the field of drug delivery (Paudel et. al., 2013). Spray drying method generally yield the microparticles of narrow size distribution and characterized by high encapsulation efficiency (Rattes et. al., 2007). Spray drying technique has inconveniences related to processing variables that

must be well controlled to avoid difficulties such as low yields, sticking, or high moisture content. These are often encountered with laboratory scale spray dryers. The optimization of the spray drying process involves the evaluation of parameters concerning both spray-dryer and feed formulation. Spray drying is a complicated process. Understanding the interplay between process and formulation parameters is crucial for the reproducible production of high-quality material. To obtain good microencapsulation efficiency, optimal spray-drying conditions must be used. The main factors in spray drying that must be optimized are feed flow rate, feed temperature, air inlet, and outlet temperature, the concentration of solids in a solution, drying and atomization gas type and flow rate, and types of atomization nozzles. Spray drying method has already been used to prepare microparticles with polyesters, polymethacrylates, cellulose derivatives and biopolymers containing both hydrophilic and lipophilic drugs and macromolecules. Several reports in the literature are based on the concepts of spray drying microencapsulation, including consideration on the formulation materials and processing parameters effects (Stulzer et. al., 2009).

#### *1.2.3.3 Spray - congealing*

Spray congealing is a hybrid technology between spray drying and hot-melt extrusion, accordingly sharing the advantages and disadvantages of both technologies. Spray drying consists in feeding a liquid stream (solution, suspension or emulsion) into a drying chamber where it is continuously divided into very fine droplets by a process known as atomization. A hot gas enters the chamber and drying of the droplets takes place. In summary, the core substance is dispersed in a solution of coating material, which is then atomized and the solvent dried-off using heated gas in a drying chamber. Both spray drying and spray congealing have the main advantage of being rapid and single-step operations, suitable for batch or continuous production of large quantities of product. Spray drying is suitable for both thermolabile and thermostable materials and enables the production of uniform size particles. The main advantage of spray congealing when compared to spray drying is that particles are prepared without the use of an aqueous phase or organic solvents. This is an environmentally friendly process, with associated economic benefit, that is particularly attractive for processing moisture-sensitive drugs. High throughputs are achievable and hence this technology is less time and energy consuming than spray drying. Microspheres are typically ready-to-use without further need of post-processing (e.g. secondary drying, granulation, milling, and pelletization).

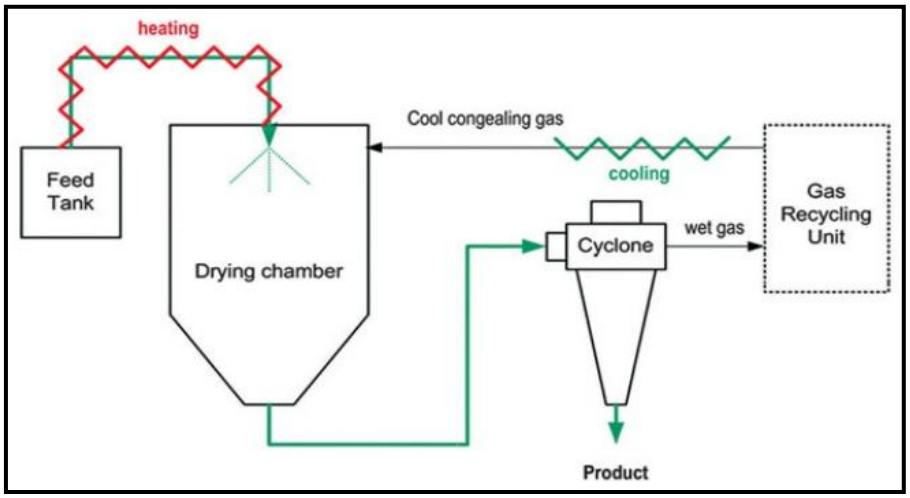



**Figure 1.4** Spray drying and congealing

(Resource: Spray congealing: applications in the Pharmaceutical Industry Hovione, R&D, Drug Product Development Group, Sete Casas, 2674, 506 Loures, Portugal)

The increasing demand for new formulations as part of drug life cycle management or to address New Chemical Entities challenges is boosting the use of spray congealing, which can be described as a combination of spray drying and hot-melt extrusion techniques. The transition of a melt from a soft or fluid state to a rigid or solid-state by cooling is called congealing.

Hence, the spray congealing process can be described by four events:

i) Atomization of the melt into droplets,

ii) Contact of the droplets with the cold congealing gas,

iii) Solidification of the droplets into particles and

iv) Separation of the particles from the congealing gas.

The platform is gaining attention driven by the generation of high-performance materials and short processing times. Compared to other "particle engineering" technologies like spray drying, process times are often shorter because solvents are not used and post-processing is typically not required. Spray drying typically produces hollow, low-density particles with irregular geometry, whereas spray congealing, with its lack of evaporative solvent effects, can produce spherical and dense microparticles suitable for tableting, capsule filling, or injection. With appropriate polymer selection, these dense microspheres can provide for diffusion-controlled or erosion-controlled drug release. Drug particles are typically dissolved, suspended or entrapped in a molten matrix. The matrix can be of hydrophilic or hydrophobic low melting point carriers, and the resultant slurry is pumped

into the spray congealing unit. The selection of a suitable carrier can mask the taste of bitter drugs or be used to modify their dissolution behaviour. The operating conditions may also impact the properties of the final product. There have been several works reported in the literature where spray congealing was assessed. Savolainen et al., (2002) prepared controlled-release tablets of a poorly soluble drug where spray congealing was used to formulate the drug and excipients into a solid dispersion which was then compressed. Changes in the physical properties of the drug such as particle size and crystallinity enabled the change of the drug release rate. Passerini et al., (2006) evaluated the suitability of spray congealing as a technique for enhancing the dissolution rate of a low water-soluble drug. Microparticles with different drug loadings were prepared with success and a higher drug dissolution rate was observed for all the microparticles when compared to the dissolution rate of the pure active ingredient and without changes of its solid-state. Moreover, this study also contemplated the examination of the microparticles shape and surface characteristics, and microparticles with a drug load higher than 10% revealed small acicular structures on their surface, suggesting that an efficient drug coating was not completely achieved for higher drug contents. Maschke et al., (2007) developed a spray congealing process for the preparation of insulin-loaded microparticles, where the impact of operating conditions, namely atomization pressure and spraying temperature, on particle size and process yield was studied. Spray congealing was proved to be an excellent platform to produce protein-loaded microparticles, taking full advantage of lipids as an alternative material for the controlled release of proteins. The choice of the appropriate matrix is a point of paramount importance in the control of the drug release profile since it impacts both the erosion rate and hydrophobicity. Usually, materials with a low HLB (Hydrophilic-Lipophilic Balance) value, i.e., with lipophilic characteristics, are the preferred choice for controlled release purposes. Passerini et al., (2003) showed that through the appropriate selection of the type and amount of carriers, microparticles having a spherical shape, good encapsulation efficiency, and a zero-order release for 8 hours in a pH 1.2 buffered solution, can be obtained without modifying the solid-state properties of the drug. Time for solidification is dependent on: (1) Particle velocity (2) Particle size (3) The specific heat capacity of the material (4) Temperature and flow rate of the cooling gas.

## 1.3 APPLICATION OF MICROENCAPSULATION

There are almost limitless applications for microencapsulated material. As shown in Fig. 1.5 microencapsulated materials are utilized in agriculture, pharmaceuticals, foods, cosmetics and fragrances, textiles, paper, paints, coatings and adhesives, printing applications, and many other industries.

Historically, carbonless copy paper was the first marketable product to employ microcapsules. A coating of microencapsulated colourless ink is applied to the top sheet of paper, and a developer is applied to the subsequent sheet. When pressure is applied by writing, the capsules break and the ink reacts with the developer to produce the dark colour of the copy.

Today's textile industry makes use of microencapsulated materials to enhance the properties of finished goods. One application increasingly utilized is the incorporation of microencapsulated phase change materials (PCMs). Phase change materials absorb and release heat in response to changes in environmental temperatures.

When temperatures rise, the phase change material melts, absorbing excess heat, and feels cool. Conversely, as temperatures fall, the PCM releases heat as it solidifies, and feels warm.

This property of microencapsulated phase change materials can be harnessed to increase the comfort level for users of sports equipment, military gear, bedding, clothing, building materials, and many other consumer products. Microencapsulated PCMs have even been used in NASA-patented thermal protection systems for spacecraft.

Pesticides are encapsulated to be released over time, allowing farmers to apply the pesticides less often rather than requiring very highly concentrated and perhaps toxic initial applications followed by repeated applications to combat the loss of efficacy due to leaching, evaporation and degradation. Protecting the pesticides from full exposure to the elements lessens the risk to the environment and those that might be exposed to the chemicals and provides a more efficient strategy to pest control.

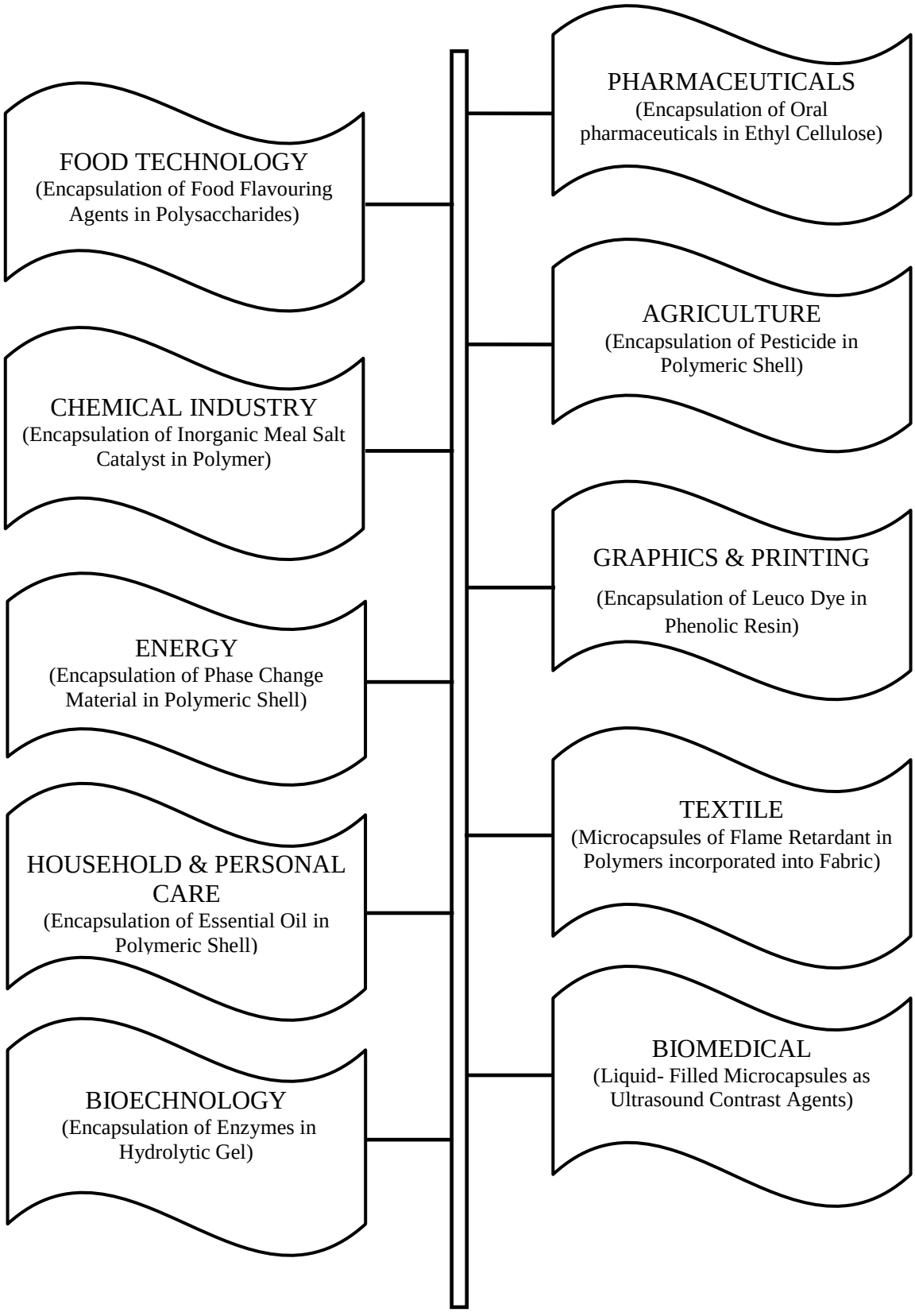



**FIGURE 1.5** Applications of microencapsulation

Ingredients in foods are encapsulated for several reasons. Most flavouring is volatile; therefore encapsulation of these components extends the shelf-life of products by retaining within the food flavours that would otherwise evaporate out and be lost. Some ingredients are encapsulated to mask the taste, such as nutrients added to fortify a product without compromising the products intended taste. Alternatively, flavours are sometimes encapsulated to last longer, as in chewing gum. The amount of encapsulated flavoring required is substantially less than liquid flavoring, as a liquid flavoring is lost and not recovered during chewing. Flavourings that are comprised of two reactive components that, when encapsulated individually, may be added to the finished product separately so that they do not react and lose flavour potential prematurely. Some flavourings must also be protected from oxidation or other reactions caused by exposure to light.

Many varieties of both oral and injected pharmaceutical formulations are microencapsulated to release over a longer period of time or at certain locations in the body. Aspirin, for example, can cause peptic ulcers and bleeding if doses are introduced all at once. Therefore aspirin tablets are often produced by compressing quantities of microcapsules that will gradually release the aspirin through their shells, decreasing the risk of stomach damage. Applications of Interfacial Polymerization for microencapsulation applications are discussed in detail in Chapter-2.

The following features further elucidate the distinctive importance of microencapsulation process as a technology:

1. Prolonged-release dosage forms. Because microencapsulation is most beneficial for the manufacture of tablets, capsules, or parenteral dosage forms, the microencapsulated drug can be delivered.
2. Microencapsulation can be utilised to make enteric-coated dosage forms, allowing the medication to be absorbed more easily in the intestine rather than the stomach (Felt et. al., 1998).
3. It can be used to mask the taste of bitter drugs (Fukushima et. al., 2000).
4. From the mechanical point of view, microencapsulation has been used to aid in the addition of oily medicines to tableted dosage forms. This has been used to overcome problems inherent in producing tablets from otherwise tacky granulations

and indirect compression to tablets (Hombreiro et. al., (2000) and Passerini et al., 2003).

5. It has been used to protect drugs from factors such as humidity, light, oxygen, and heat. Although microencapsulation cannot yet provide a perfect barrier for materials that degrade when exposed to oxygen, moisture, or heat, it can provide a high level of protection against these elements. (Arshady et. al, 1991).
6. Encapsulation has been used to achieve separations of incompatible compounds, such as pharmaceutical eutectics. This is a situation where two materials come into direct touch and form a liquid. The stability of an incompatible aspirin-chlorpheniramine maleate mixture was improved through the use of micro-encapsulating both of them before mixing.
7. Microencapsulation can be used to decrease volatility. An encapsulated volatile substance like pesticides can be stored for longer times without substantial evaporation.
8. Microencapsulation has also been used to decrease hazardous or a noxious substance poses a risk. After microencapsulation, the toxicity caused by fumigants, herbicides, insecticides, and pesticides has been reduced.
9. Microencapsulation can minimise the hygroscopic characteristics of several core materials.
10. To decrease gastric irritation, many drugs have been microencapsulated. (Carrasquillo et. al, 2001).

## 1.4 Aim and Scope of work:

### Aim:

1. Experimental studies on synthesis and characterization of polyurea microcapsules via IP at specific preparative conditions.
2. Study the effect of different solvents and different temperatures on the reaction kinetics of IP.
3. Encapsulation of selected insecticides (i.e. active ingredients (AI)) in polyurea shell to study their controlled release behaviour via experiments.
4. Correlate encapsulation efficiency and release rate of active ingredient (AI) with morphological parameters of microcapsules as well as process variables.

### Scope of Work:

The present research work is mainly an experimental work on the synthesis of polyurea microcapsules via IP at different preparative conditions and reaction temperatures which address each of the above objectives. Polyurea shell was characterized using various analytical tools like Fourier transform infrared (FTIR) spectrophotometer, X-ray diffraction analysis (XRD), Differential scanning calorimeter (DSC), and scanning electron microscope (SEM). IP reaction rate was studied using different organic solvents: (i) Cyclohexane (ii) *n*-Octane (iii) Benzene (iv) Toluene (v) *p*-Xylene and (vi) Mesitylene at three different temperature levels. Three different insecticides i.e. chlorpyriphos, cypermethrin and pretilachlor were encapsulated in polyurea shell via IP at different preparative condition i.e. R=1.2, 2.4 and $n_L/V_d$= 0.36, 0.72. Where, R is monomer mole ratio and is limiting monomer per unit volume of dispersed phase. Encapsulation efficiency was calculated and a rate of release of these insecticides into methanol was measured experimentally in controlled release experiments and correlated with % crystallinity of polyurea.

## 1.5 Outline of the thesis

The **First** chapter covers an introduction to microencapsulation and the details regarding all techniques used in Microencapsulation Processes: Chemical processes: i) Interfacial polymerization, ii) *In situ* polymerization. Physico-chemical processes: i) Coacervation - phase separation, ii) Emulsion method iii) Suspension method, iv) Pickering method,
v) Micro-fluidic method and Mechanical processes: i) Air suspension or fluidized bed coating, ii) Spray drying, iii) Spray congealing.
It also covers the aim and scope of the study: Experimental studies on synthesis and characterization of polyurea microcapsules via IP at specific preparative conditions. Study the effect of different solvents on the reaction kinetics of IP at three different temperatures. Encapsulation of selected insecticides (i.e. active ingredients (AI)) in polyurea shell to study their controlled release behaviour via experiments. Correlate encapsulation efficiency and release rate of AI, with morphological parameters of microcapsules as well as process variables.
The **second** chapter covers the details regarding the literature review of different types of interfacial polymerization, mechanism of interfacial polycondensation, the kinetics of polymer synthesis via interfacial polycondensation, and applications of interfacial polycondensation for microencapsulation.
The **third** chapter covers the details regarding Experimental and characterization. It includes physical and chemical properties of materials used in present experimental studies and experimental processes.
The **fourth** chapter covers the details regarding Results and discussions. The **Fifth** chapter covers the details regarding **Conclusions and Scope of future work.**

# CHAPTER 2

# Literature Review

Interfacial Polymerization (IP) is one of the most versatile used chemical methods for effective encapsulation of various active ingredients in polymeric shell. In this chapter a brief overview, advantages and important engineering aspects of this method is discussed.

This review provides information about polyamide, polyurea and polyurethane polymeric shell materials synthesized by IP and summary of their applications to encapsulate key active ingredients like agrochemicals, pharmaceuticals, phase change materials, dyes & ink and self healing materials. Experimental method reported in literature to study controlled/sustained release of various agrochemicals is also reviewed.

## 2.1. A Brief Overview of Interfacial Polymerization

Polycondensation can be carried out by various polymerization techniques including melt polymerization, solution polymerization, interfacial polymerization and emulsion polymerization.

In interfacial polymerization (IP), the formation of polymer takes place at the interface of two immiscible liquids in which monomers are initially dissolved separately, and it takes place almost exclusively by a diffusion mechanism. The system is usually stirred to ensure better contact of two liquids. The polymer formed at the interface is filtered off, washed and dried.

In step growth polymerization or polycondensation, polymer linkage occurs between two macromolecules containing reactive functional groups; the primary characteristic of this polymerization is that any two species containing minimum two functional end groups in a reaction mixture can react with each other (Cheremisinoff, 1998).

In this work, the generic Interfacial polymerization process is considered as Interfacial polycondensation (IP) that is step-growth polymerization reactions taking place at the interface.

### *2.1.1 Historical Perspective of Interfacial Polycondensation (IP)*

Interfacial polymerization was mainly developed toward the end of the 1960s, leading to applications in microcapsule production by the mid-1970s. The process consists in the dispersion of one phase containing a reactive monomer, into a second immiscible phase to which is added a second monomer (Perignon et al., 2014).

Polyamides, polyureas, polyesters, polyurethanes, polysulfon amides, polycarbonates etc. are polymers which can be prepared by interfacial polymerization (IP) (Cheremisinoff, 1998). Functional monomers and characteristics of these polymers as a wall material of microcapsules are given in Table: 2.1. (Khilar, 1987)

Table: 2.1 Polymers synthesized by interfacial polymerization (IP) (Khilar, 1987)

| **Polymer** | **Aqueous Phase Monomer** | **Oil Phase Monomer** | **Properties of Microcapsule Wall** |
|---|---|---|---|
| Polyamide | Diamine | Di acid chloride | Weak, Soft |
| Polyester | Diol | Di acid chloride | Tough |
| Polycarbonate | Diol | Bis (chlorocarbonate) | Tough |
| Polyurea | Diamine | Diisocyanate | Tough and Strong |
| Polyurethane | Diol | Diisocyanate | Tough and Strong |

## 2.2 Engineering Aspects of Interfacial Polycondensation

### *2.2.1 Mechanism of Interfacial Polycondensation*

Highly reactive multifunctional monomers, which constitute a large volume of the reaction mixture and regeneration of the organic phase, are required in this process. Interfacial polymerization (IP) is conveniently used to produce many type polymers with more ease and convenient compared to other methods. (Cheremisinoff, 1998).

In Interfacial Polycondensation (IP), step growth polymerization reactions occur at, or in a thin region adjacent to the interface of the two immiscible phases, and since the polymer formed is insoluble in both the phases, accumulate at the surface of contact between the phases. (Dhumal et al., 2010)

IP is a heterogeneous process of mass transfer with chemical reaction and simultaneous occurrence of polymer phase separation and film formation. The steady state concentration profiles of the aqueous phase and oil phase monomers used in a typical polycondensation reaction with concurrent phase separation of polymer formation are shown schematically in Figure-2.1. The system considered is the microencapsulation of an organic phase dispersed as drops of uniform size in an aqueous phase, by the interfacial polycondensation reaction between an aqueous phase monomer *A–R–A* and an organic phase monomer *B–R'–B*. For the polyurea system, these are, respectively HMDA and HMDI.

Considering a small section of the aqueous–organic interface with the formed polymer film separating the phases at some intermediate stage of the reaction, the concentration profiles of the monomers in the film and adjacent regions are shown schematically in Figure-2.1 (Dhumal et al., 2008).

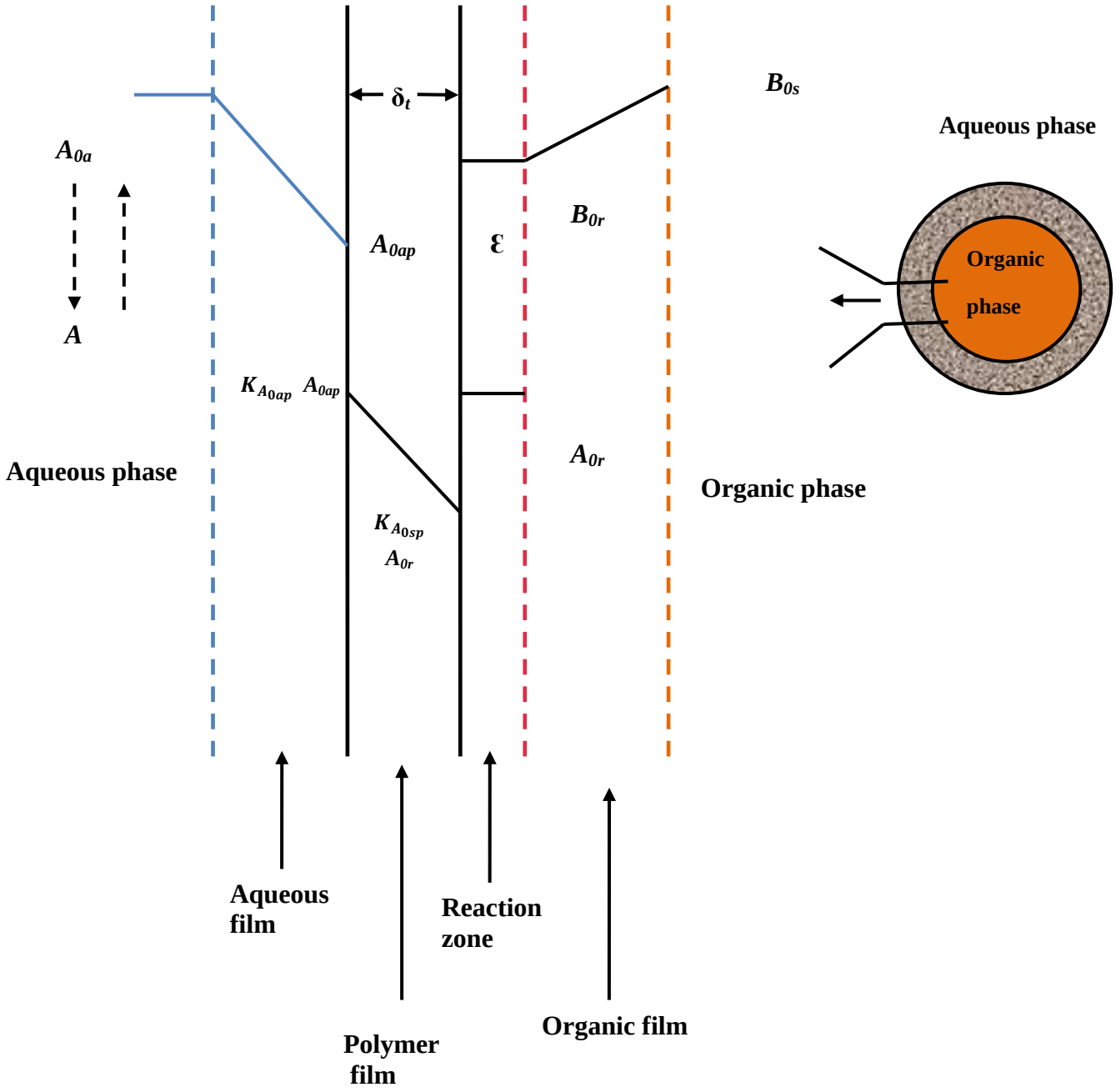



**Figure 2.1** Schematic diagram showing different regions of Interfacial Polycondensation

Where, $A_{0a}$ = unprotonated diamine concentration in bulk aqueous phase,
$A_{0ap}$ = diamine concentration at aqueous phase-polymer interface,
$A_{0r}$ = diamine concentration in reaction zone,
$A_T$ = total diamine concentration in bulk aqueous phase,
$B_{0r}$ = diisocyanate concentration in the reaction zone,
$B_{0s}$ = diisocyanate concentration in the bulk organic phase,
$K_{A_{0ap}}$ = partition coefficient of diamine between aqueous phase and polymer film
$K_{A_{0sp}}$ = partition coefficient of diamine between polymer film and organic solvent.

### *2.2.2 Merits of Interfacial Polycondensation*

Perignon et al., (2014) reported merits of interfacial polycondensation as:

- Simple and reliable process,
- Direct control of capsule mean size and membrane thickness possible,
- High active loading and tuneable delivery processes,
- Versatile and stable properties of the membrane as well as membrane permeability,
- Relatively low cost and conducive to scale- up.

IP is the technique of step polymerization which can be carried out with less stringent conditions of monomer purity, both linear or cross linked polymers are obtained under ambient conditions of temperature and pressure and with minimum or no post-processing steps (Zudiam and Shimoni, 2010).

### *2.2.3 Synthesis of Important Polymeric Shell material by IP*

Polyamide, Polyurea and Polyurethane are important shell materials which are extensively used for microencapsulation via IP. Synthesis and characterization of these polymers are reported in the sub section as below:

#### **2.2.3.1 Polyamide**:

Janssen et al., (1992) prepared oil-containing polyterephthalamide capsules by the interfacial polycondensation of diethylene triamine (DETA) with terephthaloyl dichloride (TDC). It was shown that the capsule wall membrane was asymmetric, consisting of a dense top-layer and a cellular, porous sub layer. The relative permeability of the membranes to the reacting DETA was indirectly determined from measurements of the membrane thickness or the dichloride concentration in the capsule with respect to the reaction time. It was shown that the permeability of the capsule wall membrane to DETA increased as the initial concentration ratio of DETA to TDC decreased. They reported a similar behaviour with respect to the membrane permeability to NaCl.

Janssen and Te Nijenhuis, (1992) also investigated the effect of the molar ratio of monomer i.e. ethylene diamine (EDA) or 1,6-hexamethylene diamine (HMDA) to DETA on the membrane permeability. It was found that the relative membrane permeability to the

reacting amines decreased as the diamine to DETA molar ratio increased. Furthermore, addition of HMDA to the DETA aqueous phase resulted in a significant reduction of the membrane permeability.

Sundet et al., (1993), developed aromatic polyamide membranes for desalination applications and studied morphology of the membrane. As a major conclusion they reported that asymmetry appears at surface is an inherent property of the polyamide membranes formed by interfacial polycondensation. Polyamide chains originally generated in the organic phase precipitate out, due to their low solubility, to form unstable colloidal particles, having some unreacted amine and carboxylic groups on their surface.

Toubeli and Kiparissides (1998) studied the synthesis, characterization and permeability of polyterephthalamide membranes for microencapsulation prepared by the interfacial polycondensation of an aliphatic amine (e.g. EDA, HMDA, DETA and TETRA) with terephthaloyl dichloride (TDC). In particular, the membrane morphology, its equilibrium water content and thermal behaviour, the partition coefficient and the membrane permeability to NaCl as well as effects of the ionic strength and pH of the release medium on the permeation characteristics of (DETA, TDC) membranes were investigated. It was found that the permeability of (DETA, TDC) membranes to NaCl exhibited a U-shape behaviour as the molar ratio of DETA/TDC varied from 8 to 36. Addition of a diamine (e.g. EDA or HMDA) to the DETA aqueous phase resulted in a reduction of the membrane permeability which was very pronounced in the case of HMDA. On the other hand, addition of a polyfunctional amine (e.g.TETRA) had no significant effect on the membrane permeability. Environmental conditions were also found to influence the (DETA, TDC) membrane permeability to NaCl. Thus, the permeability decreased as the ionic strength of the aqueous medium increased or the pH varied from alkaline to acidic.

Synthesis of polyamide milicapsules by interfacial polycondensation was carried out by Louis et al.,(1999) using 1,6- diaminohexane, Tetraphtaloyl Chloride and1,3,5- benzene tricarbonyl chloride using tri block copolymer Hypermer B 261 (ICI) as a surfactant and cyclohexane as a solvent. They determined polymer weight composition with regard to the capsule mass, the influence of the surfactant, the growing time and the concentration and the nature of the reagents on the thickness and the surface state of the capsules wall. Water

was encapsulated inside the capsule. Effect of surfactant concentration on capsule size was reported, as higher the surfactant concentration smaller the capsule size. Membrane wall thickness was dependent on reaction time as well as concentration of cross linking agents. Rupture strength and mechanical resistance of milicapsules were measured as a function of wall thickness. Permeability measurement methods were allowed to optimize the capsules' properties

The formation of aqueous core polyamide microcapsules via interfacial polymerization of a polyoxypropylenediamine soluble in water and sebacoyl chloride dissolved in organic phase was studied by Zydowicz et al., (2001), to determine the ideal circumstances for the production of microcapsules As a result, the emulsification process was first examined with the goal of optimising the emulsion's stability, which came before the production and regulation of microcapsule size. The monomer ratio, surfactant content, and, most importantly, the pH of the aqueous phase were all considered in the optimization of the system's formulation. FTIR, NMR, and MALDI-TOF mass spectrometry were used to examine the chemical structure of the microcapsules. Thermal gravimetric analysis was performed to examine the thermal properties of the polyamide membranes (TGA). The size of the microcapsules was determined using optical microscopy and laser light diffraction. Finally, scanning electron microscopy (SEM) was used to examine the morphology.

**2.2.3.2 Polyurea:**

Effect of emulsifying time and stirring speed reduction was studied by Peihong et al., (1995) for Polyurea microcapsules synthesized by using toluene-2,4 diisocyanate (TDI) and Ethylene diamine (EDA) or Lysine(LYS). The diameter of microcapsules decreased as the emulsifying time increased during the initial 3 min, beyond which there were no appreciable changes in the diameter and size distribution. Reducing the stirring speed after addition of DETA into reactor diminished the formation of membrane fragments, but had not any effect on the diameter of TDI-DETA microcapsules. The zeta-potential of the TDI-LYS microcapsules was higher than that of the TDI-DETA microcapsules, which improved the dispersity of microcapsules.

Yadav et al.,(1996), investigated detail kinetics of the polyurea formation by interfacial polycondensation between aqueous phase containing Hexamethylene1,6- diamine (

HMDA), water and Tween-85 emulsifier and dispersed phase containing Hexamethylene diisocyanate(HMDI) with solvent cyclohexane using technique of on line pH measurement as a function of time. Kinetic data were obtained over a range of concentrations, monomer mole ratios and polymer film thicknesses. A model was proposed for the reaction that considers ionic equilibria in the external aqueous phase in addition to the resistances due to external mass transfer, diffusion through the formed polymer and surface reaction. Further, the structure of the polymer has been studied through X-Ray diffraction (XRD). The results obtained provide clues on how the structure can be manipulated through the rate of polymerization. They also determined the permeability of the polyurea microcapsules containing cyclohexane as a core material, which synthesized at constant conditions. The degree of crystallinity of the polymer forming the membrane can be altered to change the product of permeability and membrane thickness. Release of cyclohexane was due to diffusion through polymeric shell wall.

Influence of the synthesis parameters on the polyurea membrane formation for the system based on reaction between Hexamethylene1, 6- diamine (HMDA) and Hexamethylene diisocyanate (HMDI) was reported by Wagh et. al., (2009) and Dhumal et. al., (2010) Hexamethylene1, 6- diamine (HMDA), water and Tween-85 emulsifier and Dispersed phase containing Hexamethylene diisocyanate (HMDI). The rate of reaction was controlled by the reaction kinetics until the limiting monomer conversion of about 80%. Wagh et. al., also discussed the effect of organic solvent nature on reaction rate.

Stover et al., (2011) developed simple T-junction type microfluidic device which was easy to operate in order to get mono dispersed emulsions of xylene and Isophorone diiso cynate (IPDI) which was further used in interfacial polycondensation with monomer diethylene triamine (DETA) resulted into polyurea microcapsules.Postmodification of PUMC with acetoacetyle functional polyanion attached to residual amine group was carried out to improve capsule wall properties

### 2.2.3.3 Polyurethane:

Bouchemal et al. (2003) synthesized polyurethane and poly (ether urethane) copolymers by interfacial reaction between two monomers. Interfacial polycondensation combined with spontaneous emulsification is a new technique for nanoparticles formation. Nanocapsules were characterized by studying particle size (150–500 nm), pH, yield of encapsulation and morphologies. Polyurethanes (PUR) were obtained from the condensation of diisocyanate (isophorone diisocyanate: IPDI) and polyol: 1, 2-ethanediol (EG), 1, 4-butanediol (BD), 1, 6-hexanediol (HD). Poly (ether urethane) copolymers were obtained by replacing diols by polyethylene glycol oligomers (PEG) M200, 300, 400 and 600. Molecular weights of di- and polyols have a considerable Influence on nanocapsules characteristics cited above. The increase of molecular weight of polyols tends to increase the mean size of nanocapsules from (232 ±3) nm using EG to (615 ±39) nm using PEG 600, and led to the apparition of a population of agglomerate particles. It was also noted that the yield of encapsulation increases with the increase of polyol length (from 85.6 to 92.2% w/w). Microscopic observations confirmed particle size analysis, but cannot predict the membrane structure owing the small size of the particles. These polymers were effectively used for microencapsulation of anti oxidants.

Series of polyurea–urethane microparticles containing xylitol were synthesized by interfacial polymerization from reaction between diphenyl methylene diisocyanate (MDI) and xylitol. This research was conducted to clarify the influence of different parameters on the encapsulation process, i.e. during the emulsion formation step and during the shell formation using contact angle measurement, FTIR, DSC and TGA. By carefully analyzing the influencing factors stirring rate and feeding weight ratio of core/shell monomers, the optimum synthetic conditions were found out. The results show that core/shell weight ratio influences not only the shell formation mechanism but also the mean diameter, microcapsule morphology, the encapsulation yield and the xylitol content Saloun et al., (2004).

Kinetics of the interfacial step polymerization in direct miniemulsion between 1, 6-hexanediol and isophorone diisocyanate, at different temperatures and with different organic solvents phase was investigated by Gaudin et al, (2012). Despite the complexity of

the reaction system due to the specific experimental conditions, the profiles of consumption of the isocyanate groups and diisocyanate monomer, chemical structure of the being formed polymer membrane, were concurrently determined by gas chromatography, FTIR spectroscopy, $^{13}$C-NMR and MALDI-TOF mass spectrometry.

## 2.3 Applications of Interfacial Polymerization for Encapsulation of Different Active Ingredients (AI)

### 2.3.1 Agrochemicals:

Polyurethane microcapsules containing insecticide sumithion as a core material were developed by Tsuji et al. (1984) to study its controlled release.

Release rate of pesticide dichlorovos (DDVP) from microcapsules was studied by Chang et al. (1988) by forming polyurethane as a shell wall barrier.

Interfacial polymerization and In situ polymerization were found as best suitable methods as per summary of industrial applications of various encapsulation technologies in agrochemicals formulations discussed by Bob Perrin et al., (2000).

Study on effect monomer ratio on capsule wall characteristics of polyurea microcapsules prepared by interfacial polycondensation of methylene bis (phenyl Isocyanate) with Hexamethylene diamine (HMDA) and release behaviour of insecticide acetamide as a core material was carried out by Jabbari E., 2001.

Microencapsulation of the water soluble pesticide monocrotophos (MCR), using polyurethane as the carrier polymer, has been developed using two types of steric stabilizers, namely PLMA macrodiol and PLMA-g-PEO graft copolymer. The microencapsulation process is carried out in non-aqueous medium and at a moderate temperature to avoid any chemical degradation of monocrotophos during the encapsulation process. Microcapsules were characterized by optical microscopy and SEM for particle size and morphology, respectively. (Shukla et al., 2002)

Controlled release systems (CRSs) of a spongy core material enriched with liquid pyriproxyfen (an effective insect growth regulator against mosquito larvae) encapsulated in

Polyurethane and Polyurea hydro gels (as an external coating) were designed by Liliana Schwartz et al., (2003). This formulation easily floated on water- and thus came in contact with the larvae- on the surface of water and was more effective. Dissolution tests were conducted to study influence of amount of polymeric coatings and surfactant concentration on cumulative release of pyriproxyfen against the larvae of culex pipiens mosquito. Rate of release of pyriproxyfen was increased with increase in amount of polymeric coating and higher concentration of emulsifier.

A two-effect product composed by microcapsules containing insecticide suspended in concentrated disinfectant solution was developed by Hirech et al., (2003). A two-stage microencapsulation procedure was used, with the first step including the production of an oil/water (o/w) dispersion in a static mixer and the second step involving the microencapsulation of the o/w dispersion in a stirred tank reactor. Microcapsules have a mean diameter of 30 m to ensure that they stay floating in the disinfecting solution. The microcapsules' walls are made of polyurea, and release rates measured by pH in the disinfectant solution are found to be very low, indicating that the insecticide and disinfectant are compatible. (Hirech et al., 2003).

T. Takahashi et al., (2007), synthesized polyurea microcapsules from oil phase monomer Hexamethylene diisocyanate (HMDI) and aqueous phase monomer Ethylene diamine (EDA) to encapsulate a pyrethroid insecticide using a two-step microencapsulation process by interfacial polymerisation. This study was performed to establish the operational conditions of preparing microcapsules by interfacial polymerization and to investigate how the operational conditions affected the characteristics of microcapsules such as the morphology, wall thickness, mean diameter, and particle size distribution. Microcapsules prepared in this study were found to be spherical and monocore. The microcapsule yields was ranging from 94 to 98%, were almost equal to the theoretical values. The wall thickness of the microcapsules increased with the diameter of the microcapsules and the concentration of hexamethylene diisocyanate isocyanurate. In comparison with the results for microcapsules prepared with a mixture of hexamethylene diisocyanate uretidione and isocyanurate, the diameters and wall thickness of the microcapsules were found to be larger. The size distribution of microcapsules at 3000RPM was 0.3µ to 46 µ while at 6000RPM 0.4µ to 14µ.

Zhu et al, (2010) developed a method with trimer of isophorone diisocyanate and triethylene tetramine as wall-forming materials, sodium dodecylsulfate and xanthan gum as stabilizers, and an emulsifying speed of 3000 rpm for 12 min, chlorpyrifos containing microcapsules, with a diameter ranging 2–7μm and an initial encapsulation rate of 94.7%, were prepared by fast interfacial polymerization at room temperature. Formulations based on the prepared microcapsules are stable in neutral medium and release chlorpyrifos in both acidic and alkaline media was studied. The results of bioassay against 3$^{rd}$-instar Spodoptera litura larvae showed that microcapsule formulations had more sustainable efficacy than that of conventional emulsion formulations.

Bagle et al., (2013) synthesized nanocapsules containing biological pesticide, neem oil as a core material inside phenol formaldehyde shell by an in-situ polymerization process in oil-in-water emulsion. The synthesis was proceeding in two parts, namely emulsification of the oil and wall formation. The synthesized microcapsules were characterized by FTIR, SEM, TGA, and particle size analyzer. The controlled release was monitored by measuring optical observation in the UV range. Resulting microcapsules were more effective than synthetic pesticide in controlling pests.

Microcapsules of pesticide abamectin in polyurea shell with encapsulation efficiency of 90% were synthesized by Wang et al., (2013). In his research work polyurea was synthesized via interfacial polymerization of oil phase monomer Tolylene-2, 4-diisocyanate (TDI) and aqueous phase monomer hexamethylenetetramine (HMDA), emulsifier Tween-80 and solvent chloroform. Effect of different stirring speed on particle size was studied. Stable microcapsules of abamectin were obtained at stirring speed of 500 RPM and 1000 RPM, while at stirring speed of 2000 RPM the microcapsules got agglomerated. Defoaming effect of different amount of emulsifier was studied. Orthogonal design of wrapping material, dispersant and solvent consumption at three different levels was developed to determine the best amount of each of this material. Optimum value of encapsulation efficiency of microcapsules was 90%.

Bruno et al., (2013), reported control release and effectiveness of various agrochemicals through polymeric nanoparticle based formulations synthesized from both natural and synthetic polymers.

Complete release characteristics of insecticides Paclobutrazol and Prochloraze were studied for comparison of both coated and uncoated slab like and microcapsule formulations of Polyurethane and Polyurea synthesized by Interfacial polycondensation was analysed by Slawomir and Wybraniec (2014).

Acetachlor is an important herbicide for gramineous weeds Controlled-release formulations of herbicide are highly desirable not only for attaining the most effective utilization of the weed control, but also for reducing environmental pollution. Acetachlor was incorporated in poly (butyl methacrylate-diacetone acrylamide) based formulation via nanoemulsion polymerization to obtain controlled release properties. The acetachlor nanocapsules were characterized by size distribution, infrared spectroscopy (IR) and field emission scanning electron microscopy (FESEM), and factors related to loading efficiency, swelling behavior of the formulation were investigated (Guo et al., 2014)

### 2.3.2 Pharmaceuticals:

Enzyme, invertase was incorporated into polyamide microcapsules. Different process parameters were studied: pH of the aqueous phase during interfacial polymerization; duration of the polymerization; surfactant concentration; stirring rate; for improvements in the isolation procedure; effect of lyophilisation (P. Rambourg et al., 1982).

Interfacial polymerization process effectively used to produced individual cross-linked albumin microcapsules, the particle size of which depended on the emulsification stirring rate. The variation in cross-linking agent concentration altered the microcapsule wall properties (Benita et al., 1984). Porous microcapsules of albumin with tuneable pore sizes were prepared using interfacial polymerization by employing a temperature-responsive cross-linking agent above its so-called cloud point temperature (Tscp). The influences of porosity on the surface morphology, release profile and biological activity of the microcapsules were investigated (Y. Zhang et al., 2012).

Aboubakar et al., 1999 developed insulin-loaded poly (alkylcyanoacrylate) nanocapsules were found to reduce the blood glucose level after oral administration to diabetic rats and dogs. The reduction of the glycaemia induced by the nanocapsules was the same regardless of the insulin doses administered, but the effect appeared only after a delay of a few days.

Polyurethane polymers and poly (ether urethane) copolymers were chosen as drug carriers for α-tocopherol. This active ingredient is widely used as a strong antioxidant in many medical and cosmetic applications, but is rapidly degraded, because of its light, heat and oxygen sensitivity. Polyurethane and poly (ether urethane)-based nanocapsules were synthesized by interfacial reaction between two monomers, (Bouchemal et al., 2004).

Xi. Zhou, & Fei, 2012; reported the method of interfacial polymerization in emulsion was employed to fabricate chondroitin sulfate-methacrylate (ChSMA) nanocapsules, in which poor water-soluble drug of indomethacin could be effectively encapsulated.

New polyurethane microcapsules incorporated with an antituberculous drug, isoniazid, have been synthesized through the interfacial polycondensation of toluene 2, 4-diisocyanate with different poly (ethylene glycols) in a water–toluene emulsion. As the poly (ethylene glycol) chain is elongated, the conversion of diisocyanate decreases with time; the content of urea groups in polyurethanes increases; and the morphology of capsule walls changes, with the walls becoming looser. At high poly (ethylene glycol) concentrations, the efficiency of isoniazid encapsulation decreases owing to displacement of the drug into the organic phase. An increase in the poly(ethylene glycol) concentration above 50 vol % leads to densification of polymer capsule walls because of enhancement of the diffusive accessibility of the monomer. As a result, the release of isoniazid decelerates almost twofold (Kim et al., 2006).

Double-layer polyurethane/poly (urea-formaldehyde) (PU/PUF) shell microcapsules containing clove oil with antibacterial properties were successfully synthesized via in situ and interfacial polymerization reactions in an oil-in-water emulsion. The morphology, core-shell structure, and composition of the microcapsules were systematically investigated by (Y. Zhang et al., 2018).

### 2.3.3 Phase Change Materials (PCMs):

Formulation of nanocapsules based on polyureas and polyamides have been tested using a patented process. This method based on polycondensation reaction of two complementary monomers and spontaneous formation of oil in water emulsion, is an alternative concept to the known technique based on the same type of reaction used for the formulation of

microcapsules, and in which the lipophilic monomer was emulsified in the organic phase before the formation of the polymeric membrane. Nanocapsules can be prepared from different monomers. Wall based on cross-linked polymer contributes to the stability of nanocapsules during and after formulation. The permeability of the polymeric wall is connected to crystallinity and helps to develop the nanocapsule membrane by allowing hydrophilic monomers to diffuse into stable colloidal suspensions. (Montasser, et al., 2007).

Encapsulation of Butyl Stearate, a phase change material (PCM), in polyurea shell was carried out by Shaofeng et al., 2013. Toluene-2, 4 diisocyanate (TDI) and Diethylene Triamine (DETA) monomers were used to conduct interfacial polycondensation at $23.3^0$C. Stable and compact Micro PCM was obtained with the average diameter in the range of 4.5 to 10.2 µ. Characterization for phase change properties, surface morphology, chemical structure and particle size were carried out by DSC, SEM, FTIR and Malvern laser particle size analyzer.

Polyurethane microcapsules were prepared by mini-emulsion interfacial polymerization for encapsulation of phase-change material (n-dodecane) for energy storage. Three steps were followed with the aim to optimize synthesis conditions of the microcapsules. First, polyurethane microcapsules based on silicone oil core as an inert template with different silicone oil/poly (ethylene glycol)/4, 4′-diphenylmethane diisocyanate wt% ratio were synthesized (Brown et al., 2003).

Microcapsules produced by interfacial polycondensation of p-phenylenediamine (PPD) and sebacoyl chloride (SC) were studied. The products were characterized in terms of morphology, mean diameter and effectiveness of PCM, dodecane encapsulation (Rosa, et al., 2015).

Microencapsulation technology for thermal energy storage was developed by (Yoo et al, 2017) by incorporating a phase change material (PCM) in a composite wall shell, which can be used to create a stable environment and allow the PCM to undergo phase change without any outside influence. Surface modification of cellulose nanocrystals (CNCs) was conducted by grafting poly(lactic acid) oligomers and oleic acid to improve the dispersion of nanoparticles in a polymeric shell.

### 2.3.4 Dyes and Ink:

A viscous organic phase, containing up to 65 per cent solid pigment, was dispersed into water with an emulsifier by a rotor-stator homogenizer and the droplets formed were encapsulated by interfacial polymerization. Microcapsules with volume median diameters d50 ranging from 10 to 25 μm and geometric standard deviation (GSD), from 1.25 to 1.65, were obtained depending on emulsification conditions. Larger impellers gave smaller d50 and slightly narrowed GSD; d50 decreased and GSD increased as volume fraction of dispersed phase is decreased. (Mahabadi et al, 1991).

Microcapsules containing pigment and polymer were prepared by dispersing a viscous mixture of pigment as a core monomers, initiators and oil-soluble shell monomer in an aqueous solution of surfactants, forming oil-in-water droplets. Subsequently, a water-soluble shell monomer was added to these droplets, encapsulating them via interfacial (IF) polycondensation. These microcapsules were then heated for free radical (FR) polymerization of the core monomers (Mahanadi et al., 1996).

### 2.3.5 Self Healing Materials:

A medical cyanoacrylate tissue adhesive was encapsulated effectively in polyurethane (PUR) and microcapsules of self-healing acrylic bone cement were prepared and characterized. Capsules were prepared by interfacial polymerization of a toluene-2, 4-diisocyanate-based polyurethane prepolymer with 1, 4-butanediol to encapsulate 2-octylcyanoacrylate. (Brochu et al., 2012)

Urea-formaldehyde microcapsules containing dicyclopentadiene were prepared by in situ polymerization in an oil-in-water emulsion that meet these requirements for self-healing epoxy. Self-healing materials require microencapsulated healing agents with sufficient strength, a long shelf life, and excellent bonding to the host material. (Scot et al., 2012)

### 2.3.6 Recent Developments in Applications of Interfacial Polymerization for Microencapsulation:

A detailed review on physicochemical, structural, and mechanical properties determination of microcapsules was presented. To truly understand the characteristics of microcapsules in connection to their specific uses, it is vital to determine their physicochemical, structural, and mechanical qualities. Depending on the application, the relative importance of various

properties may change. Microcapsules containing fragrance, for example, are used in the laundry industry to prolong the fresh scent on clothing. It is desirable for microcapsules containing fragrance to remain intact until the optimum time, at which point they are broken by mechanical force after the drying process, so mechanical properties are critical. When it comes to the pharmaceutical industry, microcapsules could release the active ingredient through a diffusive process, and mechanical properties are still significant, the release rate, which is dependent on porosity, is the most relevant property in this scenario. It's also worth noting how these traits interact with one another. The mechanical strength of a particular microcapsule composition is mostly determined by the shell composition, structure, thickness, and particle size. For the physicochemical and structural characterization of microcapsules, there are a variety of approaches available, each with its own capabilities and limits, and the technique chosen relies on the type of information and accuracy required. Physicochemical properties like microcapsules size and size distribution, surface roughness and determination of morphological properties of microcapsules, techniques for surface charge and zeta potential measurements were effectively reviewed. Structural properties of microcapsules i.e. pore size, shell thickness and release rate of core material was studied in detail.(Gray et al., 2015)

Antibacterial, antifungal, antiviral, insecticidal, and antioxidant activities have been reported in essential oils. Essential oils have a lot of biologically active components in them. Interfacial polymerization allows for the creation of spherical microcapsules with an active component core inside (oil). However, the size of microcapsules and the amount of oil encapsulated fluctuate significantly depending on oil properties. The polymerization procedure for the wall material has been carried out correctly, as reported by FTIR analysis. Particle size of microcapsules had a significant effect on amount of oil encapsulated. (Marcela et al., 2015)

Raaijmakers & Benes, 2016; reviewed structures and layers with high lateral dimensions and small thicknesses of different components used for interfacial polymerization synthesis. Materials that redissolved after preparation were not included since they were not used in the same way as interfacial polymerization. Effective applications of interfacial polymerization for synthesis of nanocomposites and hybrid materials were reported.

Interfacial Polymerization method was applied to encapsulate phoxim, an easily photo

degradable pesticide in polyurea shell. An optimum and versatile method was developed for controlled release studies of encapsulated core material with use of an artificial, simulative condition. A dissolution device equipped with syringes and syringe filters were designed. At predefined intervals, samples were extracted. Validation testing showed that this method was universally applicable to a variety of wall and core materials, with standard errors of less than 3.4 percent across the span. They showed that it was a dependable, convenient, and diverse technique for speeding up the time-consuming dissolving testing process. This newly developed design was found more effective compared to dynamic dialysis method. (Cui et al., 2017)

A new insecticide formulation of imidacloprid a neonicotinoid insecticide microcapsule using dopamine and diisocyanate to produce a stable dispersion and long-term release in water was studied. Step-by-step preparation of three types of imidacloprid formulations (IMFs): imidacloprid suspension (IMSC), polydopamine coated imidacloprid (IMPDA), and polyurea coated IMPDA (IMPU). A wet grinding technique had been used to obtain IMSC in the first step. In the second stage, dopamine was employed to create a layer on the surface of IMSC through oxidative self-polymerization. On the PDA layer, the resulting product (named IMPAD) has a lot of amino and hydroxyl groups, making it easier to disperse in water and react with diisocyanate. The entrapment rate and pesticide loading was determined. Fourier infrared transform analysis, TGA analysis and contact angle analysis were conducted to confirm the encapsulation of imidacloprid. Dynamic light scattering showed that the microcapsule size ranged from hundreds of nm to several mm, which was similar to the results obtained by scanning electron microscopy. The microcapsule had a stable dispersion up to one month in the aqueous solution. Moreover, the microcapsule was able to release imidacloprid in a sustainable manner, as the release was much slower than the non-encapsulated imidacloprid.(Gao et al., 2017)

Interfacial polymerization was used to make polyurea/polyurethane double-composition shell microcapsules with n-Octadecane as the major core ingredient. Polymerization of toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) produced the outer polyurea shell, whereas polymerization of TDI and polypropylene glycol 2000 produced the inner polyurethane shell (PPG2000). Differential scanning calorimetry (DSC), FTIR, SEM, TEM, and thermal gravimetric analysis were used to evaluate the phase change

property, chemical structure, surface morphology, and thermal stability of microcapsules. The melting temperature and melting enthalpies of double-composition shell micro caps were found to be similar. (Lu et al., 2017)

Interfacial polymerization was used to make the cypermethrin microcapsules. Polyurethane and Polyurea shell were effectively used to encapsulate cypermethrin, which took place at the oil-water interface. At various levels, controllable parameters such as core to shell ratio, surfactant concentration (%), and surfactant type were examined. HPLC was used to study controlled release of cypermethrin in water. Over the course of a 60-day study, a sustained release of cypermethrin was found for various score to shell ratios. Faster release was found with a core to shell ratio of 5:1, which provides a thinner shell material, resulting in a significant amount of cypermethrin diffusion through the shell as compared to other formulations. (Kamble et al., 2018)

Isocyanate microcapsules have become an ideal additive for usage in chemical and manufacturing materials because of their outstanding bonding properties and stability. A one-step interfacial polymerization process was utilised to make isocyanate microcapsules, in which only one type of isocyanate was used and microcapsules were created by a crosslinking reaction between the isocyanate group and water. In our work, we used liquid polymethylene polyphenyl polyisocyanates (PAPI), which has a lower toxicity and vapour pressure than other isocyanates. The isocyanate microcapsules were used as a high-performance wood adhesive for plywood after the stability of the encapsulated isocyanate was greatly increased. Isocyanate microcapsules allow for the regulated release of isocyanate in plywood, allowing for intelligent cross-linking. (Ma et al., 2019)

## 2.4 Controlled/Sustained Release of Agrochemicals from Product Synthesized by Interfacial Polymerization:

Shukla et al., (1999) patented formulation of polyurethane microcapsules (1-100μm) containing monocrotophos pesticide (unstable in aqueous medium) by IP method. Release of monocrotophos was studied by 0.45 g sample of paraffin oil containing 60% microcapsules is weight accurately in 30 mL glass sample bottle with screw type cap and 20 mL distilled water is added. The bottle is kept in a shaking water bath at 30°C. After 6 hours the solution is filtered through G3 sintered crucible into a 250mL conical flask. The

bottle is gently rinsed with 2 mL of distilled water. The filtrate is then transferred into a 100 mL volumetric flask. The contents of the conical flask is rinsed with 25 mL of distilled water and transferred to a 100 mL volumetric flask. To this solution 13 mL of acetonitrile is added and the solution is diluted with distilled water up to the mark and analyzed by HPLC. The results indicate only 0.6 wt% release of monocrotophos.

Hirech et al., (2003) have investigated controlled release of insecticide diazinon encapsulated in polyurea shell synthesized by IP method. The initial insecticide concentration was to 80 g/l (diazinon in hexane) from which diazinon was released in the disinfectant solution (constituted by quaternary ammonium and glutaraldehyde), release from microcapsules in the disinfectant solution has been determined by measuring the time evolution of pH. Microcapsules with average particle size of 30-40μm were able to stay in suspension in the disinfectant solution without stirring and the release rate of the insecticide in the disinfectant solution is very low, about 4%.

Schwartz et al., (2003) have demonstrated preparation of controlled-release systems (CRSs) of an insect growth regulator pyriproxyfen by applying coating of polyurethane synthesized by IP. The chemical release of pyriproxyfen from the CRSs was performed in a dissolution test system (model 2100B, Distek, North Brunswick, NJ), comprising six glasses (11.5 cm high ×10.2 cm i.d.), each filled with 800 mL of distilled water. Each glass was fitted with a basket, which held 1.0 g of a formulation containing 0.03 g of pyriproxyfen. The dissolution system was held at 25 °C and operated at a basket rotation of 50 rpm. Due to the very low solubility of pyriproxyfen in water, the water in each glass was replaced every 24 h at the beginning, a step that prevented saturation and thus facilitated analysis of the entire amount of active ingredient released into the water. The interval between the changing of water was gradually increased during the course of each experiment as in the case of taking of the samples for HPLC analysis. This way the dissolution system was kept below the saturation level.

In vitro release at irregular time intervals, liquid samples were withdrawn from the upper layers of each glass (because the aqueous solution was stirred, the concentration of pyriproxyfen was the same in any part of the solution), and the amount of pyriproxyfen released into the water was determined by HPLC. Effect of polymer composition and emulsifier concentration was correlated with controlled release of pyriproxyfen.

Li et al., (2013) prepared pendimethalin polyurethane microcapsules via interfacial polymerization with average microcapsule particle size was 4.75 μm. Drying method was applied and results for the cumulative release of the sample after drying for four hours at 20 °C was 96.57%, while that of samples dried at 130 °C was only 43.56%.

Hedaoo et. al.,(2014) synthesized microcapsules of herbicide pendimethalin encapsulated in dendritic PAMAM-based novel novel polyurea as a wall material. The release rate of encapsulated pendimethalin microcapsules was carried by three different methods viz. weight loss on drying, UV (UV-3600 spectrophotometer) as described and subsequently by gas chromatographic (GC) methods.

Marcela et al., (2015) have studied the controlled release of oregano and sage essential oils as core materials through polyurea shell prepared by interfacial polymerization technique. In release study 0.1 mg of washed microcapsules were taken and were dissolved in 10 mL sulphuric acid (pH =0.8). The monitoring of the release of the essential oil concentration of various compounds present in the oils was followed by analyzing samples collected during 120 hours. The measurements were made with a 7890 A gas chromatograph coupled to mass spectrometer. Release kinetics of both essential oils through polyurea microcapsules was best fitted to first order release kinetics with release rate constant of 0.274 $hr^{-1}$ and 0.109 $hr^{-1}$ for oregano oil and sage oil respectively.

Microcapsules of carbosulfan, a carbamate insecticide in a polyurethane shell using interfacial polymerization method were synthesized Yong Xu et al., (2016). The encapsulation efficiency (EE %) was calculated as ratio of mass of carbosulfan in microcapsules to initial mass. The carbosulfan microsphere suspension was dispersed in a certain amount of xylene. The release rate of loaded carbosulfan from the prepared microcapsules was investigated by added them to a dialysis bag which was placed in a constant volume (20 ml) of a release medium (the volume ratio of acetonitrile: water was 30:70). At different time intervals, 1 mL of solution was sampled, and 1 mL of fresh acetonitrile– water solution was added to the reagent bottle to maintain a constant volume and unsaturated conditions. The sampled solution was analyzed by HPLC. Cumulative release of carbosulfan was reported for different values of pH of release medium at constant temperature of 25 °C. The release rate was highest at lower value of pH.

Gao et al., (2017) have encapsulated pesticide imidacloprid in polyurea and release experiment was carried out by injecting 100 mL IMF suspension (5 wt%) of each type (in triplicate) into a dialysis bag (molecular weights: 8000–14 000) and placing the bag in a PP centrifuge tube (50 mL) containing 50 mL deionized water as the release medium. The experiment was conducted under static condition at 25 °C until a steady state of imidacloprid release was achieved. Imidacloprid released into water was measured by an ultraviolet-visible spectrophotometer.

Controlled-release formulations via microencapsulation of many pesticides offered advantages such as improved shelf life, reduced toxicity and environmental damage, reduction in the number of required applications, and enhanced efficacy.

Such formulations enable smaller quantities of pesticide to be used more effectively over a given time interval and in that their design enables them to resist the severe environmental processes, i.e., leaching, evaporation, and photolytic, hydrolytic, and microbial degradation, that act to eliminate conventionally applied pesticides.

## 2.5 Status of Interfacial Polycondensation in Present Research Work:

It is known from earlier works that polyurea synthesized by IP offers good flexibility in desirable properties of microcapsules for required release rates of active ingredient (AI), S. Yadav et al., (1997); S. Yadav et al., (1996) . Various researchers have studied different operating parameters e.g. reactivity of monomers, types and concentration of surfactant, speed of agitation, different reaction parameters on reaction kinetics of synthesis of polyurea membrane by IP through experimental and modelling studies correlating rate of reaction with polymer film properties like film thickness, crystallinity and molecular weight distribution (MWD) (Janssen et al., 1992; Takahashi et al., 2008 and Sopena et al., 2005).

Study of the reported literature makes it clear that the Interfacial Polycondensation (IP) reaction for synthesis of polyurea can be effectively used to make a polymer shell to encapsulate different core materials in it for controlled/sustained release. Several process conditions, such as monomer concentration ratio, phase volume ratio and number of moles of limiting monomer, and intrinsic properties like polarity of organic solvents and partition coefficient of aqueous phase monomer have significant effect on product properties. The available literature on polyurea synthesis via IP shows that sufficient experimental work is still required to prove legitimate claim of IP for making effective formulation of polyurea microcapsules.

# CHAPTER 3

# Experimental and Characterization

As mentioned in the scope/objective part of the present work, the main aim is directed towards the study of controlled/sustained release behavior of microcapsules synthesized by IP reaction, this chapter intends to give necessary information about the core practical aspects of the research work.

This chapter is divided into four sections. In section 3.1 properties of different chemicals used for synthesis of polyurea microcapsules by interfacial polycondensation (IP) method, and physical and chemical properties of three different insecticides selected as core material are listed. Section 3.2 provides information about different laboratory scale equipments used for current experimental studies as well as different analytical and sophisticated equipments required for characterization. Section 3.3 covers detailed experimental procedure and experimental parameters studied for reaction kinetics of interfacial polycondensation (IP) at specific preparative conditions. And in section 3.4 experimental process for encapsulation of selected insecticides in polyurea microcapsules in order to study their controlled/sustained release behaviour is explained.

## 3.1 Materials

### 3.1.1 Chemicals used in the present work for synthesis of polyurea shell*:*

Chemicals (AR Grade) used for synthesis of polyurea shell are given in Table 3.1.

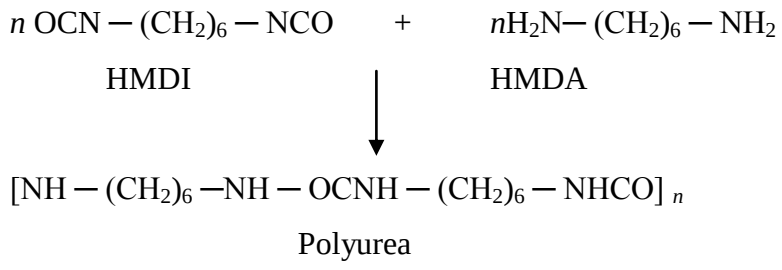
**TABLE 3.1:** Chemicals used for Synthesis of Polyurea Shell

| Sr. No. | Chemicals | Make |
|---|---|---|
| 1 | Hexamethylene-1, 6-diamine (HMDA) | Sigma-Aldrich, USA |
| 2 | Hexamethylene-1, 6-diisocyanate (HMDI) | Sigma-Aldrich, USA |
| 3 | Tween-85 | Sigma-Aldrich, USA |
| 4 | Methanol | Merck, Germany |
| 5 | *n*-Octane | S D fine chemicals Ltd. India |
| 6 | Cyclohexane | S D fine chemicals Ltd. India |
| 7 | Benzene | S D fine chemicals Ltd. India |
| 8 | Toluene | S D fine chemicals Ltd. India |
| 9 | *p*-Xylene | S D fine chemicals Ltd. India |
| 10 | Mesitylene | S D fine chemicals Ltd. India |

All above chemicals were used as supplied without further purification in the laboratory.

### *3.1.1.1 Monomers and their properties:*

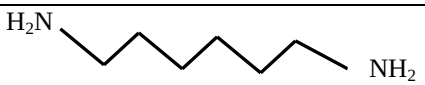
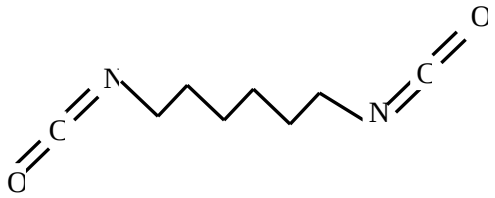
Polyurea has been synthesized by interfacial polycondensation of hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI). The reaction is:




Unlike many polycondensation reactions, this reaction produces no other low molecular weight product such as $H_2O$.

Physical and chemical properties of monomers hexamethylene-1, 6-diamine (aqueous phase monomer) and hexamethylene-1, 6-diisocyanate (oil phase monomer) of AR grade with purity>99% are listed in Table 3.2.

**TABLE 3.2:** Properties of monomers

| **Properties** | **Hexamethylene Diamine(HMDA)** | **Hexamethylene-1,6-diisocyanate (HMDI)** |
|---|---|---|
| Chemical formula | $C_6H_{16}N_2$ | $C_8H_{12}N_2O_2$ |
| Molecular weight | 116.208 gm/mol | 168.196 gm/mol |
| Appearance | colorless crystalline solid | colorless liquid |
| Density | 0.89 gm/cm$^3$, at 25°C | 1.048 gm/cm$^3$, at 25°C |
| Boiling point | 204°C | 255°C |
| Vapour pressure | 0.256 mm Hg, at 25°C | 0.05 mm Hg, at 25°C |
| Water solubility | Freely soluble in water | Reacts with water |
| IUPAC name | Hexane-1,6-diamine | 1,6-Diisocyanatohexane |
| Structure |  |  |

***3.1.1.3 Properties of emulsifier Tween-85:*** An oil/water emulsifier (purity > 99%)

Molecular formula: $C_{100}H_{188}O_{28}$

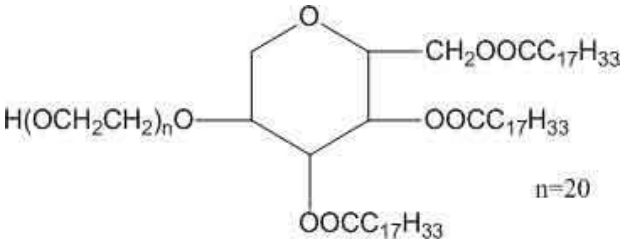
Molecular Weight: 1836 gm/mol

Synonym: Polyoxyethylenesorbitan trioleate

HLB value: 11

Density: 1.028 gm/cm$^3$, at 25°C

Structure:




***3.1.1.4 Properties of different organic solvents used in kinetic study of IP reaction:***

Different organic solvents: Cyclohexane, *n*-Octane, Benzene, Toluene, *p*-Xylene and Mesitylene used in experimental studies of reaction kinetics of interfacial

polycondensation of polyurea synthesis were of AR grade and were used without any additional processing. Their properties are listed in Table 3.3.

**TABLE 3.3:** Properties of different organic solvents used in kinetic study of IP reaction

| **Properties** | **Cyclohexane** | ***n*-Octane** | **Benzene** | **Toluene** | ***p*-Xylene** | **Mesitylene** |
|---|---|---|---|---|---|---|
| Chemical formula | $C_6H_{12}$ | $C_8H_{18}$ | $C_6H_6$ | $C_6H_5CH_3$ | $C_6H_4(CH_3)_2$ | $C_6H_3(CH_3)_3$ |
| Molecular weight | 84 | 114 | 78 | 92 | 106 | 120 |
| IUPAC name | Cyclohexane | Octane | Benzene | Methyl Benzene | 1,4-Di Methyl Benzene | 1,3, 5- Tri Methyl Benzene |
| Appearance | Colorless Liquid | Colorless Liquid | Colorless Liquid | Colorless Liquid | Colorless Liquid | Colorless Liquid |
| Density (gm/ $cm^3$) | 0.77 at 25°C | 0.69 at 25°C | 0.87 at 20°C | 0.87 at 20°C | 0.86 at 20°C | 0.86 at 20°C |
| Boiling Point | 80.74 °C | 125.6 °C | 80 °C | 110.6°C | 138.3°C | 164.7°C |
| Solubility in water | Insoluble | Insoluble | Insoluble | Insoluble | Insoluble | Insoluble |
| Viscosity (cP) | 1.02 at 17°C | 0.5151 at 25°C | 0.607 at 25°C | 0.56 at 25°C | 0.603 at 25°C | 0.72 at 25°C |
| Dielectric Constant | 2.0 | 1.95 | 2.28 | 2.40 | 2.30 | 2.20 |

***3.1.1.5 Insecticides as core material*:** Following three different insecticides are selected as a core material for encapsulation in polyurea shell:

(1) Chlorpyriphos (Pesticide)

(2) Cypermethrin (Pesticide)

(3) Pretilachlor (Herbicide)

These insecticides are received as gift samples from UPL Ltd. formerly United Phosphorous Ltd., Ankleshwar-Gujarat. All samples were of 98-99% purity. Properties of three insecticides are listed in Table 3.4.

**TABLE 3.4:** Physical and Chemical properties of various insecticides used as an active ingredient:

| **Properties** | **Chlorpyriphos** | **Cypermethrin** | **Pretilachlor** |
|---|---|---|---|
| Chemical formula | $C_9H_{11}Cl_3NO_3PS$ | $C_{22}H_{19}NO_3Cl_2$ | $C_{17}H_{26}NO_2Cl$ |
| Molecular weight (gm/mol) | 350.6 | 416.3 | 311.9 |
| Type of Insecticide | Organic Phosphate Pesticide | Pyrethroid Pesticide | Cloroacetamide Herbicide |
| Appearance | Colorless to white crystalline solid. | Pale yellow color semisolid | Colorless liquid |
| Vapour pressure | $2.02 \times 10^{-5}$ mmHg at 25°C | $1.70 \times 10^{-9}$ mmHg at 20°C | $9.97 \times 10^{-7}$ mmHg at 20°C |
| Density (gm/ $cm^3$) | 1.4 at 20°C | 1.25 at 20°C | 0.93 at 20°C |
| Solubility in water | 1.4 mg/L at 25°C. | 0.9 mg/L at 20 °C | 0.5 mg/L at 20 °C |
| Solvents | *i*-Octane, *n*-Octane, Methanol, Acetone, Benzene, Diethyl Ether | Ethyl Acetate, *n*-Hexane, *i*-Octane, *n*-Octane, Methanol, Acetone, Xylene | Diethyl Ether, *n*-Octane, Xylene, *i*-Octane, Methanol, Acetonitrile |
| Soil Sorption Coefficient (Koc) | 360 to 31,000 depending on soil type and environmental conditions | 60 to 24, 000 depending on soil type and environmental conditions | 50 to 542 depending on soil type and environmental conditions |
| Octanol-water partition coefficient (log | 4.70 | 6.60 | 4.08 |
| $LD_{50}$ | 135 mg/kg (for rats) | 250 mg/kg (for rats) | 1120 (for rats) |
| Soil Half-life (days) | 30 | 30 | 20 |

## 3.2 Equipments used for laboratory scale synthesis and characterization of microcapsules:

Following laboratory scale equipments were used in this experimental work.

### 3.2.1 Equipments and Instruments

#### *3.2.1.1 High Speed Emulsifier*

Mechanical stirrer, (REMI 120-D) equipped with a shrouded, four-bladed, pitched turbine type impeller as shown in Fig. 3.1 was used for emulsion preparation.

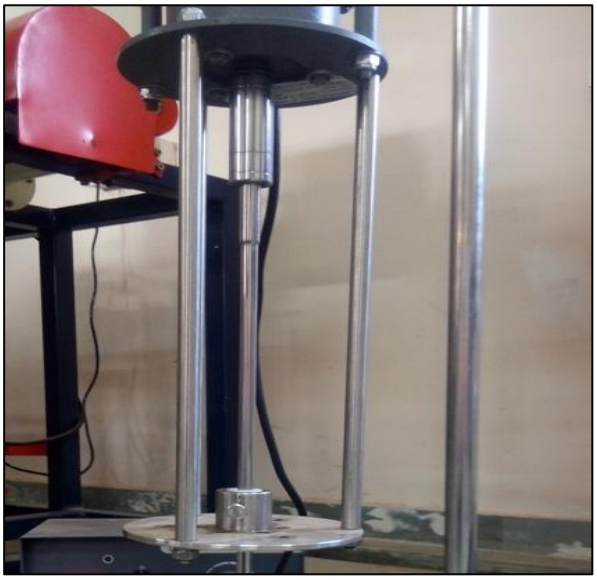


**Figure 3.1** High speed emulsifier

#### *3.2.1.2 High precision analytical balance*

Analytical balance with high accuracy (Mettler Toledo: MS105DU/M), has readability of 0.1 mg to 0.001 mg.

#### *3.2.1.3 Magnetic stirrer*

Laboratory scale magnetic stirrer as shown in Fig. 3.2 equipped with speed stability and control with high accuracy (REMI: 5MLH) was used in this experimental work.


**Figure 3.2** Magnetic stirrer with speed controller

### *3.2.1.4 Water Bath*

A laboratory scale water bath made of S.S. (Labline, India) was used equipped with microprocessor based temperature controller for operating temperature 5°C to 99 °C, 230 V, AC, 50 Hz, with accuracy of ± 0.5°C

### *3.2.1.5 Advanced PLC based pH Logger based data acquisition system:*

This equipment was used for reliable measurement of true pH and temperature. It stores the results in a data acquisition system. Advanced PLC based pH logger as shown in Fig. 3.3 (A) equipped with high responsive pH probe (which is constructed from chemically-resistant Ryton Polyphenylene Sulfide (PPS), accuracy ± 0.1 pH, in range of 0-14 pH with a resolution of 0.01 digit) as shown in Fig. 3.3 (B) was used. The logger was also equipped with an RTD sensor for constant and accurate monitoring of temperature (operating range 0°C to 150 °C).


**Figure 3.3 (A)**
Advanced PLC based pH logger


**Figure 3.3 (B)**
pH probe

### *3.2.1.6 Vacuum Filtration Assembly*

Vacuum filtration apparatus for clamp seals filter membrane between flanges on funnel top and funnel stem, filter medium support, aluminum clamp, stopper (except standard taper units) and filtration flask was used for filtering the polymer formed during the reaction.

### *3.2.1.7 Vacuum Dryer*

A laboratory scale vacuum dryer (Labline, India) with heating range of 5 ºC to 200 ºC, 230 V, AC, 50 Hz equipped with a vacuum pump was used for drying the polymer microcapsules.

## 3.2.2 Analytical and sophisticated instruments for characterization:

### *3.2.2.1 Fourier Transform Infrared Spectrophotometer*

Fourier Transform-Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures. In this experimental work the functional groups of polyurea were examined using FTIR spectrophotometer (Spectrum One, Perkin Elmer).

The spectrum was recorded utilizing infrared light in the range of 400 $cm^{-1}$ to 4000 $cm^{-1}$.

### *3.2.2.2 X-Ray Diffractometer*

The powder X-ray analysis of polyurea samples was recorded using Bruker powder X-ray diffractometer (Model D2 Phaser, Bruker, USA). X-ray diffraction at with high intensity CuKα1 radiation (ʎ=1.54060$A^0$). The XRD spectrum was noted for 2θ= 5º to 50º.

### *3.2.2.3 Differential Scanning Calorimeter (DSC)*

DSC analysis is used to measure melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, precipitation energy and temperature. In this experimental work, thermal stability of polyurea was checked with DSC-1 METLER TOLEDO in the range of temperature $30^0$C to 500 $^0$C at a heating rate of $10^0$C/min. Nitrogen is used as a purging gas.

### *3.2.2.4 Optical Microscope*

Appearance of polyurea microcapsules was observed under bright field microscope (Leica microscope DM750) and recorded for different resolution 40X to 100 X using a digital camera (Canon A 3100, 14.2 Mega Pixels) connected through LSM image browser in computer system.

### *3.2.2.5 Scanning Electron Microscope*

To measure surface morphology of polymeric microcapsules field emission scanning electron microscopy JEOL FESEM (JSM-6701F) at 5 KV and scanning electron microscope (FEG SEM, Phillips) were used. Particles as a dry powder were mounted onto aluminium stubs and their surface was coated with gold film (thickness of 20 nm) in an argon atmosphere using a gold sputter module in a high vacuum.

### *3.2.2.6 Particle Size Analyzer*

A particle size analyzer (Malvern Mastersizer 2000, UK) was used and Particle Size Distribution (PSD) was prepared by laser diffraction method. Sample was diluted and loaded to the sample distribution unit under constant agitation until an obscuration of 10-15 units was reached. The size distribution was performed five times for an individual samples. Size distribution of particles was characterized using the volume mean diameter (μm) and the width of particle size distribution is given by the span.

### 3.2.3 Equipments used for studies on controlled/sustained release of insecticides:

#### *3.2.3.1 Sonicator*

1 gm of microcapsules in 100ml methanol was stirred using a single probe sonicator, UP200S for 20 min. To avoid the rise of temperature during sonication, a water bath was used so that the temperature was maintained at (28-30) $^{o}$C.

#### *3.2.3.2 UV Spectrophotometer*

For spectroscopy measurement and analysis of controlled/sustained release of selected insecticides through polyurea shell in methanol, UV-1800, UV-VIS Shimadzu, Japan was used.

Details of analytical method for various equipments listed in section 3.2.8 and 3.2.9, their important construction features and applications are given in Appendix-I.

### 3.2.4 Software used

Microsoft excel (Windows 2007) was used to construct the different plots of experimental data points. X-ray diffractogram peaks were analyzed using ORIGIN-Pro-8.5.1 (a data analysis and graphing software).

## 3.3 Experimental process for synthesis of polyurea microcapsules:

### 3.3.1 Experimental set-up

Experiments were conducted in a laboratory scale interfacial polycondensation (IP) reaction set-up as shown in Fig. 3.4.

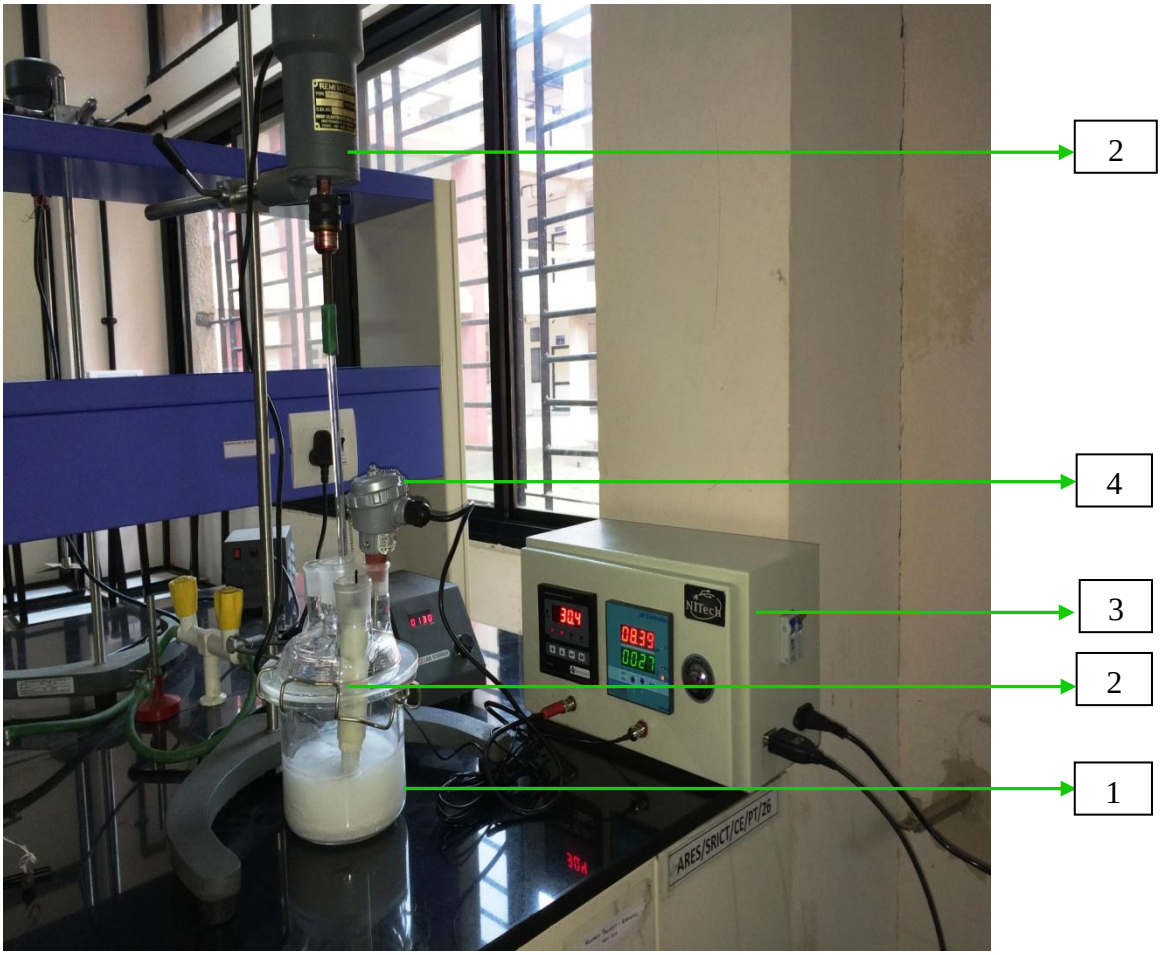



**Figure 3.4** Experimental set up

Equipment used in this experimental set up:

1- Three-neck borosilicate flat bottom glass reactor equipped with lid

2- High responsive pH probe

3- Advanced PLC based pH logger connected to computer accessories

4- Tank RTD temperature probe

5- Overhead mechanical stirrer

### 3.3.2 Experimental preparative conditions/process variables

Following experimental parameters were considered to study interfacial polycondensation reaction kinetics for constant volume of aqueous phase of 110 ml.

1) Monomer Mole Ratio=R
2) Limiting Monomer per unit volume of dispersed phase= $n_L/V_d$
3) Phase volume ratio= $[V_d/V_c]$
4) Reaction Temperature=T $^0$C

Values of specific preparative conditions studied in the IP reaction experiments are as mentioned in Table 3.5.

**TABLE 3.5** Experimental parameters employed in IP reaction

| **Sr. No.** | **R** | **$n_L/V_d$ (Kmol/ $m^3$)** | **$[V_d/V_c]$** | **T ($^0$C)** |
|---|---|---|---|---|
| 1 | 0.6 | 0.18 | 0.05 | 20 |
| 2 | 1.2 | 0.36 | 0.1 | 25 |
| 3 | 2.4 | 0.72 | 0.2 | 35 |

### 3.3.3 Experimental procedure

The polyurea microcapsules were synthesized by interfacial polycondensation of Hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI) according to the procedure reported in the literature (Yadav et al., 1997; Wagh et al., 2009; Dhumal and Suresh, 2010).

A two- step procedure is adopted and total volume of aqueous phase is constant in all experiments. In the first step, oil-in-water emulsion (oil: water: 1:2 v/v) was prepared by dispersing the organic phase; a solution of a desired concentration of HMDI in solvent n-octane in distilled water, with Tween-85 (4 % v/v, distilled water) as the emulsifying agent. The emulsification of organic phase and aqueous phase was carried out using a mechanical stirrer equipped with a shrouded, four bladed, pitched turbine impeller, stirring at 3000 ± 20 rpm for 15 min. This step was identically performed for all of the experiments to obtain the same drop size distribution of emulsion and particle size of microcapsules as reported in the literature (Yadav *et al.*, 1996).

In the second step, an appropriate volume of this emulsion (as per set value of phase volume ratio, $V_d/V_c$) was added to an aqueous solution of HMDA, and the reaction mixture was continuously stirred at 200 rpm. Interfacial polycondensation was carried out between HMDI in dispersed phase (present in the emulsion) and HMDA in aqueous phase. The

reaction temperature was continuously monitored and controlled with a temperature probe attached to a data acquisition system. The progress of reaction was monitored by measuring the change of pH of the reaction mixture with the use of an advanced Programmable Logical Controller based pH Logger equipped with a high responsive pH probe until it reached a constant value. Polyurea microcapsules were of an average particle size of 3.20 μm finally filtered, washed with n-octane, dried under vacuum and stored in a moisture free environment. Table-3.5 shows the experimental conditions employed to study effect of various preparative parameters on the rate of reaction and properties of polyurea shell formed influencing the release of active ingredient (AI).

Four different solvents were used (i.e. Benzene, Toluene, *p*- Xylene and Mesitylene) in this experimental work, experiments for some selected parameters from Table 3.5 at constant phase volume ratio of 0.05 were conducted for all four solvent systems.

## 3.4 Experimental process for synthesis of insecticide- loaded polyurea microcapsules:

A selected active ingredient (AI) from amongst chlorpyriphos, cypermethrin and pretilachlor was dissolved in *n*-octane (4 % w/v) and encapsulated as the core material in polyurea microcapsules that were synthesized in a sequence of steps as shown in Fig. 3.5 for the condition of bulk mole ratio of monomers (R) = 1.2 and 2.4 and number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$) = 0.18, 0.36, and 0.72 at constant temperatures of 28 to 30 ºC.

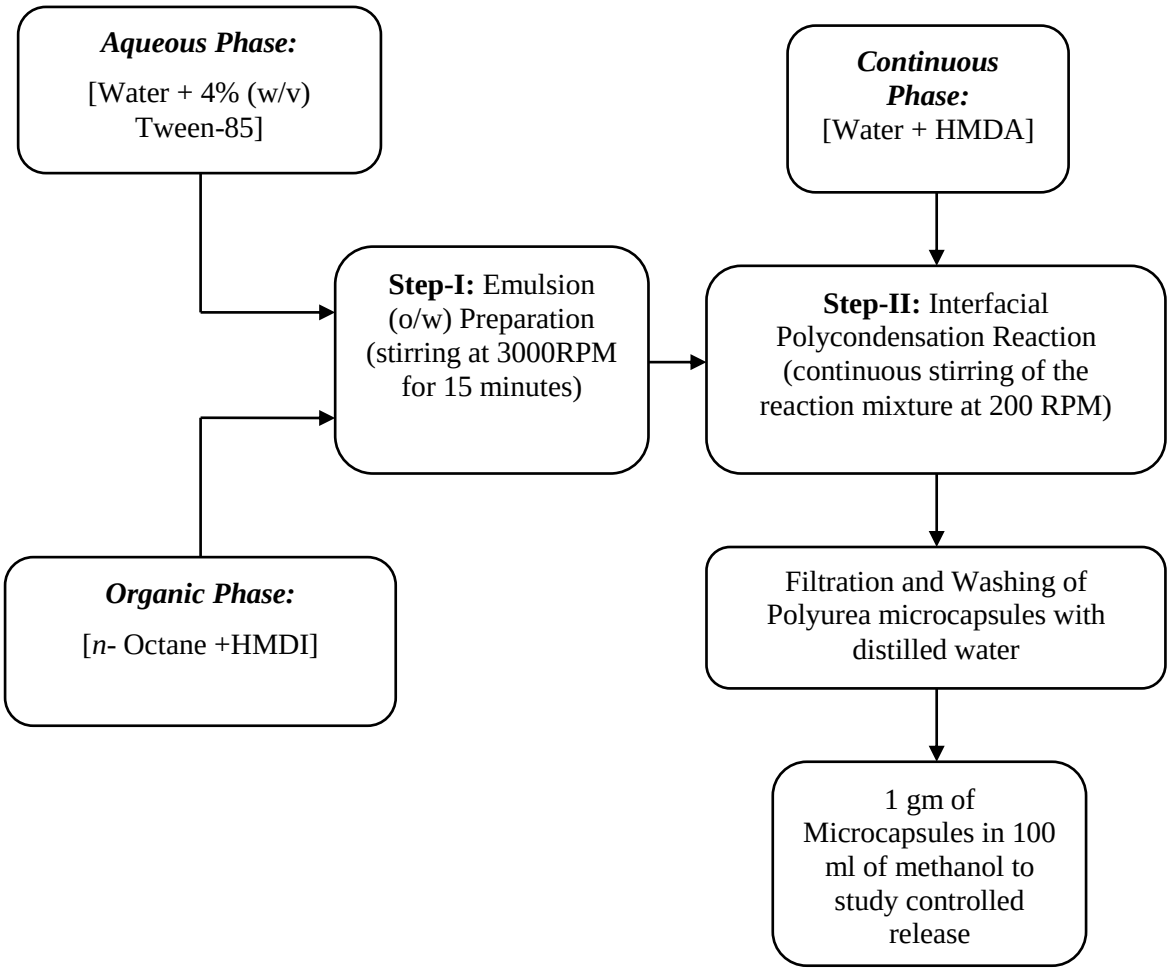



**Figure 3.5** Steps in the synthesis of polyurea microcapsules containing insecticide as a core material via interfacial polycondensation (IP)

### 3.4.1 Release rate measurement

Fig. 3.6 represents steps in the measurement of release rate of insecticide through polyurea shell. Polyurea microcapsules containing insecticide sample (as an active ingredient (AI) and core material) with constant loading content of 4% (w/v) were filtered, washed with

distilled water and lightly blotted to remove excess surface moisture. The microcapsule (1 gm) was added into the release cell containing 100 mL methanol and kept in a sonicated bath at 28 ºC. At regular intervals, 10 mL of sample was withdrawn using a syringe, filtered with filter paper and its absorbance recorded using a pre-calibrated UV-spectrophotometer (UV- 1800, UV-VIS Shimadzu, Japan). Fresh methanol was added to the cell to maintain constant volume of the continuous phase.

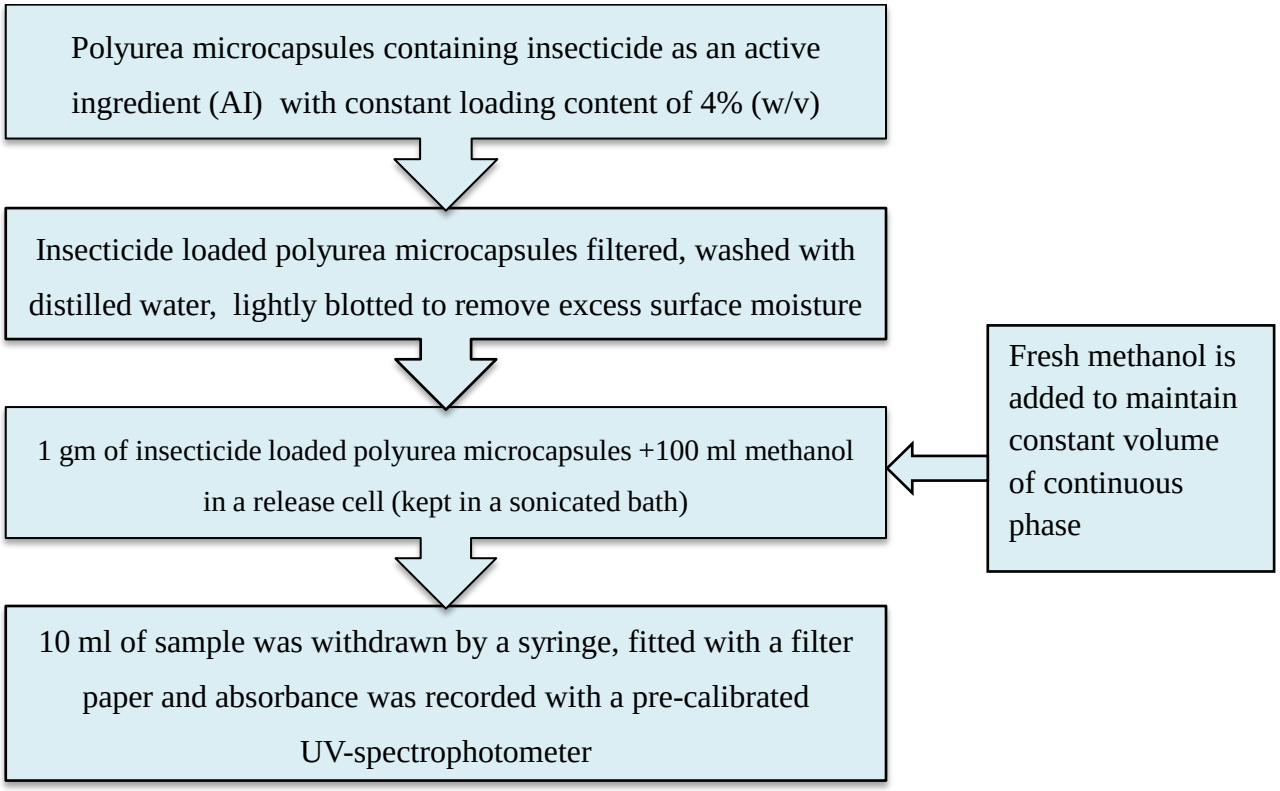



**Figure 3.6** Steps in measurement of release rate of insecticide through polyurea shell

The method of (Takashi et al., 2000) and (Scopena et al., 2005) were followed to determine encapsulation efficiency (%) and cumulative release rate (%) of insecticide on the basis of initial input of insecticide to the feed.

### 3.4.2 Calculation of encapsulation efficiency (%)

It indicates how effectively an active ingredient (AI) as a core material has been encapsulated inside the polyurea shell. It measures the percentage of core material present in the microcapsules and mathematically expressed as:

$$\text{Encapsulation efficiency (\%)} = \left[\frac{\text{weight of insecticide encapsulated in microcapsules}}{\text{Total weight of insecticide taken in feed}}\right] \times 100$$

(Takahashi et al., 2000); (Xiao et al., 2018)

### 3.4.3 Calculation of cumulative release (%)

In release rate experimental studies as discussed in 3.4.1, concentration of insecticide released from microcapsules at time (t) was determined using the observed wavelength in standard calibration curve of UV absorption for sample insecticide in methanol solvent system. Mathematically this release rate of insecticide is represented as:

Release of insecticide (%)

$$= \left[\frac{\text{weight of insecticide released from microcapsules at any time, t}}{\text{Total weight of insecticide encapsulated in microcapsules}}\right] \times 100$$

(Scopena et al., 2005); (Xiao et al., 2018).

In the present experimental work encapsulation efficiency (%) and cumulative release (%) were calculated for chlorpyriphos, cypermethrin and pretilachlor for their constant loading 4% (w/v) formulation in polyurea microcapsules synthesized under different preparative parameters.

# CHAPTER 4

# Results and Discussions

In the present chapter experimental results of polyurea microcapsule synthesis by interfacial polycondensation (IP) method using hexamethylene-1, 6-diamine (HMDA) as an aqueous phase monomer and hexamethylene-1, 6-diisocyanate (HMDI) as an oil phase monomer under different preparative conditions of several bulk mole ratios of the monomers (R) (i.e., initial moles of HMDI to initial moles of HMDA), the number of moles of limiting monomer per unit volume of the dispersed phase ($n_L/V_d$), and reaction temperature (T) are discussed in section 4.1.

Experimental findings to study effect of four different organic solvents i.e. Benzene, Toluene, *p*-Xylene and Mesitylene on IP reaction kinetics are presented in section 4.2.

Polyurea samples synthesized under different preparative conditions were characterized by several characterization techniques like FTIR, XRD, DSC PSD, SEM and TGA their results are discussed in section 4.3.

In section 4.4, results of controlled release experiments are discussed to study encapsulation efficiency of three different insecticides chlorpyriphos, cypermethrin and pretilachlor in polyurea shell and their rates of release, into methanol. The influence of preparative conditions on Polyurea shell and the release rate of insecticide is discussed in detail in this section.

## 4.1 Studies on reaction kinetics of synthesis of polyurea microcapsules by Interfacial Polymerization (IP)

### 4.1.1 Measurement of rate of IP reaction

Polyurea microcapsules were synthesized according to procedure discussed in 3.3. Reaction of hexamethylene-1, 6-diamine (HMDA) as an aqueous phase monomer and hexamethylene-1, 6-diisocyanate (HMDI) was carried out at ambient condition of temperature and pressure. In this reaction the diamine has a very high nucleophilic character and superior reactivity with diisocyanate (Caraculacu and Coseri, 2001) which results into a faster reaction. Reaction starts as soon as the addition of emulsion containing HMDI is completed in an aqueous solution of HMDA. Solution of HMDA is alkaline in nature, as it was consumed during IP reaction, value of pH decreased in from 11 to 7. End of the reaction was indicated by attainment of a constant value of pH.

Kinetic data for the progress of the reaction was monitored by measuring the change of pH of the reaction mixture (i.e. decrease in concentration of HMDA in aqueous phase) and plotted against reaction time. Several such plots are made. One sample plot for polyurea synthesis by IP with *n*-Octane as a solvent is shown in Fig. 4.1.

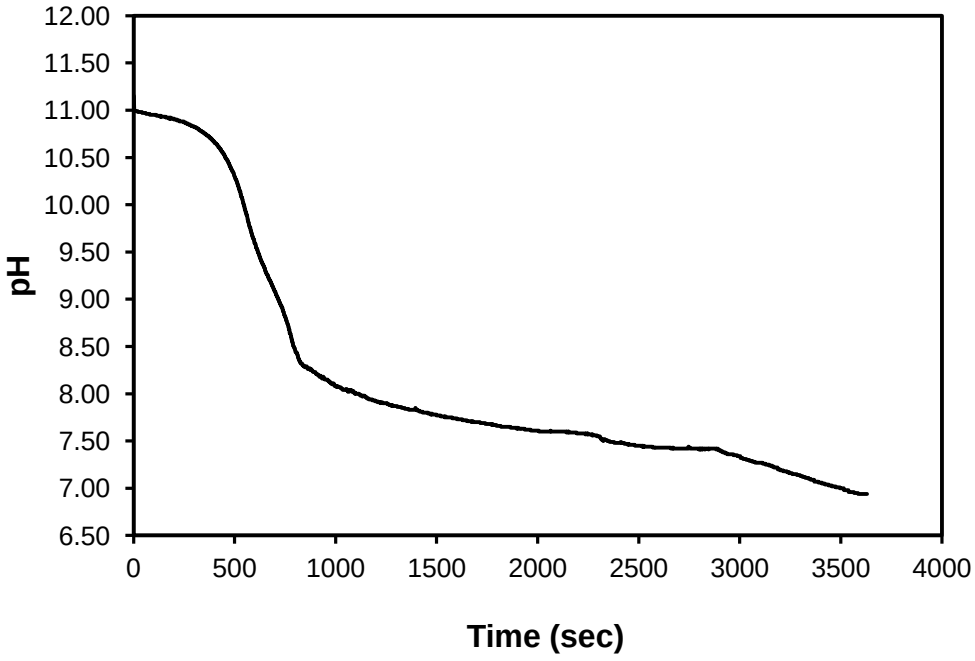



**Figure 4.1** Rate of IP reaction for monomer mole ratio, R=2.4
(Other conditions: $n_L/V_d$ =0.72, T=25°C, $V_d/V_c$=0.05, solvent *n*-Octane)

### 4.1.2 Effect of monomer mole ratio

Bulk monomer mole ratio (R) represents the ratio of concentration of HMDI to that of HMDA. In this experimental work three different values of R i.e. 0.06, 1.2 and 2.4 were studied for sample number R18, R21 and R27 respectively. All other parameters were constant. For R<1, the limiting monomer is HMDI and for R>1 the limiting monomer is HMDA. Organic solvent selected was *n*-Octane for this study which was further used as a solvent for insecticide samples encapsulated as a core material in polyurea.

Fig. 4.2 shows the effect of R on reaction rate for constant conditions of $V_d/V_c$ = 0.05, $(n_L/V_d)$ =0.36 and T=25 $^0$C. Since the reaction takes place on the organic side of the interface and reaction is kinetically controlled; the variation in concentration of HMDI results into change in R (Wagh et al., 2008 and Dhumal & Suresh, 2010). High value of R results into increase in concentration of HMDI and reaction is accelerated therefore reaction rate is highest for R=2.4 than that of R=0.6 and R=1.2.

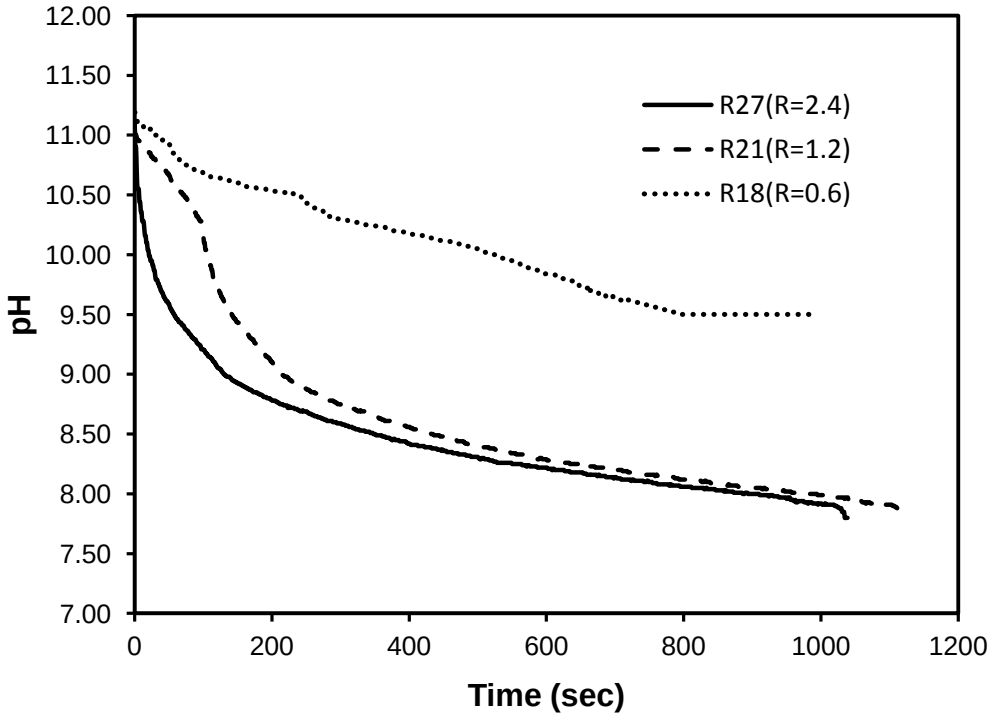



**Figure 4.2** Effect of monomer mole ratio (R) (other conditions $n_L/V_d$ =0.36, T=25$^0$C, $V_d/V_c$=0.05, Solvent: *n*-Octane)

For other sets of data where mesitylene is used as an organic solvent (sample number R28 and R38) reaction rate also increases with the increase in the value of monomer mole ratio (R) as shown in Fig. 4.3

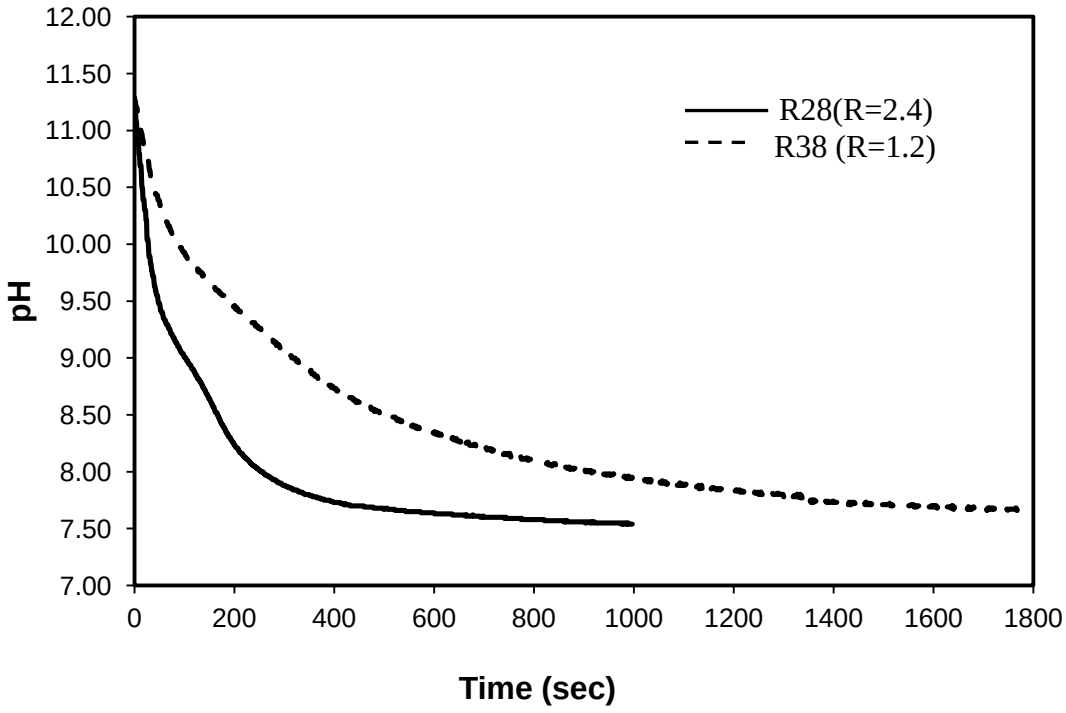



**Figure 4.3** Effect of monomer mole ratio (R) (other conditions $n_L/V_d$ =0.36, T=35$^0$C, $V_d/V_c$=0.05, Solvent: Mesitylene)

### 4.1.3 Effect of moles of limiting monomer per unit volume of dispersed phase

As shown in Fig. 4.4, increase in number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$) decreases the rate due to increase in polymer film thickness as diffusion mechanism is responsible for lowering the reaction rate in case of thicker film.

The visual observation of Fig. 4.2, Fig. 4.3 and Fig. 4.4 show that there always appears a hump in the pH-time plot. The same observation had been noted by Wagh et al., 2009, the time at which the hump appears may be an insinuation of solid polymer phase appearance creating an instantaneous resistance to the transfer of aqueous phase monomer molecule across the phase-interface.

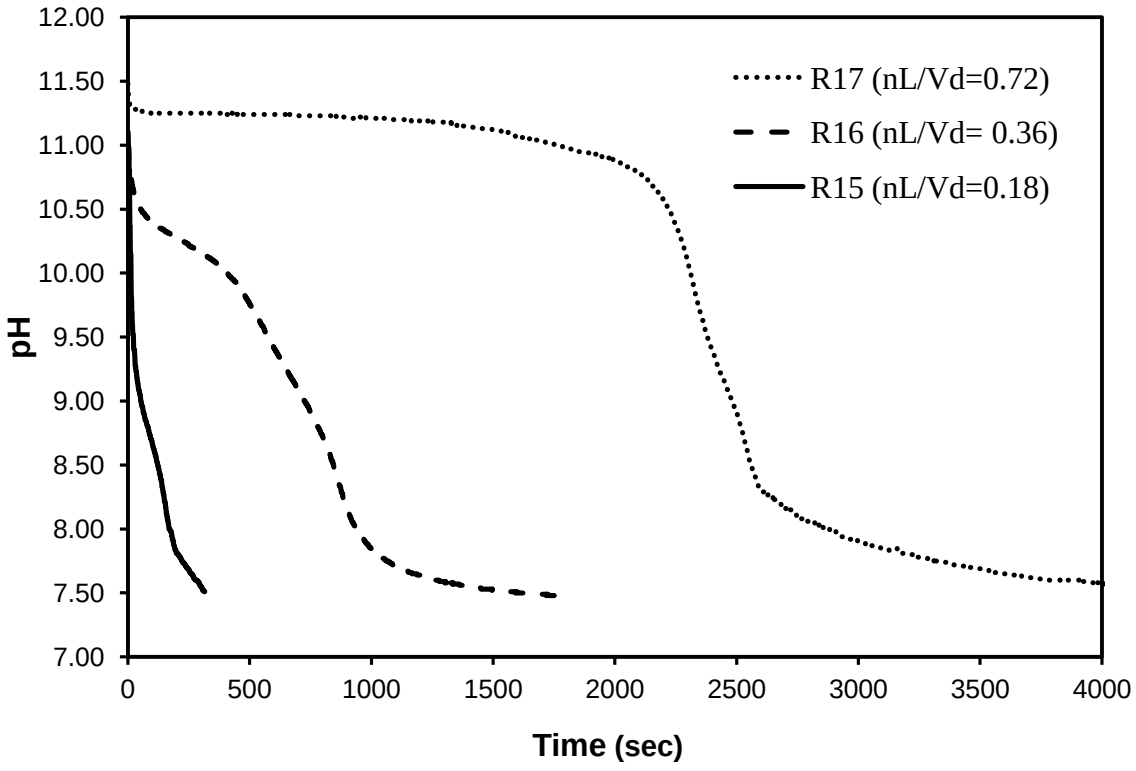



**Figure 4.4** Effect of ($n_L/V_d$) on the rate of IP reaction (other conditions R=2.4, T=$20^0$C and $V_d/V_c$=0.05, Solvent: *n*-Octane)

### 4.1.4 Effect of phase volume ratio

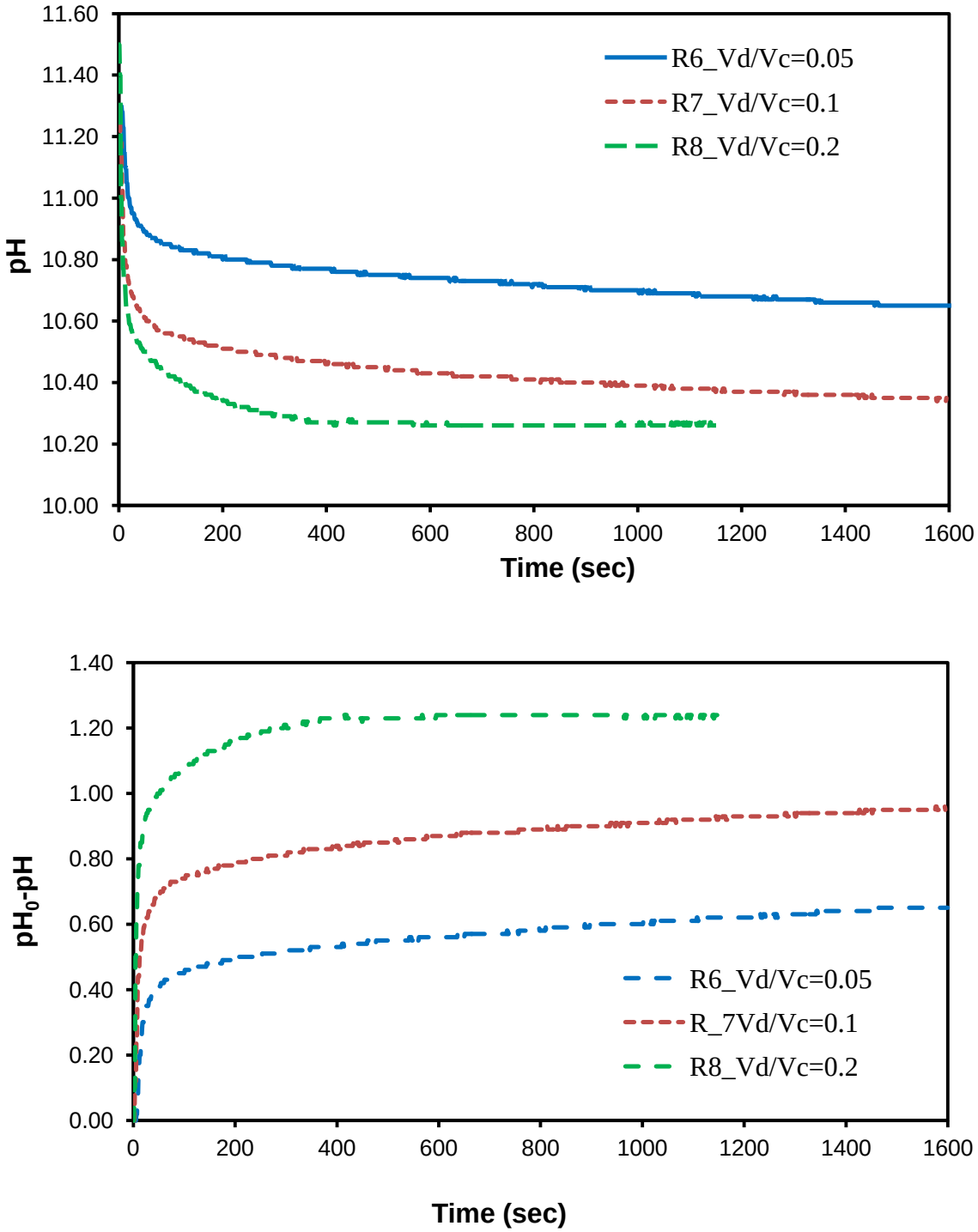



**Figure 4.5** Effect of phase volume ratio ($V_d/V_c$) on the rate of IP reaction (other conditions: R=0.6, T=25$^0$C and ($n_L/V_d$) =0.18, Solvent: cyclohexane)

Fig. 4.5 shows effect of ratio of volume of dispersed phase to that of continuous phase i.e.

$V_d/V_c$ .Cyclohexane was used as a solvent and by maintaining other conditions at, R=0.6, T=$25^0$C and ($n_L/V_d$) =0.18. Phase volume ratio is directly correlated with interfacial area per unit of dispersion volume as well as initial concentration of aqueous phase monomer HMDA. In this case for R=0.6, HMDI is limiting monomer and with increment in volume of dispersed phase the concentration of HMDI as well as interfacial area increases the reaction rate of interfacial polycondensation. The similar effect has been discussed for R=0.8 and $n_L/V_d$ =0.5 (Wagh et al., 2008).

*n*-Octane was used as organic solvent for runs R24 and R25, monomer mole ratio value R=2.4 and the limiting monomer is HMDA ($n_L/V_d$ =0.36) the reaction rate was found to be increased with increment in phase volume ratio from 0.05 to 0.1 as shown in Fig. 4.6. Therefore, it is observed that the overall reaction of polyurea synthesis via interfacial polycondensation by and large, is a mass transfer controlled reaction.

Intial value of hexamethylene diamine (HMDA) in aqueous phase is indicated by $pH_0$. As interfacial polycondensation reaction proceeds pH falls rapidly and the rate of reaction can be indicated by the value of ($pH_0$-pH).

Polyurea formed under condition of R=0.6 and $n_L/V_d$ = 0.18 is of very less yield since R<1, HMDI is a limiting monomer and the reaction occurs on the organic side of the interface leaves HMDA unreacted. These preparative conditions were omitted from the rest of experimental work.

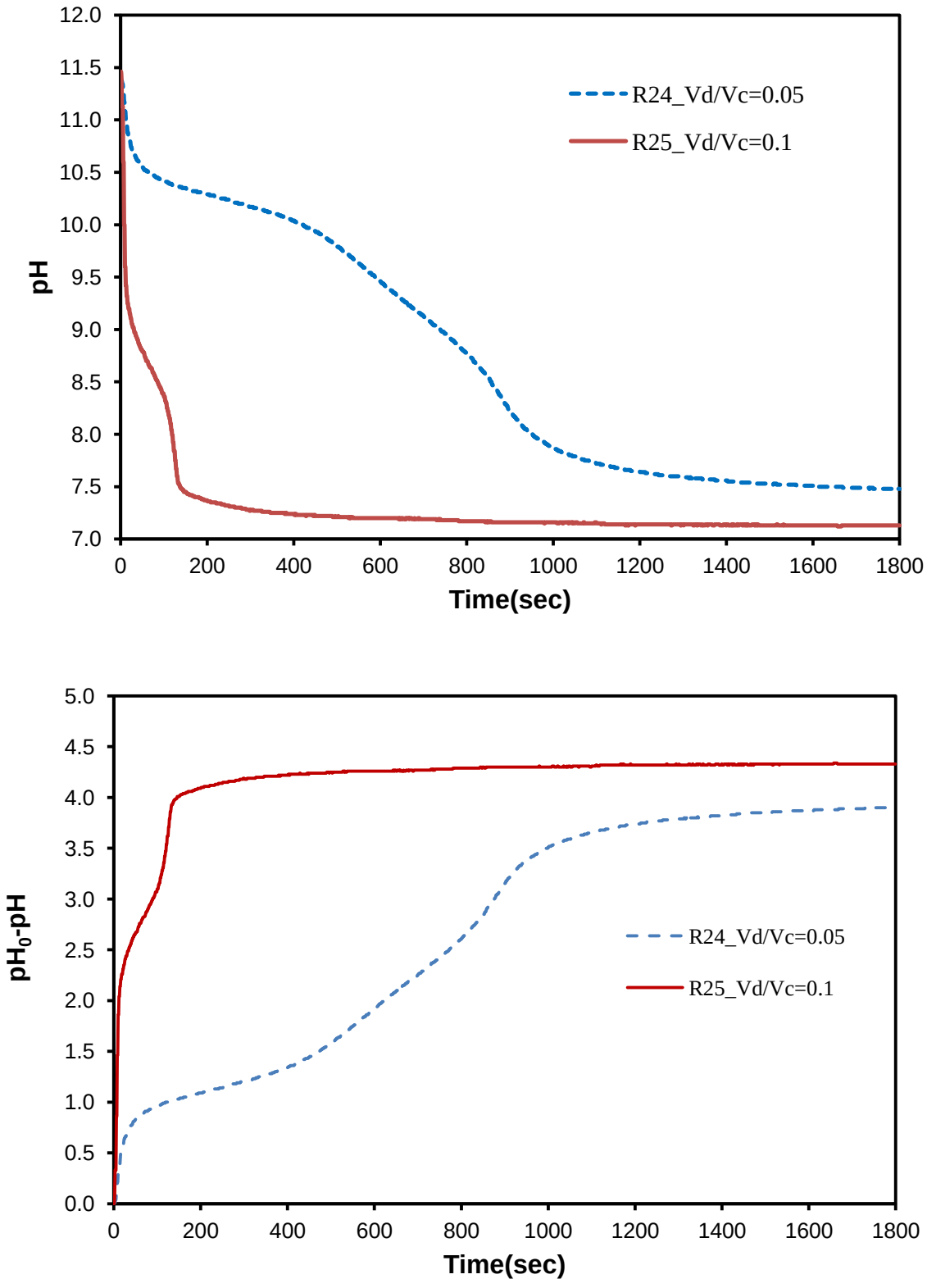



**Figure 4.6** Effect of phase volume ratio ($V_d/V_c$) on the rate of IP reaction (other conditions: R=2.4, T=25$^0$C and ($n_L/V_d$) =0.36, Solvent: *n*-Octane)

### 4.1.5 Effect of reaction temperature

One of the objectives of the present research work is to study the effect of reaction temperature on reaction kinetics of interfacial polycondensation (IP). As reported in literature polyurea microcapsules were synthesized from different monomers at ambient temperature conditions; Yan et al., 1995, Moghbeli et al., 2011,synthesized polyurea microcapsules using toluene 2,4,-diisocyanate (TDI) and diethyle triamine (DETA) monomers at 298K; polyurea microcapsules from monomers hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI) at reaction temperature of 28°C to 30°C were synthesized by Yadav et al.,1996 and Wagh et al., 2009. Reaction temperature is one of the important process variables and to our knowledge, no experimental data are available on the effect of temperature on polyurea synthesis via IP reaction. Therefore, experimental kinetic data are reported for three different reaction temperatures i.e. 20°C, 25°C and 35°C to study effect of reaction temperature on polyurea synthesis by IP.

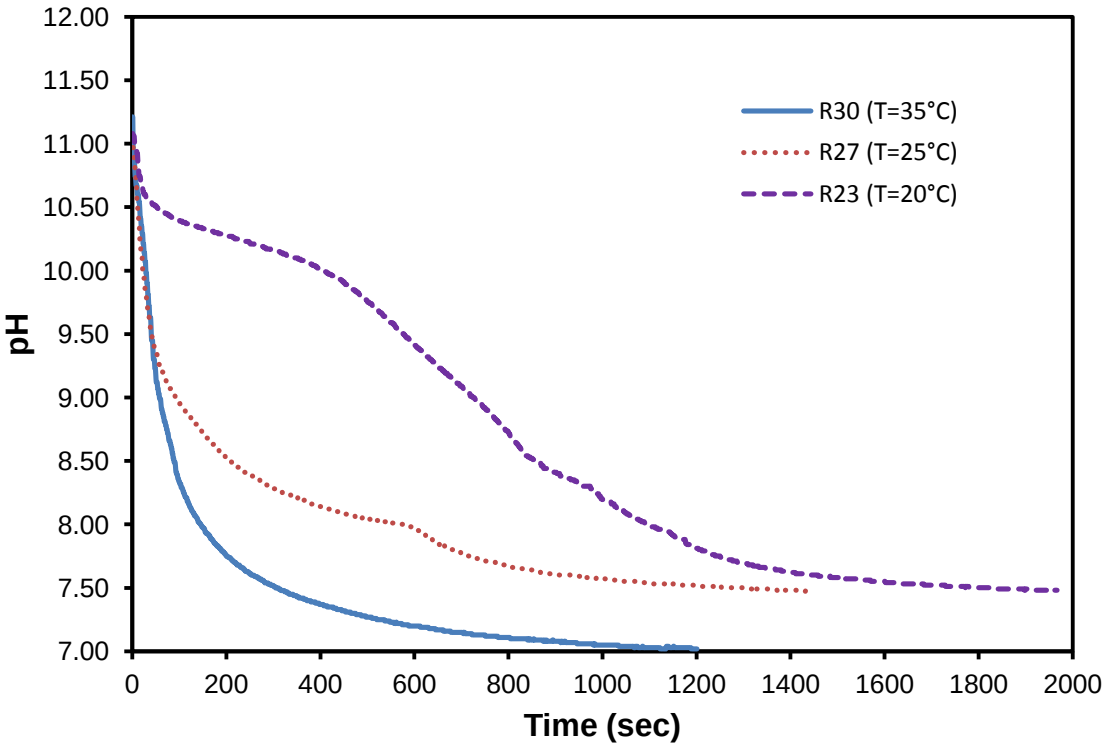



**Figure 4.7** Effect of temperature on rate of IP reaction (other conditions: R= 2.4, $n_L/V_d$ = 0.36, Vd/Vc = 0.05, Solvent *n*-Octane).

In our experiments, as expected, it is observed (Fig. 4.7) that the reaction is faster at 35°C compared to that at other two temperatures (25°C and 20°C). Increase in reaction temperature promotes transfer of HMDA from aqueous phase to organic phase by increasing its diffusion coefficient and its partition coefficient which results into increase in reaction rate. Simillar results were obtained in the case of polyamide formation where the diffusion of diamine was increased with increase in temperature resulted into higher rate of formation of polyamide membrane. Gaudin F., 2012, observed that the partition coefficient of diol increased with increase in temperature during formation of poly (urethane-urea) nanocapsules membrane. This resulted into increase in diisocyanate monomer conversion rate due to increase in temperature.

As shown in Fig. 4.7 for run number R30 at 1200 second, reaction is almost complete at 35 °C while for run number R23 the reaction is only 60% completed at 20 °C and for run number R27 reacttion is 65% completed at 25 °C.

## 4.2 Effect of different organic solvents on reaction kinetics

One of the objectives of the current research work is to study the effect of different organic solvents (for organic phase monomer, HMDI) on reaction kinetics. Four different organic solvents, (i) Benzene (ii) Toluene (iii) p-Xylene and (iv) Mesitylene with incremental order of methyl pendant group were selected, experiments for some selected parameters from

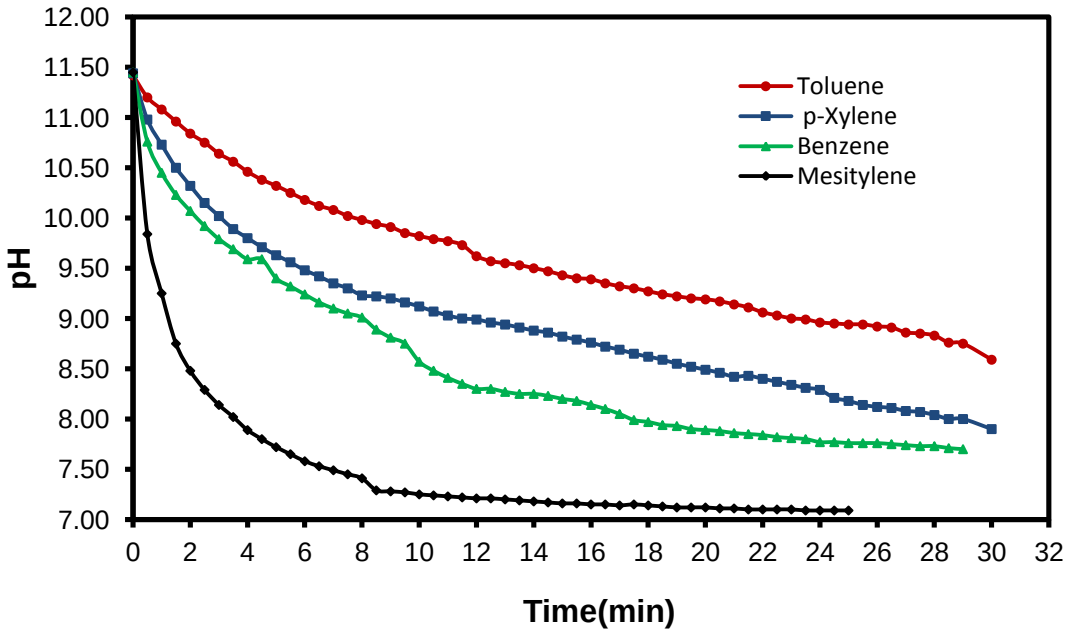



**Figure 4.8** Effect of different organic solvents on rate of IP reaction
(other conditions:R = 1.2, $n_L/V_d$ = 0.72, $V_d/V_c$ = 0.05 and T= $30^0$C)

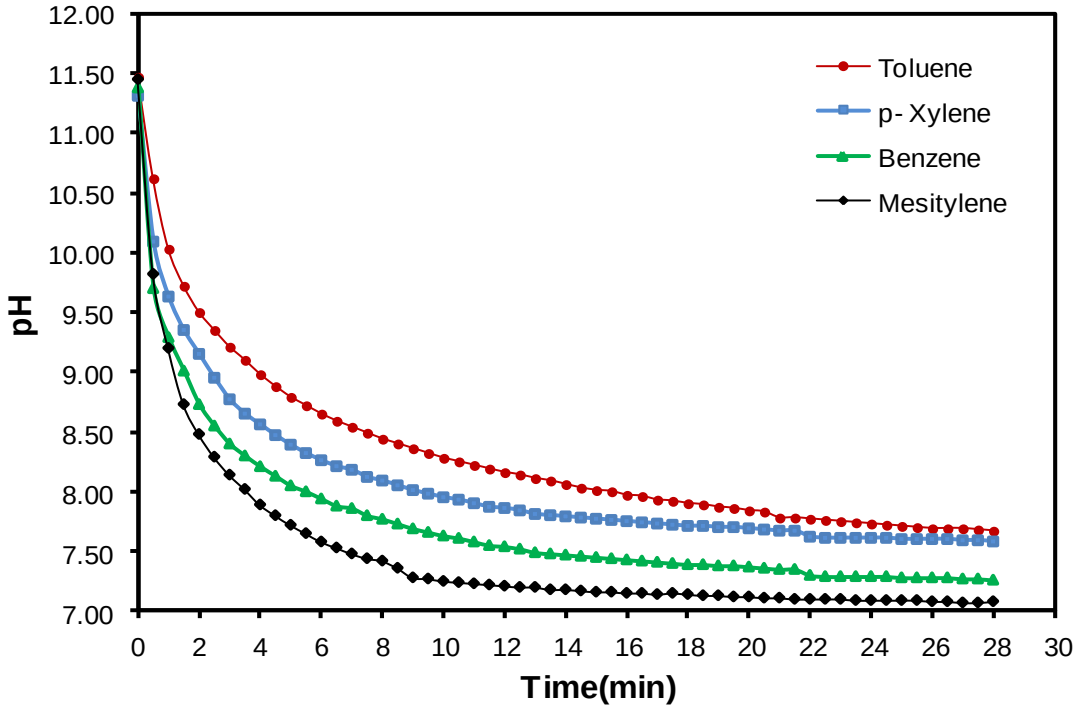



**Figure 4.9** Effect of different organic solvents on rate of IP reaction
(other conditions: R = 2.4, $n_L/V_d$ = 0.36, $V_d/V_c$ = 0.05 and T= $30^0$C)

Table 3.5 at constant phase volume ratio of 0.05 were conducted for all four solvent systems and the experimental kinetic data plotted as shown in Fig. 4.8 and Fig. 4.9. Dielectric constants for selected organic solvents reported in the literature (T. J. Bruno, P. D.N. Svoronos, 2011 and D. R Lide, 2004) are as shown in Table 4.1:

**TABLE 4.1:** Value of dielectric constant of different organic solvents:

| **Organic solvent used to study reaction kinetics** | Benzene | Toluene | p-Xylene | Mesitylene |
|---|---|---|---|---|
| **Dielectric Constant** | 2.28 | 2.40 | 2.30 | 2.20 |

Order of increment in dielectric constant of four different organic solvents used in this study is represented as: Toluene (2.40) > p-Xylene (2.30) > Benzene (2.28) > Mesitylene (2.20). Dielectric constant for water is 80 at 20°C.

Polarity of solvent is directly related with its dielectric constant. As value of dielectric constant increases polarity of solvent is also increases. Water has high polarity so its dielectric constant value is high. In present studies toluene has the highest polarity and mesitylene has the lowest polarity.

From Fig. 4.8 (R = 1.2, $n_L/V_d$ = 0.72, $V_d/V_c$ = 0.05 and T= $30^0$C and Fig. 4.9 (R = 2.4, $n_L/V_d$ = 0.36, $V_d/V_c$ = 0.05 and T= $30^0$C) it was observed that reaction rate decreases with the increase in the polarity of organic solvent irrespective of number of methyl pendant group associated in molecular structure of organic solvent.

It can be therefore, said that solvent polarity with respect to aqueous medium is a more influencing parameter on the rate of reaction than the pendant group in its molecular structure.

Hughes- Ingold rules (Christian Reichardt and Thomas Welton, 2011) for homogeneous reactions of similar type where an increase in solvent polarity decreases the rates of reactions is valid in this condition. This experimental observation of our work can also be considered as a corroborative evidence for the reaction taking place on the organic phase side.

## 4.3 Characterization

**4.3.1 FTIR Analysis**Fig. 4.10 shows FTIR scan of polyurea. A systematic peak analysis is represented in Table 4.2 which confirms presence of specific functional groups. It reveals complete conversion of monomers to polyurea.

**TABLE 4.2:** Data of FTIR spectrum of Polyurea

| **Wave number ($cm^{-1}$)** | **Band Assignments** |
|---|---|
| 3400-3307 | Stretching & vibration of –NH |
| 1600-1800 | Stretching & vibration of C=O |
| 1600=1500 | Stretching & vibration of C–N |
| 2220~2280 | No obvious peak is present which suggests N=C=O was completely reacted |
| 2956-2853 | Stretching & vibration of –CH |
| 1257.25 | Stretching & vibration of C-O-C |
| 1654 | Bending & vibration of –NH |

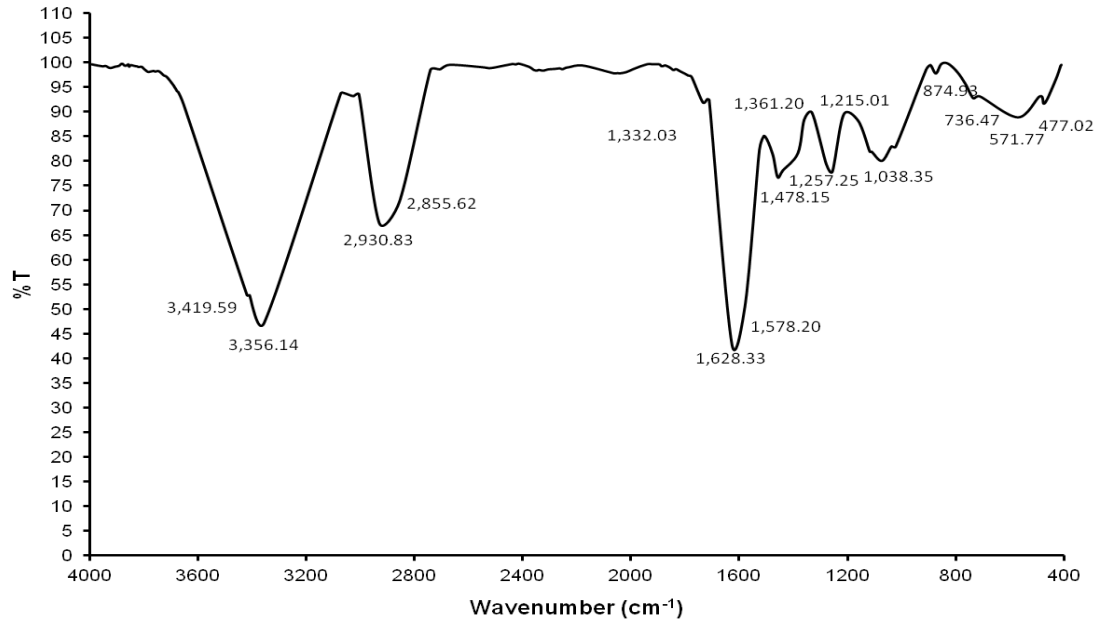



**Figure 4.10** FTIR spectrum of polyurea sample (synthesized at conditions, R=2.4, T=25$^0$C and ($n_L/V_d$) =0.36, Solvent: *n*-Octane)

### 4.3.2 Characterization of polyurea by XRD analysis

X-ray diffraction (XRD) estimation was applied to examine the crystallinity of polyurea shell. Highly crystalline phase was represented by sharp peaks in diffractogram while the broad peaks characterized amorphous phase of polymer.

***Determination of percentage crystallinity:***

Powder X-ray analysis of one sample was recorded and percentage crystallinity was calculated from X-ray diffractogram using RIGAKU-software. The same was determined by curve fitting method using ORIGIN-85 software as:

$$\%\, Crystallinity = \left[\frac{A_c}{(A_c + A_a)}\right] = \left[\frac{A_c}{A_{Total}}\right]$$

Where, $A_c$ = Area of crystalline phase of polymer
$A_a$ = Area of amorphous phase of polymer
$A_{Total}$ = Total Area of both crystalline and amorphous phase

Detail calculations of the above method are given in Appendix-II. ORIGIN-85 based method validate with reasonable level of accuracy therefore for all other samples (synthesized under different preparative conditions) the same method was used to determine % crystallinity.

***Effect of various reaction parameters on percentage crystallinity of polyurea:***

Percentage crystallinity of polyurea samples synthesized using organic solvent *n*-Octane at constant phase volume ratio of 0.05 was calculated and effect of following three reaction parameters on percentage crystallinity was studied:

(i) Monomer mole ratio (R).

(ii) Moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$).

(iii) Reaction temperature (T).

Effect of change in monomer mole ratio (R) for two samples of polyurea, for run number R17 and R22 on % crystallinity is listed in Table 4.3.

**TABLE 4.3:** Effect of different monomer mole ratio (R) on % crystallinity of Polyurea

| **Sample No.** | **R** | **$n_L/V_d$** | **T ($^0$C)** | **% Crystallinity ( $X_c$)** |
|---|---|---|---|---|
| R17 | 2.4 | 0.72 | 25 | 21.54 |
| R22 | 1.2 | 0.72 | 25 | 27.98 |

The pattern of X-ray diffractograms of these samples are as shown in Fig. 4.11 (a) to (d)

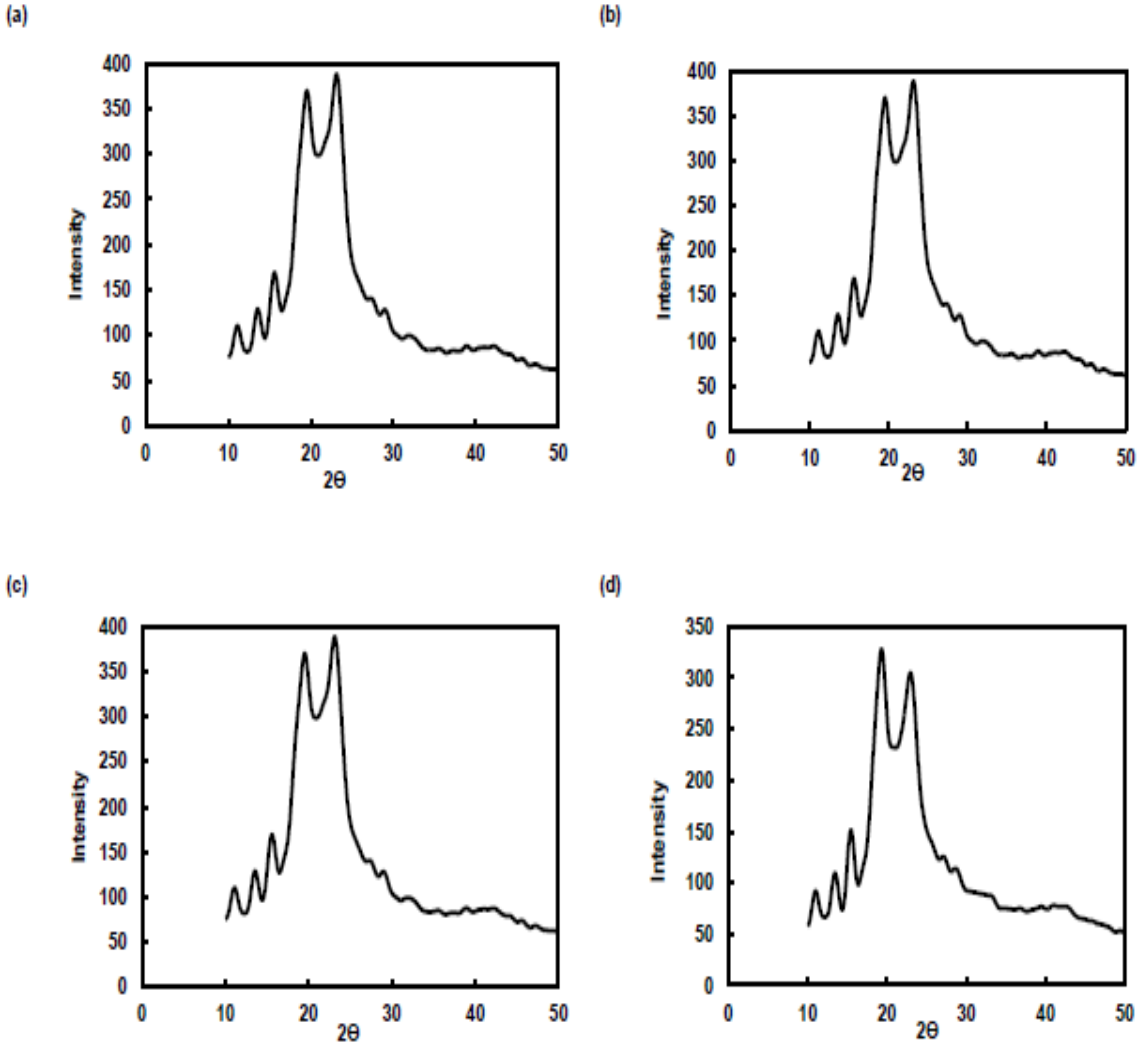



**Figure 4.11** X- ray diffractograms of polyurea samples: (a) R15 (R=2.4, ($n_L/V_d$) =0.18, T=25 °C); (b) R17 (R=2.4, (nL/Vd) =0.72, T=25 °C); (c) R22 (R= 1.2, ($n_L/V_d$) =0.72, T=25 °C); and (d) R24 (R=2.4, (nL/Vd) =0.72, T=20 °C). Phase volume ratio=0.05 and organic solvent is n-Octane.

These XRD patterns confirm formation of semi crystalline structure of polyurea samples. Percentage crystallinity calculation of each case was done by comparing area under crystalline peaks to total area as reported in literature (Yadav et al., 1996; Wagh et al., 20019; Dhumal et al., 2010).

Sample no. R17 bulk monomer mole ratio (R=2.4) while for run no. R22 bulk monomer mole ratio (R=1.2), other conditions were kept constant (i.e. T=$25^0$C and ($n_L/V_d$) =0.72). Percentage crystallinity of R17 was 21.54% and that of R22 was 27.98%.

As discussed in section number 4.1.2, rate of polymerization is high for large values of bulk monomer mole ratio, R polyurea molecules do not get enough time to arrange themselves in orderly lattice structure so % crystallinity decreases.

Effect of change in number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$) for two samples of polyurea, for run number R15 and R17 on % crystallinity is listed in Table 4.4.

Ratio of moles of limiting monomer to volume of dispersed phase ($n_L/V_d$) for sample no. R15 was 0.18 while that for run no. R17 was 0.72, other conditions (i.e. T=25$^0$C and (R) =2.4) for synthesis of polyurea using organic solvent *n*-Octane. Percentage crystallinity of R15 was 14.17% and that of R17 was 21.54%

**TABLE 4.4:** Effect of ratio of moles of limiting monomer to volume of dispersed phase ($n_L/V_d$) on % crystallinity of Polyurea

| **Sample No.** | **R** | **$n_L/V_d$** | **T ($^0$C)** | **% Crystallinity ( $X_c$)** |
|---|---|---|---|---|
| R15 | 2.4 | 0.18 | 25 | 14.17 |
| R17 | 2.4 | 0.72 | 25 | 21.54 |

As discussed in section number 4.1.3, number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$), directly controls the thickness of polymer film ($\delta_t$) formed during reaction through which the aqueous phase monomer (HMDA) diffuses as interfacial polymerization progresses. Low value of limiting monomer reduced the thickness of polymeric film and HMDA can diffuse through it with less resistance which results into high rate of polymerization and more amorphous structure of polyurea. Therefore the percentage (%) crystallinity decreases with decrease in value of moles of limiting monomer to volume of dispersed phase ($n_L/V_d$).

Effect of change in reaction temperature (T) for two samples of polyurea, for run number R17 and R24 on % crystallinity is listed in Table 4.5.

**TABLE 4.5:** Effect of different reaction temperature (T) on % crystallinity of Polyurea

| Sample No. | R | $n_L/V_d$ | T ($^0$C) | % Crystallinity ( $X_c$) |
|---|---|---|---|---|
| R17 | 2.4 | 0.72 | 25 | 21.54 |
| R24 | 2.4 | 0.72 | 20 | 24.97 |

Sample no. R17 was synthesized at reaction temperature of $25^0$C while that for run number R24 was $20^0$C other conditions (i.e. (R) =2.4 and $n_L/V_d$ = 0.72). Percentage crystallinity of R17 was 21.54% and that of R24 was 24.97%.

As discussed in section number 4.1.5, rate of polymerization increases with increase in reaction temperature so for polyurea synthesized at $25^0$C had less percentage crystallinity due to less orderly arrangement of molecules in the lattice structure and polyurea synthesized at $20^0$C had high percentage crystallinity. However, the effect of temperature is somewhat masked because of high value of $n_L/V_d$ causing lower rate of reaction.

Crystalline or amorphous structure of polyurea shell which governs the release rate of encapsulated core material was correlated and value of % crystallinity was governed by all three preparative conditions of parameters i.e. the monomer mole ratio (R), the number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$) and the reaction temperature (T).

### 4.3.3 DSC analysis

Thermal behavior of polymer samples was characterized by Differential Scanning Calorimeter (DSC). In this analysis polyurea behavior on heating is examined. DSC scans for samples R15, R17, R24, R22 and R21 are as shown in Fig. 4.12 and Fig. 4.16 respectively. Results of two different endothermic peaks are noted in Table 4.6 for scan in temperature range of 0°C to 500°C.

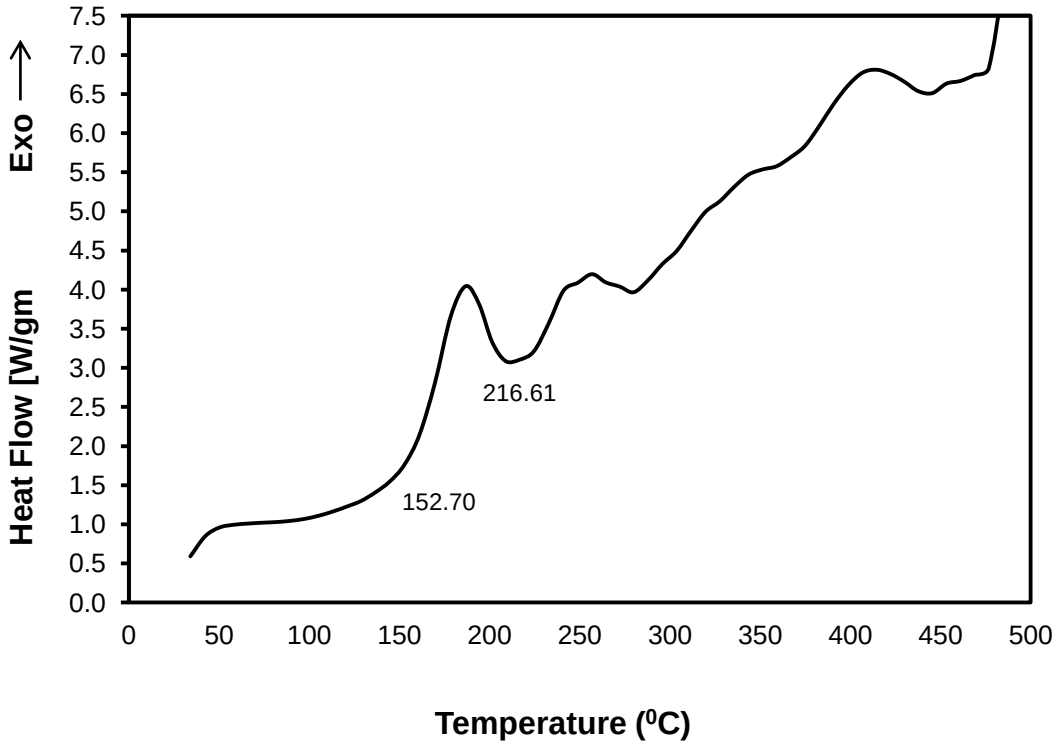



**Figure 4.12** DSC thermogram of polyurea sample **R15** (R= 2.4, $(n_L/V_d)$=0.18,T=25$^0$C), Phase volume ratio=0.05 and organic solvent is *n*-Octane.

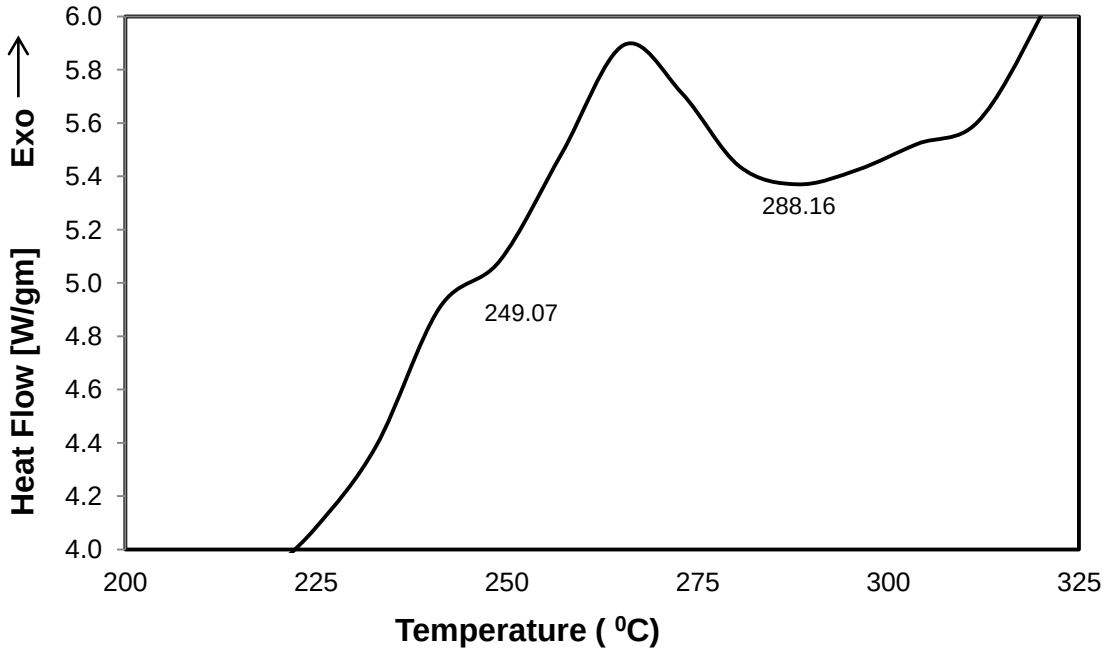



**Figure 4.13** DSC thermogram of polyurea sample **R17** (R= 2.4, $(n_L/V_d)$=0.72,T=25$^0$C), Phase volume ratio=0.05 and organic solvent is *n*-Octane.

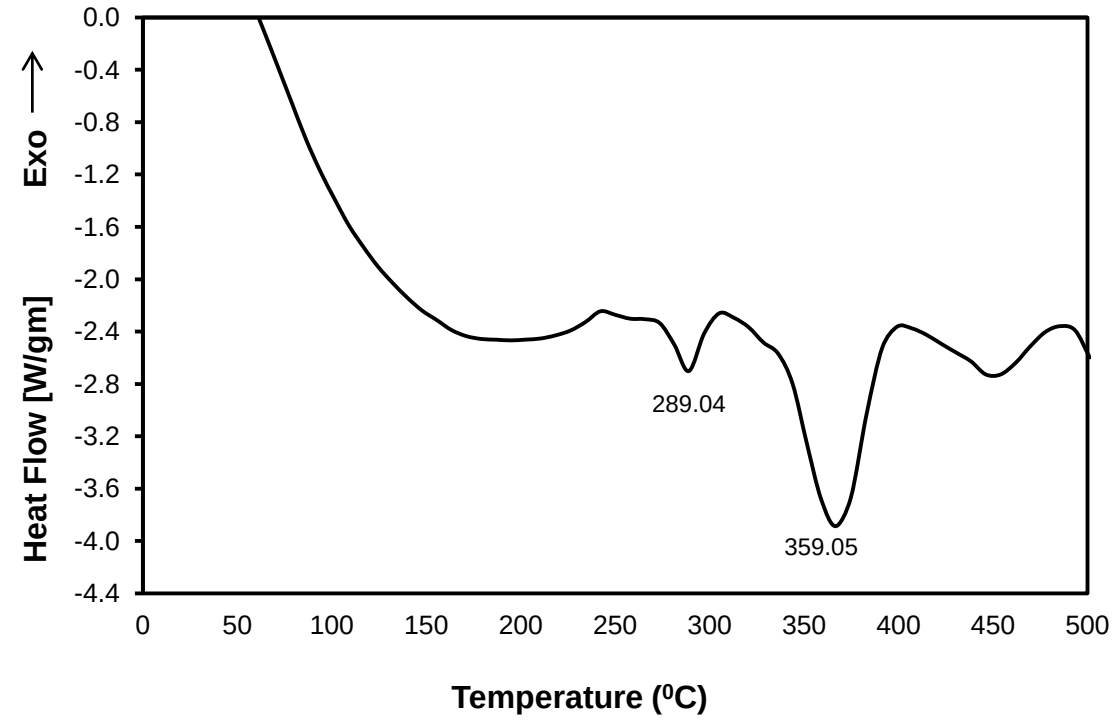



**Figure 4.14** DSC thermogram of polyurea sample for run **R24** (R=2.4, $(n_L/V_d)$ =0.72, T=20°C). Phase volume ratio=0.05 and organic solvent is *n*-Octane.

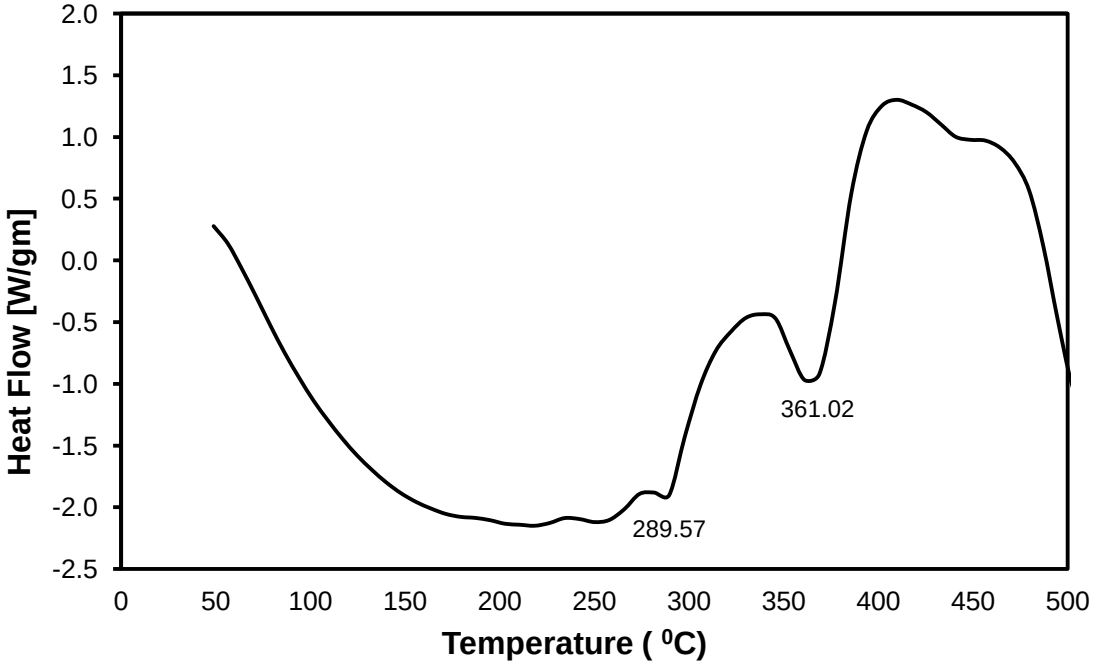



**Figure 4.15** DSC thermogram of polyurea sample **R22** (R= 1.2, $(n_L/V_d)$ =0.72, T=25$^0$C), Phase volume ratio=0.05 and organic solvent is *n*-Octane.

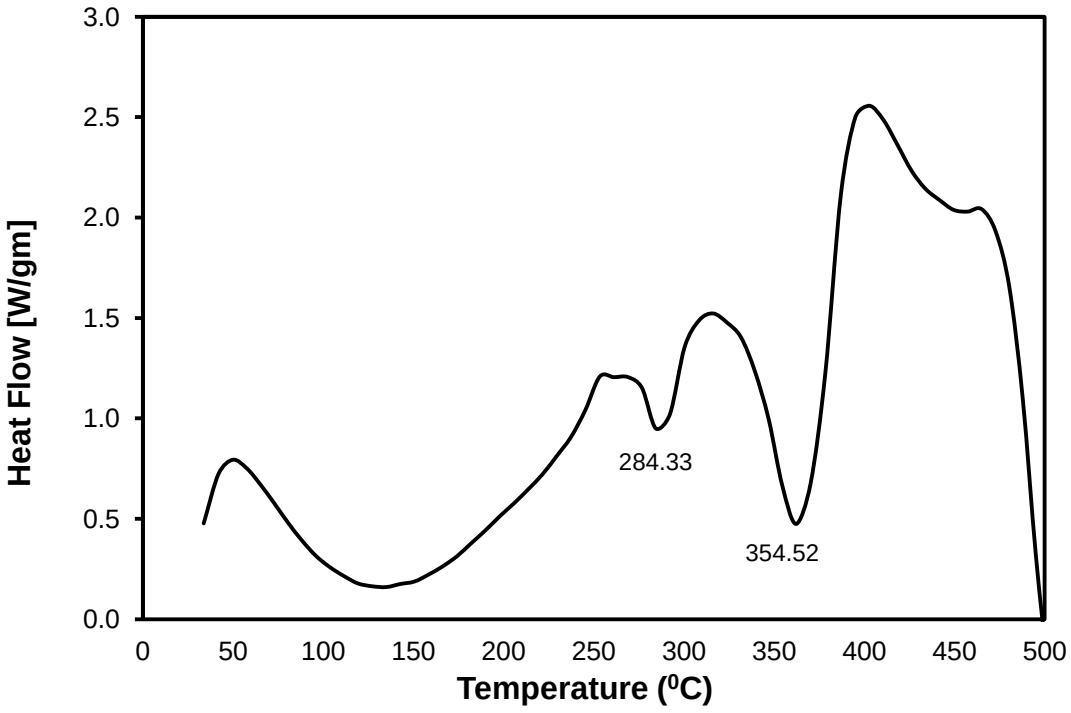



**Figure 4.16** DSC thermogram of polyurea sample for run **R21** (R=1.2, ($n_L$/Vd) =0.36, T=25°C). Phase volume ratio=0.05 and organic solvent is *n*-Octane.

Table 4.6 shows summary of peak analysis of DSC Thermogram for polyurea synthesized with n-Octane as solvent and Vd/Vc = 0.05. The data can be analyzed in the light of the theory of polyurea crystallization and the effect of various preparative conditions used in this work.

**TABLE 4.6:** Summary of peak analysis of DSC Thermogram for polyurea synthesized with *n*-Octane as solvent and $V_d/V_c$ = 0.05

| Sr. No. | Run No. | R | $n_L/V_d$ | T ($^0$C) | % Crystallinity ($X_c$) | 1st Endothermic Peak ($^0$C) | 2rd Endothermic Peak ($^0$C) |
|---|---|---|---|---|---|---|---|
| 1 | R15 | 2.4 | 0.18 | 25 | 14.17 | 152.70 | 216.61 |
| 2 | R17 | 2.4 | 0.72 | 25 | 21.54 | 249.07 | 288.15 |
| 3 | R24 | 2.4 | 0.72 | 20 | 24.97 | 289.04 | 359.05 |
| 4 | R22 | 1.2 | 0.72 | 25 | 27.98 | 289.57 | 361.02 |
| 5 | R21 | 1.2 | 0.36 | 25 | 21.20 | 284.33 | 354.52 |

Results of DSC thermograms confirmed that a highly thermally stable polyurea thermoplastic was formed (Yadav et al., 1996) with a semi crystalline structure. Total two endothermic peaks were observed. First endothermic peak was indicator of glass transition temperature ($T_g$) which is unique property for semi crystalline polymer. Melting temperature ($T_m$) of polyurea sample was obtained from the second endothermic sharp peak. If a polymer is amorphous, on heating the polymer sample, the solid-to-liquid transition occurs very gradually, going through an intermediate "rubbery" state. The transition from hard and brittle glassy state into softer rubbery state occurs over a narrow temperature range referred to as glass transition temperature ($T_g$). For semi crystalline polymers this transformation occurs in its amorphous region only. The crystalline zones remain unchanged and making the sample hard and tough. If heating is continued a temperature is reached at which the crystalline zone begin to melt. The equilibrium crystalline melting point, $T_m$ for polymers corresponds to the temperature at which last crystallite starts melting.

In contrast to simple material, the value of melting point, $T_m$ for polymers depends on its percentage crystallinity. As monomer mole ratio value, R increased from 1.2 to 2.4 (from sample no. R22 and R17) initial rate of polymerization was faster and shorter polymeric chains easily arranged themselves in a crystalline form resulted into increase in crystallinity as well as melting temperature.

As listed in Table 4.6, different polyurea samples were synthesized with constant phase volume ratio of 0.05 and organic solvent was *n*-Octane. Sample no. R17 was synthesized at reaction temperature of $25^0$C while that for sample no. R24 was $20^0$C and maintaining other conditions (R) =2.4 and $n_L/V_d$ = 0.72 same. Percentage crystallinity of sample no. R17 was 21.54% and that of sample no. R24 was 24.72% therefore melting point of R24 was higher than that of R17. Value of $n_L/V_d$ was increased from 0.36 to 0.72 for sample no. R21, and sample no. R22, for which other conditions (R) =1.2, T=$25^0$C same, this has resulted into increase in initial rate of polymerization and hence melting point, $T_m$ of polyurea; percentage crystallinity of R21 was 21.20% and that of R22 was 27.98% therefore melting point of R22 was 6.9 $^0$C higher than that of R21.Similarly value of $n_L/V_d$ was increased from 0.18 to 0.72 in sample no. R15 and sample no.R17 for which other conditions (R) =2.4, T=$25^0$C same, this has resulted into increase in initial rate of polymerization and hence melting point, $T_m$ of polyurea. Percentage crystallinity of R15 was 14.17% and that of R17 was 21.54% therefore melting point of R17 was higher than that of R15.

### 4.3.4 Optical micrographs

Optical images of polyurea microcapsule without drying were observed by Leica DM4B Digital Microscope was recorded using digital camera (Canon A 3100) at 40-100 X resolution. Representative images as shown in Fig. 4.14 confirmed formation of polyurea shell wall.

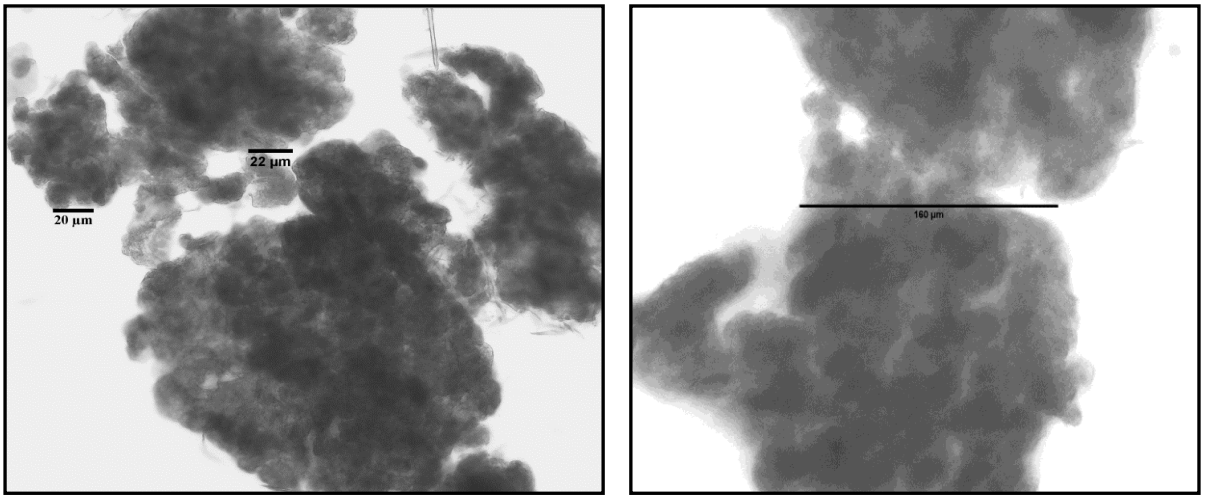



**Figure 4.17** Optical images of polyurea microcapsules of sample R23 (R=2.4, $n_L/V_d$=0.36 and T=$20^0$C)

### 4.3.5 Surface morphology by scanning electron microscope (SEM)

The results presented in Fig. 4.18 (a-d) are for scanning electron microscope (SEM) images of PU at different magnifications. Polyurea capsules formed with use of Tween-85 as an emulsifier under different preoperative parameters were more probable to deform under sample preparation protocols (especially during drying) used for SEM analysis. SEM micrographs at different magnification confirmed porous and fibrous internal structure of polyurea shell.

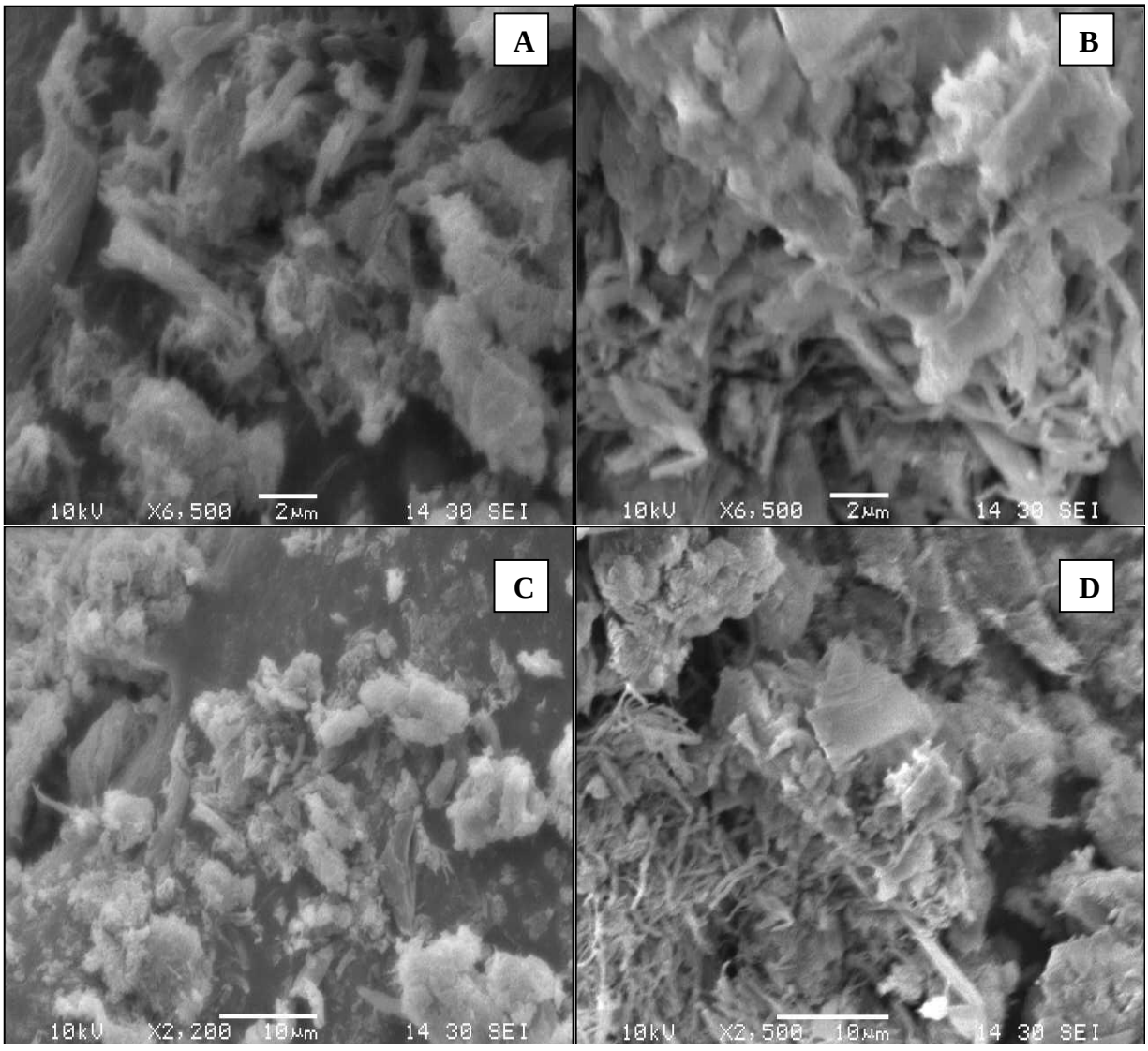



**Figure 4.18** SEM micrographs (A) sample R23 (R=2.4, $n_L/V_d$=0.36 and T=$20^0$C) magnification x6500
(B) sample R30(R=2.4,$n_L/V_d$=0.36and T=$30^0$C) magnification x6500
(C) sample R23 (R=2.4,$n_L/V_d$=0.36andT=$20^0$C) magnification x2200
(D) R30 (R=2.4, $n_L/V_d$=0.36 and T=$30^0$C) magnification x2200

### 4.3.6 Particle size analysis:

Particle size analysis of one sample of polyurea microcapsules was carried out by laser diffraction based particle size analyzer (Malvern Mastersizer 2000). Particle size distribution (PSD) plot is represented in Fig. 4.19. Value of different volume based particle diameters: ($d_{0.1}$) =1.91 μm, ($d_{0.5}$) =5.41 μm and ($d_{0.9}$) =24.15 μm. With overall span of 4.107 and average particle diameter was 3.76 μm. Overall narrow particle size distribution represents uniformity in particle size.

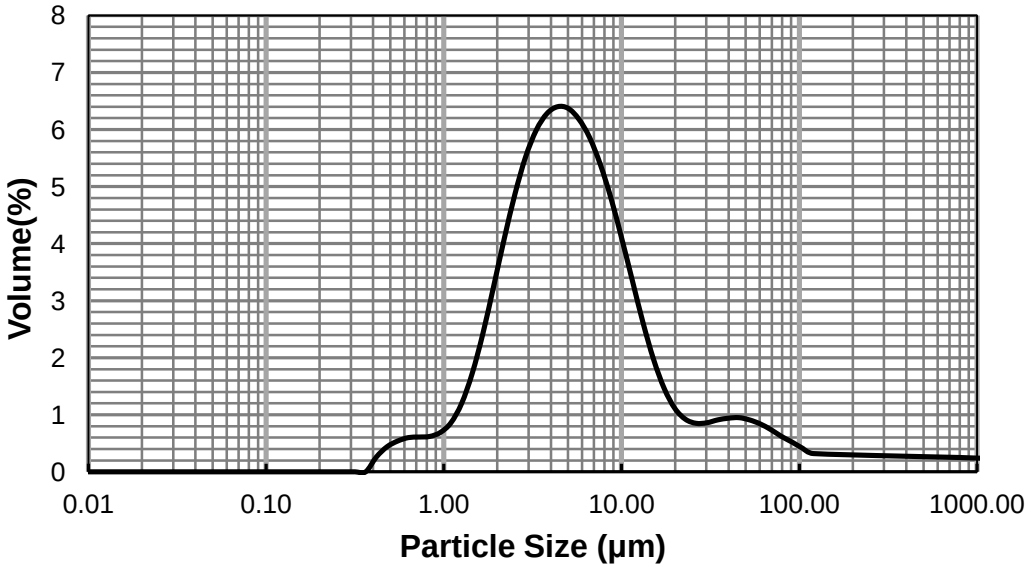



**Figure 4.19** Particle size distribution (PSD) for polyurea microcapsule

### 4.3.7 Determination of viscosity average molecular weight ($\bar{M}_v$)

0.5 gm/dl of polyurea solution were prepared in 98% concentrated $H_2SO_4$, and viscometery data were collected using Ostwald-Fenske viscometer at 25 $^0$C. Calculated value of intrinsic viscosity was 0.4463dl/gm. With use of Mark-Houwikn's constants reported in literature (Dhumal et al., 2010) the viscosity average molecular weight was 12,740.89 kg/kmol.

Detail calculations are given in Appendix-III.

## 4.4 Controlled/sustained release experimental results for encapsulation of different insecticides in polyurea shell

In this experimental work three different insecticides (i) Chlorpyriphos (ii) Cypermethrin and (iii) Pretilachlor were effectively encapsulated as a core material in polyurea shell synthesized for different preparative condition of monomer mole ratio (R) and moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$). All three insecticides were soluble in *n*-Octane therefore initial stock solution was prepared in *n*-Octane with constant loading content of 4 % (w/v) and appropriate volume of this solution was added as dispersed phase in emulsification step to maintain a constant phase volume ratio of 0.05. Temperature was kept constant at $30^0$C.

Controlled release studies of insecticides in methanol were carried out as discussed in section 3.4 and concentration of core material was determined using pre-calibrated UV-spectrophotometer (UV-1800, UV-VIS Shimadzu Japan).

### 4.4.1 Encapsulation efficiency and cumulative release rate:

As explained in section 3.4 encapsulation efficiency of polyurea shell for the insecticide as a core material is calculated for all three selected insecticides i.e. chlorpyriphos, cypermethrin and pretilachlor for constant loading ratio of 4% (w/v).

$$\text{Encapsulation efficiency (\%)} = \left[\frac{\text{weight of insecticide encapsulated in microcapsules}}{\text{Total weight of insecticide taken in feed}}\right] \times 100$$

$$\text{Release of insecticide(\%)} = \left[\frac{\text{weight of insecticide released from microcapsules at any time,t}}{\text{Total weight of insecticide encapsulated in microcapsules}}\right] \times 100$$

The ultraviolet spectrophotometric analysis was performed on a double beam (Shimadzu UV - Vis 2450) spectrophotometer equipped with a deuterium lamp as the radiation source for measurements in the ultraviolet region. It was connected to a computer with the appropriate software for recording the absorbance readings.

Calibration curve was constructed for each insecticide sample for their different known concentrations in methanol to determine the maximum wavelength ($\lambda_{max}$).

### 4.4.2 Encapsulation efficiency and cumulative release rate of Chlorpyriphos

In release studies of chlorpyriphos through polyurea shell in methanol medium, initially chlorpyriphos solution in methanol (30 mg/l) was prepared by dissolving 3 mg chlorpyriphos in 100 ml methanol. Pure methanol was used as a reference and the solution was scanned in the range of 190-400nm with a spectrophotometer UV (Shimadzu UV-Vis 2450). Absorption peak at 289nm was reported as maximum wavelength ($\lambda_{max}$). A number of chlorpyriphos methanol dilute solutions were prepared and a standard calibration curve of absorbance Vs concentration of chlorpyriphos in methanol solution as shown in Fig. 4.20 was obtained. The linear relationship between concentration and absorbance for concentration range of 5 to 30 mg/l was obtained. L. Zhu *et al.*, 2010, had developed similar method for chlorpyriphos n-hexane solution.

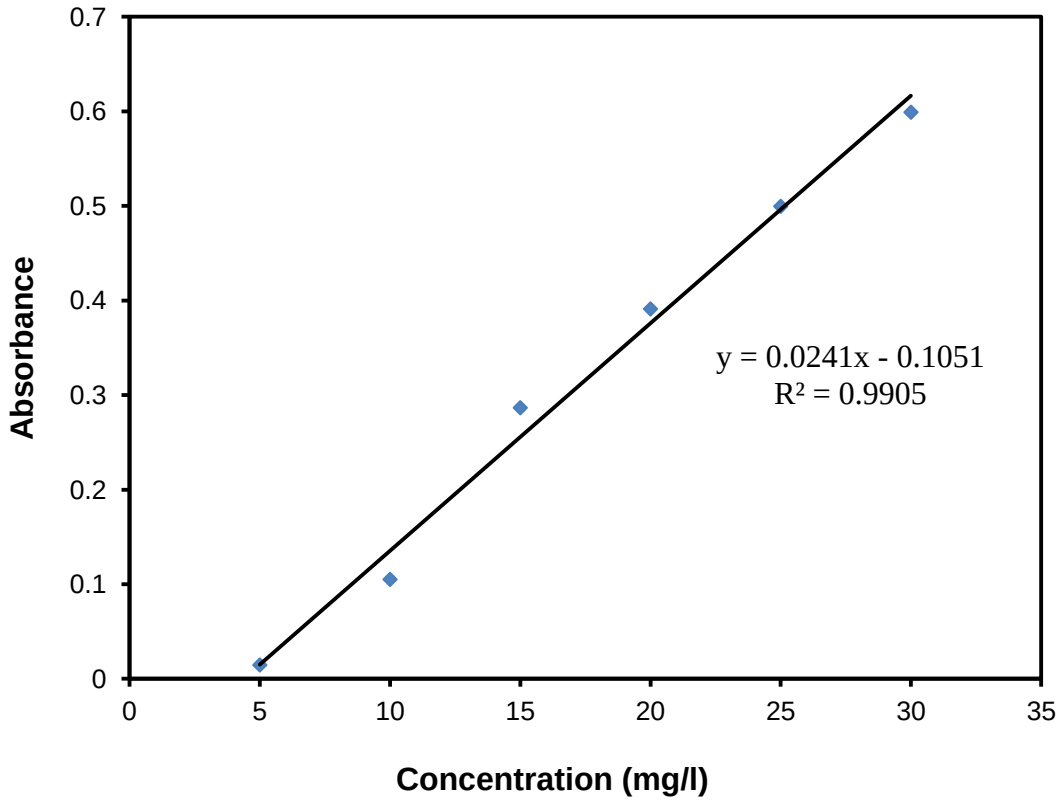



**Figure 4.20** Calibration curve for chlorpyriphos solution in methanol

Chlorpyriphos encapsulated in polyurea shell formed at different preparative conditions (Formulation no.: CLP1 to CLP5) and its release concentration in methanol was determined by calibration curve shown in Fig. 4.20 the cumulative release rate and % encapsulation efficiency are reported in Table 4.7.

**TABLE 4.7:** Controlled release data for chlorpyriphos encapsulated in polyurea shell at different preparative conditions

| Sr. no. | Formulation Notation | R | $n_L/V_d$ | % Crystallinity ($X_c$) | Encapsulation Efficiency (%) | %Cumulative Release after t=100 min. |
|---|---|---|---|---|---|---|
| 1 | CLP1 | 2.4 | 0.18 | – | 35.79 | 79.80 |
| 2 | CLP2 | 2.4 | 0.36 | 20.51 | 64.48 | 75.71 |
| 3 | CLP3 | 2.4 | 0.72 | 24.72 | 78.55 | 64.30 |
| 4 | CLP4 | 1.2 | 0.36 | 21.20 | 81.67 | 71.05 |
| 5 | CLP5 | 1.2 | 0.72 | 26.76 | 93.83 | 58.05 |

Fig.4.21 represents %cumulative release of chlorpyriphos in methanol from different formulations of constant loading. Initially cumulative release rate was fast for all formulations due to higher concentration of chlorpyriphos in the core and gradually it became steady. For constant value of R=2.4, as R>1 HMDA is limiting monomer and its diffusion towards the reactive zone will govern the rate of polymerization, lower value of $n_L/V_d$ decreased the rate off polycondensation resulted into decrease in encapsulation efficiency. Thickness of polymeric film was increased with increase in $n_L/V_d$ therefore %cumulative release rate after a constant time period of 100 minute reduced for different formulations as CLP3<CLP2<CLP1. Similar results were obtained for constant value of R=1.2, %cumulative release rate was lower for formulation CLP5 than that of CLP4.

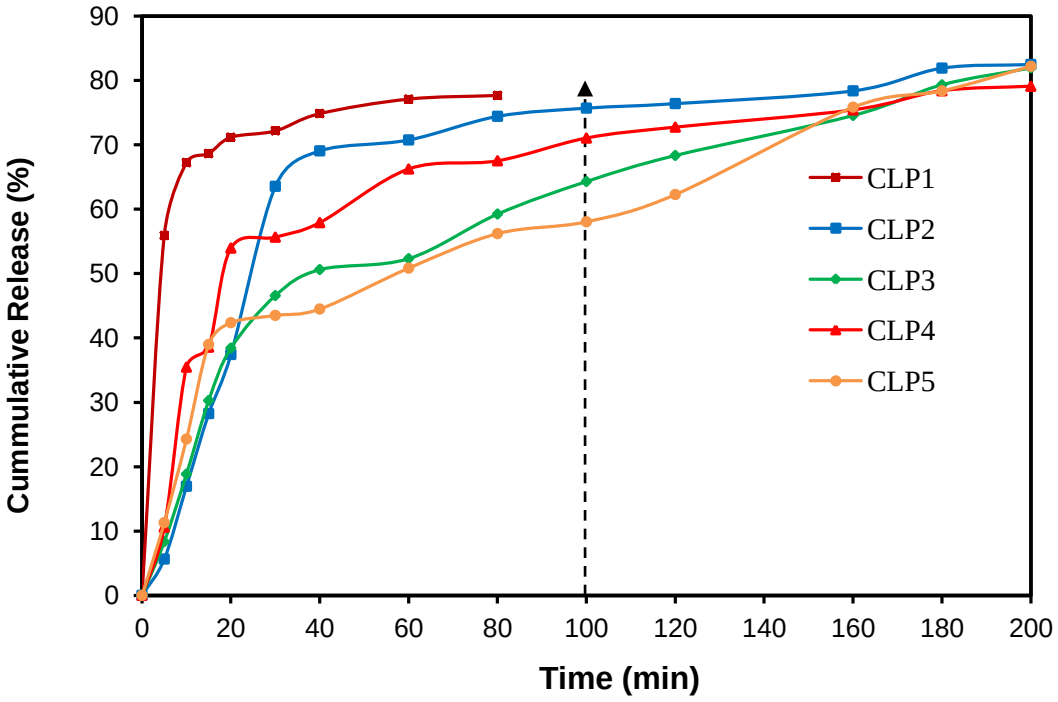



**Figure 4.21** Cumulative release curve for chlorpyriphos

With increased in monomer mole ratio R from 1.2 to 2.4 concentration of organic phase monomer, HMDI is double in case of formulation CLP2 than that of CLP4 which resulted into high crystalline polyurea shell therefore encapsulation efficiency of chlorpyriphos was increased and % cumulative release rate was decreased in CLP2 than CLP4. Similar results were obtained for formulation CLP3 and CLP5. In general, higher the crystallinity, lower is the %cumulative release of the insecticide through the polyurea shell.

### 4.4.3 Characterization of Chlorpyriphos loaded polyurea microcapsules:

***Characterization by FTIR:***

Fig. 4.22 shows the FTIR spectrum for chlorpyriphos loaded polyurea microcapsules. The transmission band at 1628.85 $cm^{-1}$ appeared for the C=O stretching of urea formation. The N—H stretching was observed at 3023.62-3355.54 $cm^{-1}$ and C—H stretching in the aliphatic methylene group of diamine was observed at 2924.47 $cm^{-1}$. There was no obvious peak observed at 2220~2280 $cm^{-1}$ which suggests N=C=O was completely reacted. Moreover, Cl—C and P=S group of chlorpyriphos were observed at 646.10 $cm^{-1}$ and 846.31 $cm^{-1}$confirmed its encapsulation.

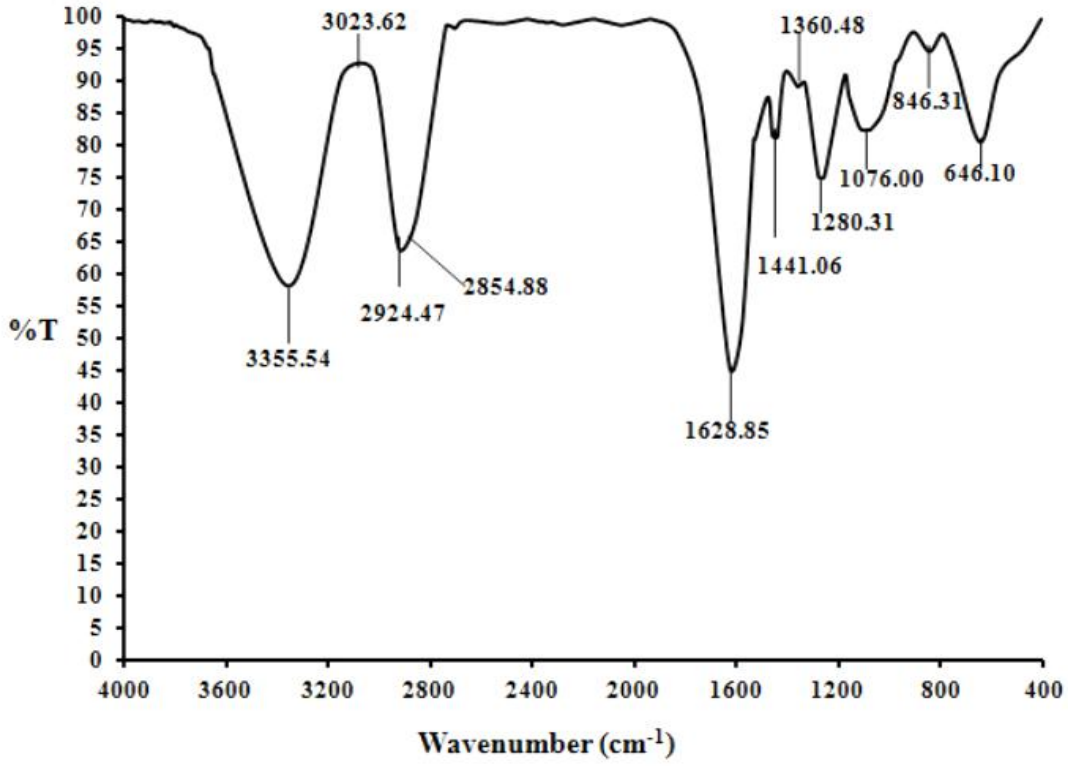



**Figure 4.22** FTIR spectrum of chlorpyriphos encapsulated in polyurea for sample CLP2 (R=2.4, $(n_L/V_d)$=0.36)

***Thermo gravimetric analysis (TGA):***

The TGA profiles for blank polyurea, pure chlorpyriphos and chlorpyriphos loaded polyurea microcapsules (CLP2) are as presented in Fig. 4.23. Weight loss of 80% to 40% occurred in the temperature range of 270°C to 325°C for pure chlorpyriphos while that for the formulation CLP2 was in the temperature range of 370°C to 430°C. Thus polyurea shell improves thermal stability of chlorpyriphos against weight loss at higher temperature.

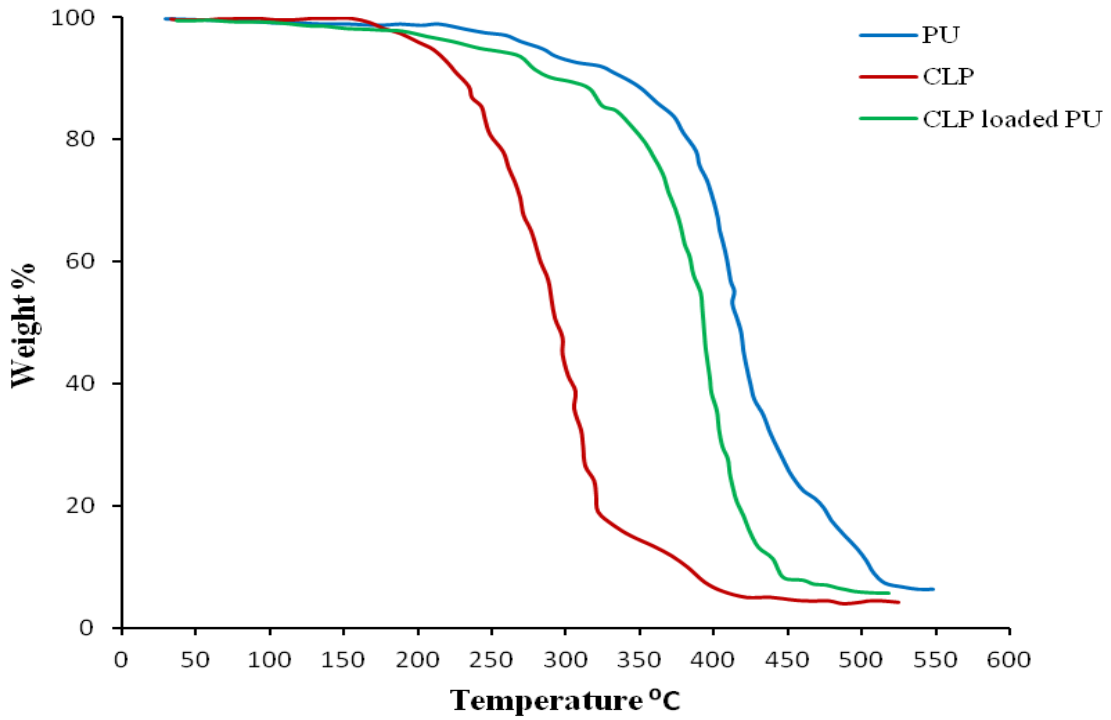



**Figure 4.23** TGA thermographs for blank polyurea sample (R=2.4 and $n_L/V_d$ =0.36), chlorpyriphos and chlorpyriphos encapsulated in polyurea formulation CLP2

### 4.4.4 Encapsulation efficiency and cumulative release rate of Cypermethrin:

Second insecticide selected for encapsulation in polyurea shell was cypermethrin. Encapsulation and controlled release of cypermethrin through polyurea shell reduce its toxic effects; minimize overall consumptions and evaporative losses. In this experimental work encapsulation efficiency of cypermethrin was calculated and its release rate in methanol was studied. Initially cypermethrin solution in methanol (2.4 mg/l) was prepared by dissolving 0.24mg cypermethrin in 100 ml methanol. Pure methanol was used as a reference and the solution was scanned in the range of 190-400nm with a spectrophotometer UV (Shimadzu UV-Vis 2450). Absorption peak at 211.51 nm was reported as maximum wavelength ($\lambda_{max}$). A number of cypermethrin methanol dilute solutions was prepared and a standard calibration curve of absorbance Vs concentration of cypermethrin in methanol solution as shown in Fig. 4.24 was obtained. The linear relationship between concentration and absorbance for concentration range of 0.4 to 2.4 mg/l was obtained.

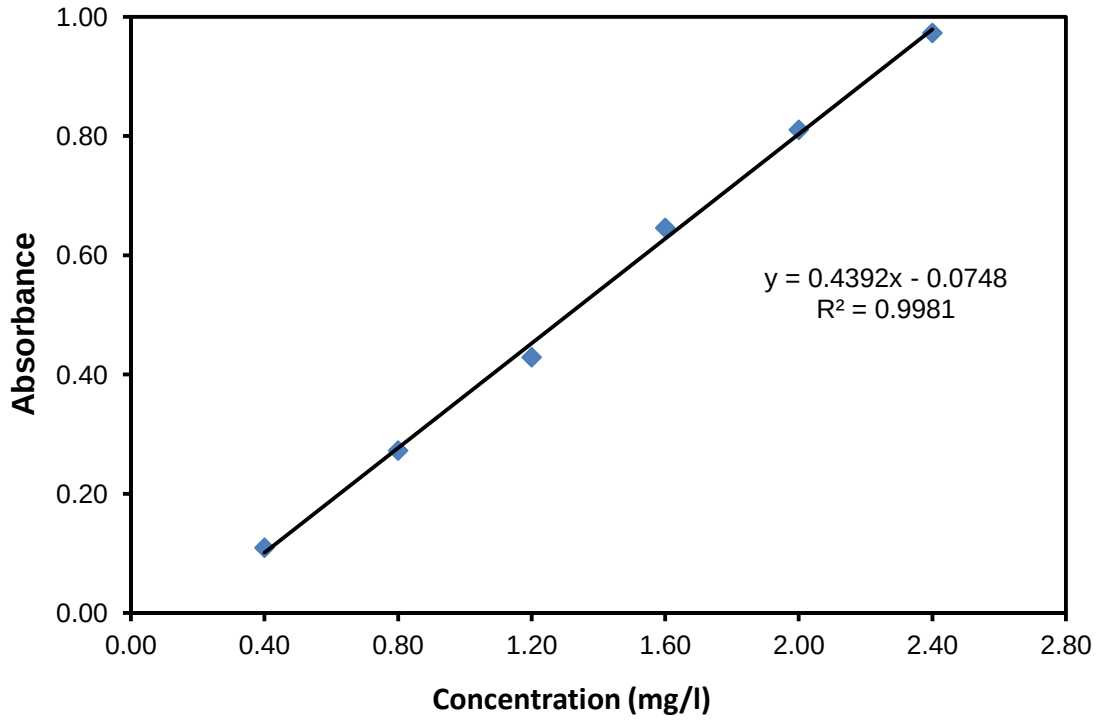



**Figure 4.24** Calibration curve for cypermethrin solution in methanol

Five different formulations of cypermethrin CYP1 to CYP5 were prepared at different preparative parameters of R, $n_L/V_d$. Release concentration in methanol was determined by

calibration curve shown in Fig. 4.25 the cumulative release rate and % encapsulation efficiency as shown in Table 4.8.

**TABLE 4.8:** Controlled release data for cypermethrin encapsulated in polyurea shell at different preparative conditions

| Sr. no. | Formulation Notation | R | $n_L/V_d$ | % Crystallinity ($X_c$) | Encapsulation Efficiency (%) | %Cumulative Release after t=100 min. |
|---|---|---|---|---|---|---|
| 1 | CYP1 | 2.4 | 0.18 | – | 22.80 | 85.15 |
| 2 | CYP2 | 2.4 | 0.36 | 20.51 | 44.46 | 80.33 |
| 3 | CYP3 | 2.4 | 0.72 | 24.72 | 52.80 | 73.25 |
| 4 | CYP4 | 1.2 | 0.36 | 21.20 | 56.74 | 78.26 |
| 5 | CYP5 | 1.2 | 0.72 | 26.76 | 66.75 | 65.25 |

Percentage encapsulation efficiency was increased with decrease in monomer mole ratio R from 2.4 to 1.2 for formulation CYP2 encapsulation efficiency was 44.46% while that of CYP4 was 56.74% for constant value of $n_L/V_d$ of 0.36. Similarly encapsulation efficiency was increased from 52.80% to 66.75% for formulation CYP3 and CYP5, while value of cumulative release rate was decreased from 73.25% to 65.25% due to increment in percentage crystallinity.

Percentage crystallinity increased from 20.51% to 24.72% with double the value of $n_L/V_d$ and therefore encapsulation efficiency was increased and cumulative release at constant time period of 100 minutes was decreased for formulation CYP1, CYP2 and CYP3. Cumulative release curve for cypermethrin is represented in Fig. 4.25.

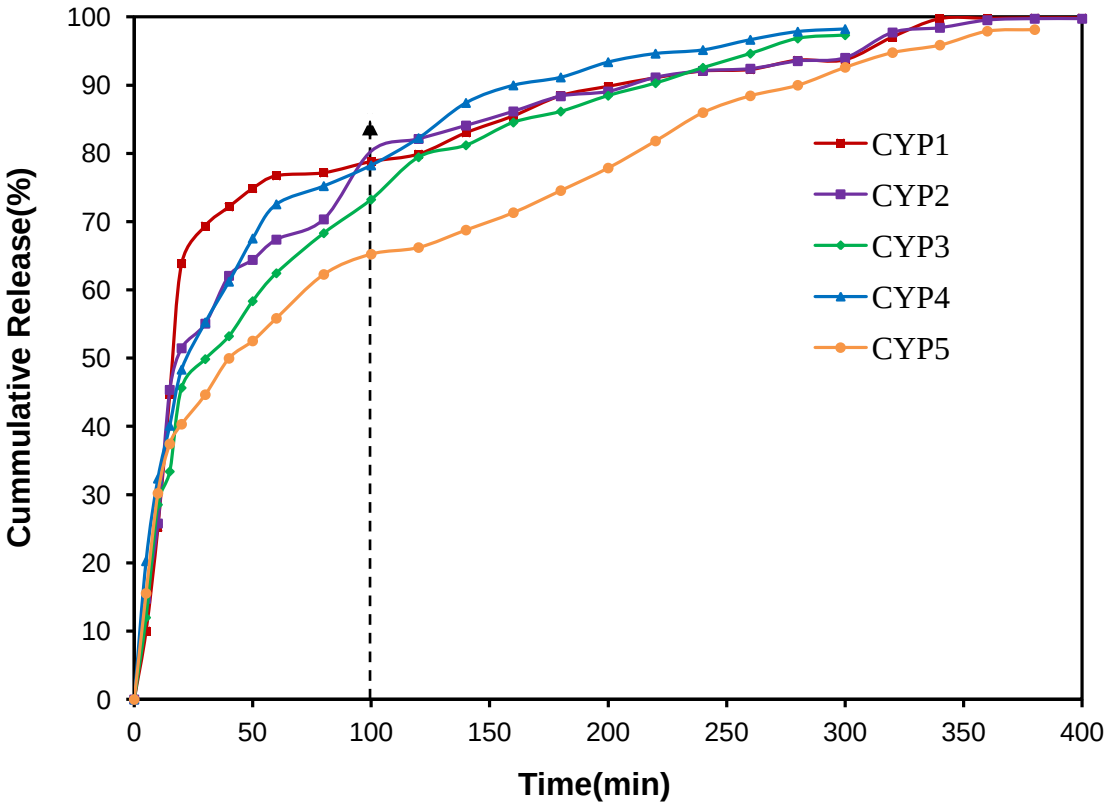



**Figure 4.25** Cumulative release curve for cypermethrin

### 4.4.5 Encapsulation efficiency and cumulative release rate of Pretilachlor:

A herbicide pretilachlor was encapsulated in polyurea shell to reduce its toxic effects; and ease of handling. In this experimental work encapsulation efficiency of pretilachlor was calculated and its release rate in methanol was studied. Initially pretilachlor solution in methanol (1.2 mg/l) was prepared by dissolving 0.12mg cypermethrin in 100 ml methanol. Pure methanol was used as a reference and the solution was scanned in the range of 190-400nm with a spectrophotometer UV (Shimadzu UV-Vis 2450). Absorption peak at 220.73 nm was reported as maximum wavelength ($\lambda_{max}$). A number of pretilachlor methanol dilute solutions were prepared and a standard calibration curve of absorbance Vs concentration of pretilachlor in methanol solution as shown in Fig. 4.26 was obtained. The linear relationship between concentration and absorbance for concentration range of 0.02 to 1.2 mg/l was obtained.

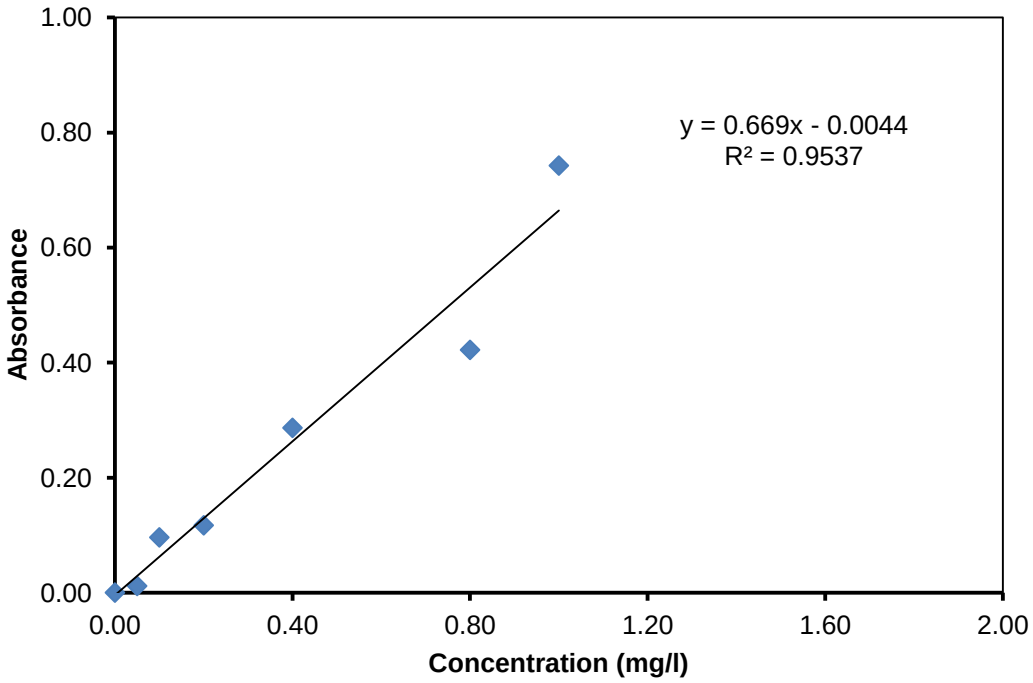



**Figure 4.26** Calibration curve for pretilachlor solution in methanol

Five different formulations of pretilachlor PTL1 to PTL5 were prepared at different preparative parameters of R, $n_L/V_d$. Release concentration in methanol was determined by calibration curve shown in Fig. 4.26 the cumulative release rate and % encapsulation efficiency as shown in Table 4.8.

**TABLE 4.9:** Controlled release data for pretilachlor encapsulated in polyurea shell at different preparative conditions

| Sr. no. | Formulation Notation | R | $n_L/V_d$ | % Crystallinity ($X_c$) | Encapsulation Efficiency (%) | %Cumulative Release after t=100 min. |
|---|---|---|---|---|---|---|
| 1 | PTL1 | 2.4 | 0.18 | – | 30.28 | 82.72 |
| 2 | PTL2 | 2.4 | 0.36 | 20.51 | 56.25 | 78.33 |
| 3 | PTL3 | 2.4 | 0.72 | 24.72 | 82.86 | 68.56 |
| 4 | PTL4 | 1.2 | 0.36 | 21.20 | 67.49 | 71.80 |
| 5 | PTL5 | 1.2 | 0.72 | 26.76 | 90.78 | 54.20 |

Percentage encapsulation efficiency was increased with decrease in monomer mole ratio R from 2.4 to 1.2 for formulation PTL2 encapsulation efficiency was 56.25% while that of PTL4 was 67.49% for constant value of $n_L/V_d$ of 0.36. Similarly encapsulation efficiency was increased from 82.86% to 90.78% for formulation PTL3 and PTL5, while value of cumulative release rate was decreased from 68.56% to 54.20% due to increment in percentage crystallinity.

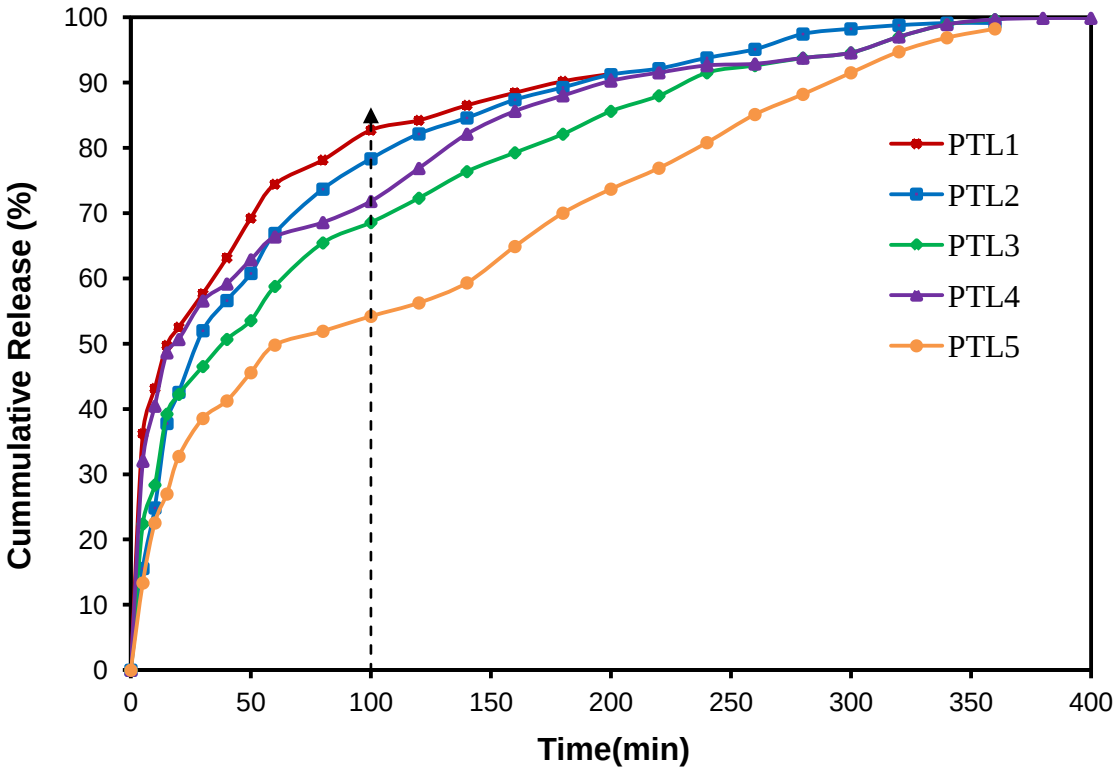



**Figure 4.27** Cumulative release curve for pretilachlor

Cumulative release curve for pretilachlor is shown in Fig. 4.27. Formulation PTL1 resulted into fastest release of pretilachlor with minimum encapsulation efficiency. Formulation PTL4 and PTL5 for constant value of R=1.2, with increase in value of $n_L/V_d$ from 0.36 to 0.72 % encapsulation efficiency increased from 67.49% to 90.78% and rate of cumulative release was decreased from 71.80% to 54.20%.

# CHAPTER-5

# Conclusions and Scope of Future Work

On the basis of results, it can be stated that interfacial polycondensation (IP) of HMDA and HMDI is one of the most effective methods which can be used to synthesize polyurea microcapsules and to encapsulate active ingredients in polymer shell. Rate of release and percentage (%) encapsulation efficiency of insecticides largely depends on structure of polymer formed which is influenced by preparative conditions.

- ✓ In this experimental work monomer mole ratio R values 1.2 and 2.4 are selected in order to ensure complete consumption of $–NH_2$ group of HMDA by excess concentration of HMDI (i.e. –NCO group).Polycondensation reaction rate increases with increase in value of R. It is a corroborative evidence of IP reaction taking place on the organic phase side of the interface.
- ✓ Diffusion of HMDA through developed polymer film governs the reaction rate as reaction occurs at organic side of interface. At low concentration of HMDA (i.e. R=2.4), diffusion resistance is less so reaction rate is faster than high concentration of HMDA (i.e. R=1.2).
- ✓ Phase volume ratio ($V_d/V_c$) for cyclohexane as an organic solvent is the key experimental parameters controlling the kinetics of IP reactions. Phase volume ratio ($V_d/V_c$) influences interfacial area and therefore increase in ($V_d/V_c$) results in faster reaction rate.
- ✓ Reaction temperature is an important condition which has a strong effect on reaction kinetics of polyurea synthesis via IP. In this experimental study increase in reaction temperature promotes transfer of HMDA from aqueous phase to organic phase by increasing its diffusion coefficient and its partition coefficient which accelerates

polymer membrane formation. At a low temperature, reaction rate decreases resulting into a more orderly structural molecular arrangement which increases % crystallinity of polyurea.

- ✓ Polarity of organic solvent governs reaction rate of IP, as reaction occurs on the organic phase side of the interface. Reaction rate decreases with increase in solvent polarity irrespective of number of methyl pendant group present in molecular structure of the solvent molecule.
- ✓ Controlled release of encapsulated insecticide largely depends on the properties of semicrystalline polyurea shell. Encapsulation efficiency and release rate of chlorpyriphos, cypermethrin and pretilachlor increases with decrease in R and increase in $n_L/V_d$. Crystallinity of Polyurea has inverse correlation with shell permeability. Increment in % crystallinity reduced diffusive losses of core material through polymeric shell and increased % encapsulation efficiency. The present work, therefore, provides a pathway based on experimental work to making a tailor made polyurea capsules loaded with insecticides.
- ✓ FTIR, XRD and DSC analyses show that the synthesized polyurea microcapsules have a semicrystalline and thermally stable polymer as a shell material.
- ✓ Polyurea microcapsules synthesized via interfacial polycondensation of HMDA and HMDI using *n*-Octane as an organic solvent can effectively encapsulate various insecticides as a core material, including selective pesticides (cypermethrin and chlorpyriphos) and a selective herbicide (pretilachlor). The kinetics of polyurea synthesis is governed by the bulk mole ratio of monomers (R), the number of moles of limiting monomer per unit volume of dispersed phase ($n_L/V_d$) and reaction temperature under the constant ratio of volume of dispersed phase to the volume of continuous phase ($V_d/V_c$=0.05). The reaction rate increases with increase in R, increase in temperature and decrease in $n_L/V_d$. Semi-crystalline polyurea is obtained and the percent crystallinity is higher with high values of $n_L/V_d$ and low values of R. The encapsulation efficiency of various insecticides increases with decrease in R and increase in $n_L/V_d$. The controlled release of the active ingredient largely depends on the properties of the polymer shell, especially the crystallinity.

- ✓ In future, kinetics data obtained in this experimental work can be utilized and tested for mathematical model development.
- ✓ Ionic liquid medium can be used for synthesis of polyurea microcapsules by interfacial polycondensation in order to reduce consumption of organic solvents.
- ✓ Pre polymer based method can be effectively developed and utilized as a greener process development approach to eliminate use of various organic solvents and it can be effective for encapsulation of different insecticides.

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# APPENDIX-I

# Details of Analytical Equipments

FTIR spectrophotometer (Spectrum One, Perkin Elmer) was used to examine functional groups of polyurea. The powder X-ray analysis of polyurea samples was recorded using Bruker powder X-ray diffractometer (Model D2 Phaser, Bruker, USA). Percentage crystallinity was calculated from X-ray diffractogram using ORIGIN-Pro-8.5. TGA/DTA1 METLER TOLEDO was used to evaluate thermal stability of polyurea in the range of temperature $30^0$C to 500 $^0$C at a heating rate of 100C/min.

## 1. Fourier Transform-Infrared Spectroscopy (FTIR):

Fourier Transform-Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.

When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The FTIR spectrometer uses an interferometer to modulate the wavelength from a broadband infrared source. A detector measures the intensity of transmitted or reflected light as a function of its wavelength. The signal obtained from the detector is an interferogram, which must be analyzed with a computer using Fourier transforms to obtain a single-beam infrared spectrum. The FTIR spectra are usually presented as plots of intensity versus wave number (in cm-1). Wave number is the reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wave number.

## 2. X-ray diffraction (XRD):

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of $2\theta$angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

## 3. Differential Scanning Calorimeter (DSC):

DSC analysis is used to measure melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, precipitation energy and temperature, denaturisation temperatures, oxidation induction times, and specific heat or heat capacity.

DSC analysis measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes.

Only non-corrosive samples can be analyzed in this very sensitive instrument. No organic or other materials containing F, Cl, Br, or I may be submitted for DSC analysis without our knowledge. The customer must either tell us what the material is or at least that it is non-corrosive to metals and assume responsibility for possible replacement of a $3000 DSC cell if a cell is destroyed as a result of the analysis of their sample. Or, you may have us perform such analysis as may be needed to determine what the material is and whether it can be analyzed in the DSC. Sometimes a higher temperature DSC to which we have

access may be able to handle somewhat more corrosive samples in the lower temperature range.

The sample is placed in a suitable pan and sits upon a constantan disc on a platform in the DSC analysis cell with a chromel wafer immediately underneath. A chromel-alumel thermocouple under the constantan disc measures the sample temperature. An empty reference pan sits on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow is measured by comparing the difference in temperature across the sample and the reference chromel wafers.

Temperature can range from -120°C to 725°C, though an inert atmosphere is required above 600°C. The temperature is measured with a repeatability of ±0.1°C. We have access to a higher temperature DSC/DTA instrument capable of a maximum temperature of 1500°C, though it has a lower sensitivity at temperatures below 725°C compared to our primary DSC.

Pans of Al, Cu, Au, Pt, alumina, and graphite are available and need to be chosen to avoid reactions with samples and with regard to the temperature range of the measurement.

Atmospheres: nitrogen, air, oxygen, argon, vacuum, controlled mixed gases.

**4. Scanning Electron Microscope (SEM):**

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal

orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence --CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete ortitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

# APPENDIX-II

# Determination of Percentage Crystallinity

A sample of Polyurea was characterized and XRD data using RIGAKU Software

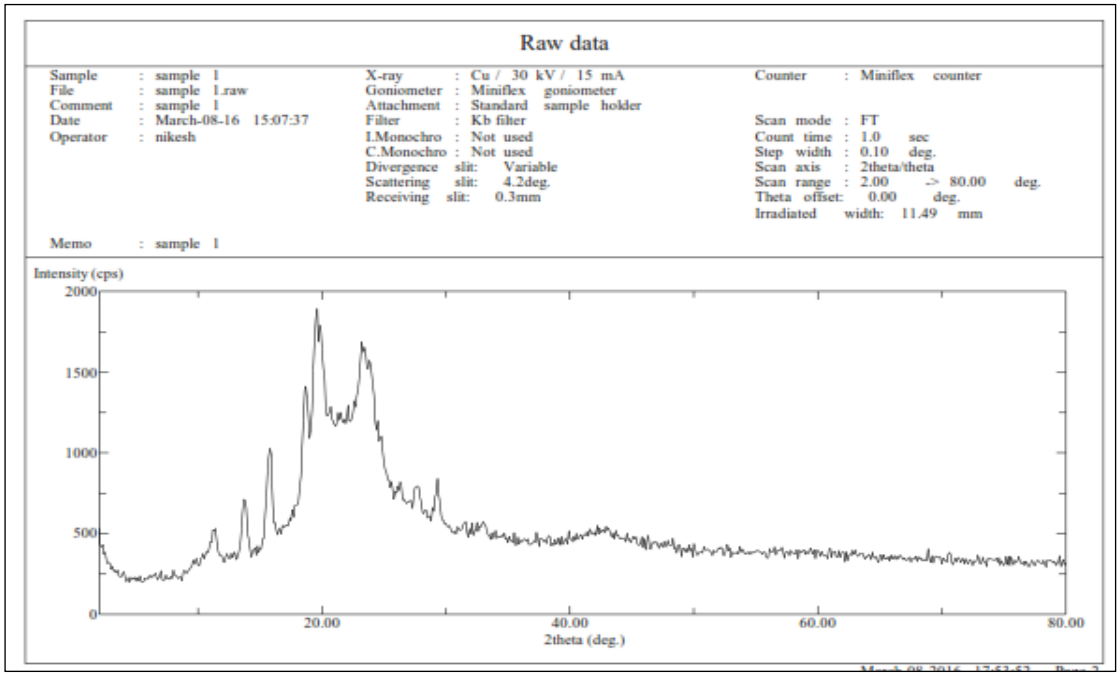



**Fig. 1 (a)**

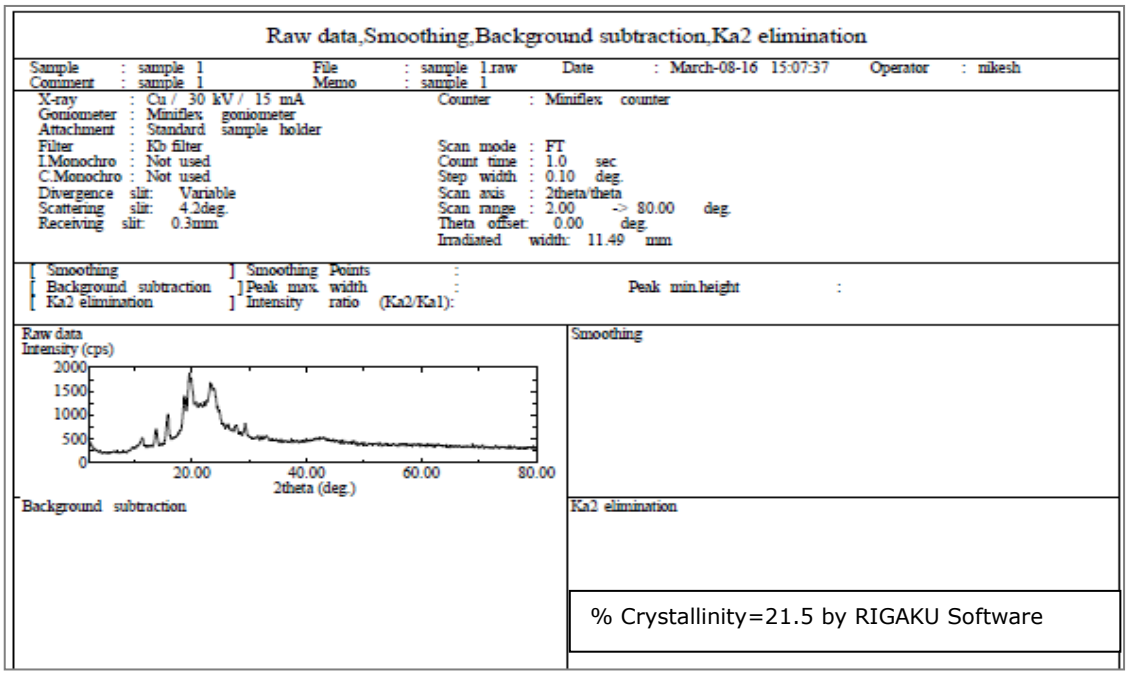
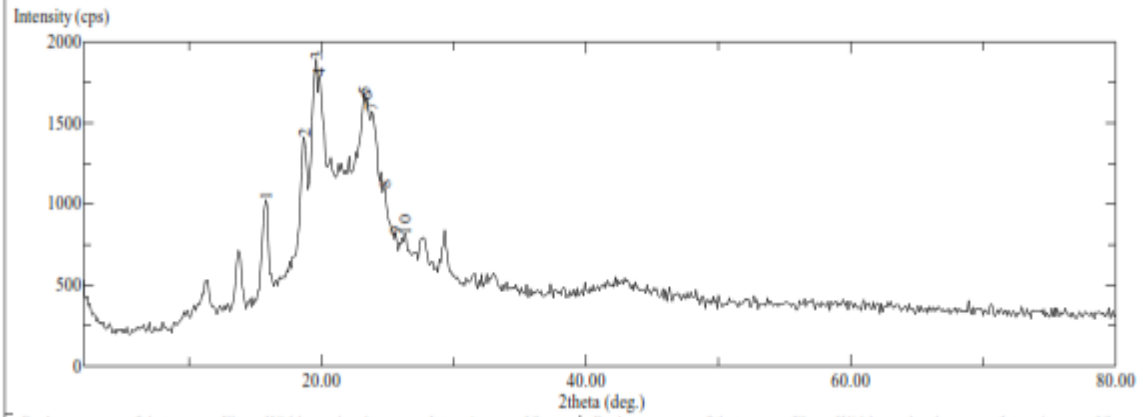



**Fig. 1 (b)**

Peak Search

| | | | | | |
|---|---|---|---|---|---|
| Sample | : sample 1 | File | : sample 1.raw | Date | : March-08-16 15:07:37 |
| Comment | : sample 1 | Memo | : sample 1 | | |
| Method | : 2nd differential | Typical width | : 0.261 deg. | Min. height | : 422.54 cps |




| Peak no. | 2theta | Flex Width | d-value | Intensity | I/Io | Peak no. | 2theta | Flex Width | d-value | Intensity | I/Io |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 15.800 | 0.471 | 5.6043 | 1028 | 55 | | | | | | |
| 2 | 18.700 | 0.353 | 4.7412 | 1414 | 75 | | | | | | |
| 3 | 19.600 | 0.471 | 4.5255 | 1894 | 100 | | | | | | |
| 4 | 19.800 | 0.353 | 4.4802 | 1791 | 95 | | | | | | |
| 5 | 23.200 | 0.235 | 3.8308 | 1688 | 90 | | | | | | |
| 6 | 23.400 | 0.235 | 3.7985 | 1655 | 88 | | | | | | |
| 7 | 23.800 | 0.353 | 3.7355 | 1574 | 84 | | | | | | |
| 8 | 24.800 | 0.235 | 3.5871 | 1105 | 59 | | | | | | |
| 9 | 25.600 | 0.235 | 3.4768 | 820 | 44 | | | | | | |
| 10 | 26.300 | 0.235 | 3.3858 | 821 | 44 | | | | | | |

**Fig.1 (c)**

21.5 % Crystallinity of Polyurea from XRD data using RIGAKU Software is as shown in Figure 1(a) to (c).

For the same sample using ORIGIN 8.5.1 Pro - Software (to calculate integral area) and following formula, % crystallinity is 22.5 as shown in Fig. 2. Therefore the same procedure is followed for remaining all samples to calculate % crystallinity.

% Crystallinity = $\frac{A_C}{A_c + A_a}$ = $\frac{A_C}{A_{Total}}$

Where, $A_c$ = Area of Crystalline Phase of Polymer

$A_a$ = Area of Amorphous Phase of Polymer

$A_{Toal}$ = Total Area

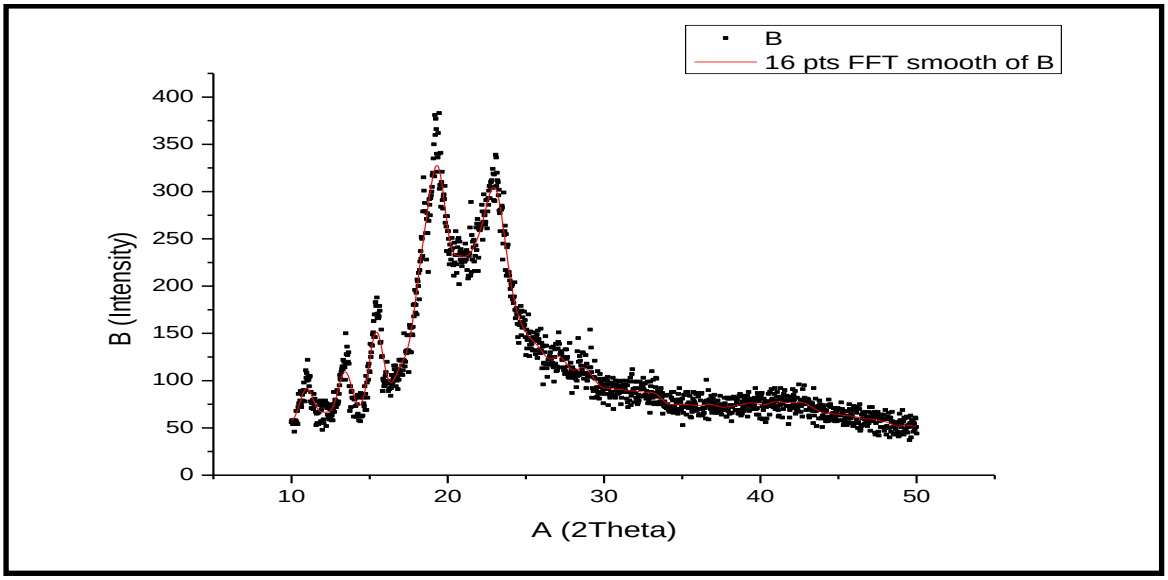



**Fig. 2** Data Smoothening by FFT Filter ORIGIN PRO-85 to ddetermine Integral Area

# APPENDIX-III

# Determination of Viscosity Average Molecular Weight ($\bar{M}_V$) of Polyurea

**Viscosity of Polyurea Solution in 98% concentrated $H_2SO_4$:**

1. 0.5 gm/dl of Polyurea solution was prepared in in 98% conc.H2SO4, and viscometery data were collected using Ostwald-Fenske viscometer at 25 $^0$C.

   Volume of sample taken = 20 ml

   Time required for reference liquid ($t_0$) = 153.53 sec

| Sr. No. | Time (t)sec | Specific Viscosity ($\eta_{sp}$) | $[\eta] = [(\eta_{sp})/c]$ |
|---|---|---|---|
| 1. | 187.2 | 0.2193 | 0.4386 |
| 2. | 186.6 | 0.2153 | 0.4306 |
| 3. | 189.6 | 0.2349 | 0.4698 |

2. Intrinsic Viscosity was calculated as: 0.4463dl/gm = 0.0965 gm/m sec
3. With use of Mark-Houwikn's constants reported in literature,

   k= $7.46 \times 10^{-5}$ and
   a= 0.92

4. the viscosity average molecular weight $\mathbf{(\bar{M}_v) = k[\eta] + a}$ = 12,740.89 Kg/Kmol

# Research Publications

***Publication in Journal:***

[1] Ujvala P. Christian, Shrikant J. Wagh, "Effect of Phase Volume Ratio on Synthesis of Polyurea Microcapsules by Interfacial Polymerization", International Journal of Advanced Research in Engineering and Technology, Vol. 9, Issue 3 (2018), 60-65. (UGC Approved Journal in 2018, ISSN: 09766480, E-ISSN: 09766499).

[2] Ujvala P. Christian, Shrikant J. Wagh, "Controlled Release of Insecticides through Polyurea Microcapsules Synthesized by Interfacial Polycondensation", *Asian Journal of Chemistry*, Vol.30, No. 11(2018), 2571-2576. (Scopus Indexed & UGC Approved Journal No.8774, ISSN:09707077) doi: 10.14233/ajchem.2018.21631

[3] Ujvala P. Christian, Shrikant J. Wagh, 'Experimental Studies on n-Octane and Cyclohexane as Organic Solvent for Synthesis of Polyurea Microcapsules by Interfacial Polycondensation', *Asian Journal of Engineering and Applied Technology* Vol. 7, No. 2(2018), 64-66. (UGC Approved Journal in 2018, ISSN: 2249068X).

***Publication in Conferences Proceeding:***

[1] Ujvala P. Christian, Shrikant J. Wagh 'Review of Experimentally Studied Systems for Synthesis of Polymer Microcapsules by Interfacial Polymerization' was presented in an International Conference 'CHEMCON-2014' at Punjab University, Chandigarh during 27$^{th}$ to 30$^{th}$ December-2014.

[2] Ujvala P. Christian 'Synthesis and Characterization of Polyurea Microcapsules derived from Hexamethylene Diamine (HMDA) and Hexamethylene Diisocyanate (HMDI)' in an International Conference International Conference Women in Science & Technology: Creating Sustainable Career (ICWSTCSC–2016) at BVM- Engineering College, V.V.NAGAR , Gujarat during 28$^{th}$ to 30$^{th}$ January-2016. Published in Indian Journal of Technical Education (IJTE), ISSN: 0971-3034.

[3] Ujvala P. Christian, Shrikant J. Wagh 'Effect of Phase Volume Ratio and Organic Solvent on Polyurea Synthesis by Interfacial Polycondensation' in an International Conference on "Paradigm shift in Chemical Engineering education, processes and technology" at organized by The Institution of Engineers India (IEI)- Gujarat State Centre, at IEI Centre, Ahmedabad-Gujarat during $16^{th}$ -$17^{th}$ September-2017.

[4] Ujvala P. Christian, Shrikant J. Wagh 'Study on the Effect of Kinetic Parameters on Controlled Release of Chlorpyriphos through Polyurea Shell Synthesis by Interfacial Polycondensation' in an International Conference GTU-ICON 2019 (Engineering and Technology), organized by Gujarat Technological University, Ahmedabad-Gujarat on $16^{th}$ March-2019.