Chapter 2

One shot kinetic studies of hyperbranched polyester as a crosslinker in polyurethane formation by in-situ FTIR

2.1 INTRODUCTION

Among the many industrial polymers, polyurethanes are known to exhibit versatile characteristics and wide applications. They are synthesized by reacting polyol (an alcohol with two or more reactive hydroxyl groups per molecule) with diisocyanate or a polymeric isocyanate in the presence / absence of suitable catalysts and additives. Polyurethanes can be prepared either by one-step or by prepolymer method. Due to the availability of different types of diisocyanates, polyols (polyester or polyether polyol with different molecular weight), chain extenders as well as methods of synthesis, a variety of polyurethanes can be produced leading to a broad spectrum of materials to meet specific applications. Polyurethanes are part of a diversified group of materials that find uses in a broad range of applications, both industrial and domestic such as foam mattresses, paints and lacquers, medical implants, rollers, electrical encapsulation, engineering components, shoe soles, seals and also in the mining industry (Clemiston 2008).

2.1.1 HISTORY AND DEVELOPMENT OF POLYURETHANES

Polyurethanes are block copolymers containing blocks of low molecular weight polyesters or polyethers covalently bonded by a urethane group. Polyurethane which follows a simple diisocyanate polyaddition reaction, was first produced by Professor Otto Bayer in the I.G.Farben laboratories in 1937 (Otto Bayer et al 1937) when he and his co-workers were trying to upgrade the properties of synthetic polyamide fibers and thus opening the door to a new class of high performance polymeric materials suitable for elastomeric, adhesives, coatings, fibers and foam applications. The basic idea which he documented in March 1937, relates to spinnable products made from hexane-1,6-diisocyanate and hexa-1,6-diamine. The polyurethane fiber formed using this reaction
had been marketed as Perlon-U by Bayer. Afterwards, DuPont and ICI chemists discovered the elastomeric properties of it. Initially, polyurethane produced was of fiber and elastomeric characteristics with enhanced properties. In order to reinforce the wings of military aircrafts with its enhanced performance during World War II, Bayer used naphthalene 1,5-diisocyanate (NDI) and polyester resins to prepare elastomeric polyurethane foams. Apart from it, polyurethane coatings were utilized for the impregnation of paper and the manufacture of mustard gas resistant garments, high-gloss airplane finishes and chemical and corrosion-resistant coatings to protect metal, wood, and masonry (Saunders and Frisch 1962).

Chemistry of polyurethane started to develop rapidly using toluene diisocyanate (TDI) with polyether polyol from Dow Chemical in 1950’s. In 1954, polyurethane fiber spandex was successfully copolymerized using polyethylene glycol and toluene 2,4-diisocyanate in presence of water by DuPont to replace natural rubber threads (Holden et al 2004). The polyurethane urea fiber synthesized from using methylene bis(4-phenylene isocyanate) and ethylene diamine was marketed under the trade name ‘Lycra’ by DuPont in 1959.

Early research on polyurethane elastomer synthesis using NDI resulted in the gummy materials because of irregular elastomeric network from low hard segment concentration. Properties of these elastomers were enhanced considerably by replacing NDI using methylene diisocyanate (MDI) and by introducing either diols or diamines. Linear polyurethane prepared from MDI, adipic acid and 1,4-butanediol in 1957, has fascinating properties like extensibility, high elasticity, abrasion resistance and solubility by Schollenberger (Schollenberger et al 1958) and he called it a “virtually crosslinked elastomer” and thus leading to a new family of thermoplastic polyurethane (TPU) elastomers. However, the structure-property relationship was still not very clearly understood. In order to understand the exact structure and its relationship with the properties, a lot of research work had been carried out. Cooper and Tobolsky (1966) were the first to reason out elasomeric properties of TPU because of phase separated hard and soft blocks in polyurethane. MDI has proven itself as a key component to fabricate elastomeric fibers during 1960’s and it resulted in the dramatic expansion of polyurethane industry. Nowadays, polyurethanes are globally marketed by four major companies,
BASF, Bayer, Dow and Huntsman. The major developments in commercial polyurethanes are given in Table 2.1. The wide range of polyurethane types, are useful in a wide variety of consumer and industrial applications as illustrated in Table 2.2.

Table 2.1: Major developments in commercial polyurethanes (Lamba et al 1997)

<table>
<thead>
<tr>
<th>Year</th>
<th>Developments of polyurethanes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1937</td>
<td>First application for polyurethane patent – I.G.Farbenindustrie</td>
<td>Bayer (1937)</td>
</tr>
<tr>
<td>1941</td>
<td>Reactions of diisocyanates and glycols</td>
<td>Lieser (1941)</td>
</tr>
<tr>
<td>1947</td>
<td>First rigid foams (Bayer)</td>
<td></td>
</tr>
<tr>
<td>1952</td>
<td>First flexible polyurethanes</td>
<td>Hochtlen (1952)</td>
</tr>
<tr>
<td>1957</td>
<td>Polyether urethanes foams commercially available</td>
<td></td>
</tr>
<tr>
<td>1958</td>
<td>Thermoplastic polyurethanes (TPU) discovered (Commercialized in 1961)</td>
<td></td>
</tr>
<tr>
<td>1960</td>
<td>US Lycra® patent awarded</td>
<td>Steuber (1960)</td>
</tr>
<tr>
<td>1972</td>
<td>Biomer® (Lycra T – 126 with a new name)</td>
<td>Boretos (1972)</td>
</tr>
<tr>
<td>1977</td>
<td>Pelletane® family of materials introduced</td>
<td></td>
</tr>
<tr>
<td>1979</td>
<td>Second generation polyurethanes disclosed</td>
<td></td>
</tr>
<tr>
<td>1983</td>
<td>First plastic-body automobile (Pontiac Fiero) in USA</td>
<td></td>
</tr>
<tr>
<td>1990s</td>
<td>Development of two-component polyurea spray elastomers</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.2: Applications of Polyurethane (Huntsman 2008)

<table>
<thead>
<tr>
<th>Type</th>
<th>Applications</th>
</tr>
</thead>
</table>
| Rigid Foam                    | • Packaging  
• Furniture  
• Buoyancy aids in boats and flotation equipments  
• Equipment housings  
• Thermal insulation for buildings, refrigerators, pipelines, deep freeze equipments and storage tanks |
| Flexible Foam                 | • Automotive seating  
• Household furniture including bedding  
• Cushioning for diverse industrial applications  
• Textile laminates |
| Semi-rigid and Low Density Structural Foam | • Steering wheels, head rests and other automotive interior trim components  
• Furniture elements  
• Sport goods such as skis and surf boards |
| Elastomers                    | • Shoe soles  
• Vehicle body panels  
• Rollers and gear wheels  
• Conveyors  
• Sealants for construction and automotive industries  
• Fibers |

2.1.2 REACTIONS OF ISOCYANATES

The high reactivity of isocyanate towards nucleophilic reagents is mainly due to pronounced electropositive character of the carbon atom caused by the delocalization of electrons onto oxygen, nitrogen and aromatic group. Aromatic isocyanates are, therefore, more reactive than aliphatic isocyanates, because of negative charge delocalization. Substitution on the aromatic ring can affect the delocalization of negative charge in case of aromatic isocyanates. Electron withdrawing groups on the ortho or para position can
increase the reactivity of the NCO group, while an electron donating group will have the
reverse effect on the reactivity of isocyanate. The presence of bulky groups in the ortho-
position on aromatic isocyanates, or branched or bulky substituents on aliphatic
molecules will sterically hinder the approach of electron donors and reduce the rate of
reaction. In diisocyanates, the rate of reaction of the second isocyanate is slower than that
of the first group. This difference is reduced considerably if the isocyanate groups are
separated by an aliphatic chain or aromatic rings (Lamba et al 1997). The electronic
structure of isocyanate group can be represented by resonating structures as shown in
Scheme 2.1.

\[
\begin{array}{c}
\text{R-N=C=O} \\
\text{R-N=C-O} \\
\text{R-N=C=O} \\
\text{R-N=C=O}
\end{array}
\]

Scheme 2.1: Resonating structures of isocyanate group.

The reactions of isocyanates can be divided into three groups: (1) primary
reactions involving urethane formation by polyaddition reaction (2) secondary reactions
involving the side reactions and (3) third reaction involves the polymerization of
isocyanates by self-addition reaction.

2.1.2.1 PRIMARY REACTIONS OF ISOCYANATES

(a) With Polyol: Addition of polyol with isocyanate is an exothermic reaction
controlled by the structure of both the reactants. Aliphatic polyols with primary hydroxyl
end groups are more (about ten times) reactive than that of secondary hydroxyl groups
(Lamba et al 1997). The reaction between phenol and isocyanate which usually proceeds
slowly, leads to the formation of unstable polyurethane, which is decomposed into the
original isocyanate and phenol upon heating. The rate of reaction between isocyanate and
polyol is dependent on the size of substituents of polyols. The reaction can be carried out
using acid catalysts such as mineral acid, acid halide, etc. or basic moieties such as
tertiary amines and metal (Sn, Zn, Fe) salts or without catalysts depending upon the
isocyanate used in the reaction. The reaction scheme of isocyanate with polyol is shown in
Scheme 2.2.
(b) **With Water:** Scheme 2.3 represents the reaction of isocyanate with water. Generally, commercial polyols contain some minimum (less than 0.05 %) amount of water. When isocyanates react with polyol having moisture, it will lead to the undesired reaction product, urea (Scheme 2.4) which could be obtained by decomposition of the formed carbamic acid as shown in Scheme 2.3 rather than the formation of urethane as the desired product. However, the reaction of isocyanate with water is necessary for the production of low density flexible foams because of the presence of carbon dioxide formed during the decomposition of carbamic acid. The primary product of the reaction with water is a substituted carbamic acid, which breaks down into an amine and carbon dioxide (Petrovic and Ferguson 1991; Lamba et al 1997).

\[
\text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-NHCONH-R'}
\]

Scheme 2.3: Reaction of isocyanate with water.

(c) **With Amines:** The reactivity of amine is greater than that of primary alcohol because of high nucleophilicity of amino group. The reactivity of amines depends on the basicity of the amine and higher the basicity, greater the reactivity of amine. Aromatic amines react much slower than that of aliphatic amines due to steric hindrance and electron withdrawing substituents. Since tertiary amines do not have active hydrogen atoms, they do not react with isocyanates. The reaction of isocyanate with amine resulting in the formation of urea is shown in Scheme 2.4.

\[
\text{R-NCO} + \text{R'}\text{NH}_2 \rightarrow \text{R-NHCONH-R'}
\]

Scheme 2.4: Reaction of isocyanate with amine (Lamba et al 1997).
2.1.2.2 SECONDARY REACTIONS OF ISOCYANATE

Depending upon the reaction condition, secondary reactions could occur to a lesser extent during polyurethane or polyurea formation. The formation of allophanate and biuret reactions (Scheme 2.5) are cross-linking reactions and occur at an appreciable rate over the temperature intervals of 120-150 °C and usually below at around 20 °C for biuret formation in comparison to that of allophanate formation (120-150 °C). Allophanate could also be formed even at lower temperature in presence of excess isocyanate. A basic property associated with allophanate and biuret is their low thermal stability. The reaction of isocyanates with urea groups is considerably faster than that with urethane groups. However, these linkages are thermally reversible and it gets dissociated into starting components at higher temperatures above 150 °C (Petrovic and Ferguson 1991).

![Scheme 2.5: Secondary reactions of isocyanate (Lamba et al 1997).](image)

2.1.2.3 ISOCYANATE POLYMERIZATION REACTIONS

The self condensation of isocyanate results in uretidione (dimer), isocyanurate (trimer) or carbodiimide as depicted in Schemes 2.6–2.8. The formation of carbodiimides is not usually considered a polymerization reaction, but it could be classified as a condensation polymerization between isocyanate molecules with the elimination of CO₂. This is due to degradation of isocyanates taking place at higher temperatures (Levchik and Weil 2004).
2.1.3 POLYOLS

Polyols are hydroxyl terminated macromolecules and of nucleophilic character. The properties of polyurethanes are determined by the structure of polyol. A broad range of polyols are used to synthesize polyurethanes and they are polyesters, polyethers, polycarbonates, hydrocarbons and polydimethylsiloxanes used for elastomer synthesis. The elastomeric nature is determined by the soft segment which is made up of polyol. However, most of them fall under two classes: hydroxyl terminated polyethers and hydroxyl terminated polyesters (Lamba et al 1997).

2.1.3.1 POLYETHER POLYOLS

The hydroxyl functionality, hydroxyl equivalent weight, the reactivity and compatibility with the other components are important characteristics of polyol to determine the polyurethane formulation. Specific applications could be resulted from tailoring the polyols by blending polyols with different functionality, molecular weight
and reactivity. Examples of commercial polyether polyols are polyethylene oxide (PEO), polypropylene oxide (PPO) and polytetramethylene oxide (PTMO) (Lamba et al 1997). The following are some of the characteristics of polyurethane synthesized by using polyether polyols (Lamba et al 1997; Voit 2001):

- Very good hydrolytic resistance
- Outstanding low temperature flexibility
- Resistance to microbial degradation
- Outstanding clarity

2.1.3.2 POLYESTER POLYOLS

The properties of the elastomers are controlled not only mainly by the overall molecular weight of the polyester but also to some extent by the molecular weight distribution. Generally, polycaprolactones and aliphatic polycarbonate are used for commercial purpose. For elastomers, linear polyester polyols having molecular weight of ca. 2000 should be preferred. Examples for commercial polyester polyols are polyethylene adipate (PEA), polytetramethylene adipate (PTMA) and polycaprolactone (PCL). The stability towards water is lower for polyester polyols in comparison to that of polyether polyols. However, they show better thermal and oxidation stabilities when compared to that of polyether polyols. The following are the characteristic features (Reed 1997) that exhibited by using polyester polyols for synthesizing polyurethane:

- Resistance to heat
- High resistance to oils and chemicals
- Excellent tear strength
- Outstanding mechanical properties

2.1.4 CHAIN EXTENDERS

Chain extenders (f=2) and crosslinkers (f=3) which play a vital role in polymer morphology, are low molecular weight hydroxyl or amine terminated compounds. They are classified into (a) aromatic diols and diamines and (b) aliphatic diols and diamines. Polyurethanes synthesized by using aliphatic chain extenders exhibit generally
elastomeric nature in comparison to that of aromatic chain extenders. Chain extenders are used to extend the length of the hard segment and to increase the H-bonding density as well as the molecular weight of the polyurethane. The mechanical properties of polyurethane are determined by the hard segment which is made up of diisocyanate and the chain extender. Common commercial chain extenders include 1,4-butanediol, ethylene diamine, ethylene glycol, hexanediol and 4,4′ methylene bis(2-chloroaniline). The diol chain extenders form well crystallized hard segments with isocyanates. Diamine chain extenders react rapidly and vigorously with isocyanates to produce urea groups and the resultant urea groups can produce a polymer crosslinked with biuret links. Polyurethane synthesized using diamine chain extenders shows higher density of secondary bonding, high hard segment, $T_g$ and high thermal stability of the polymer. Besides, trifunctional and poly functional chain extenders can also be used which usually result in branched or crosslinked polyurethane (Lamba et al 1997; Petrovic and Ferguson 1991).

2.1.5 SYNTHESIS OF SEGMENTED POLYURETHANE ELASTOMER

Segmented polyurethanes can be prepared either by ‘one shot method’ or the ‘prepolymer method’ in bulk or in solution as shown in Scheme 2.9. The synthesis of polyurethane which is an exothermic polyaddition reaction may be performed at temperatures below 80 °C to avoid the formation of biuret and allophanate. The final properties of polyurethane are dictated by the molar ratio of NCO/OH or NCO/NH$_2$, polyol structure, isocyanate and chain extender used (Lamba et al 1997). The desired properties of polyurethane are obtained only when the molar ratio of isocyanate to hydroxyl and/or amine should be maintained one. Stoichiometry of the reacting groups is very important since a slight deviation of it affects the polymer molecular weight. If the stoichiometric ratio of hydrogen bearing nucleophiles to isocyanate is less than 1 (ca. 0.96) (Meckel et al 1987), a low molecular weight product is obtained, while if it is greater than 1 (ca. 1.1) (Meckel et al 1987), a partially crosslinked product is obtained and the process will be realized a bit difficult.
In one-step method of synthesis, polyol, isocyanate and the chain extender are mixed together and allowed to polymerize whereas in the prepolymer method, isocyanate (NCO) terminated prepolymer is synthesized first by reacting excess diisocyanate with polyol and then this isocyanate terminated prepolymer formed is reacted with chain extender (dil or diamine) resulting in high molecular weight polymer. DMAc and DMF are generally employed for solution polymerization reactions. Both synthetic methods can be performed batchwise and continuously either in a mixing chamber or in an extruder (Holden and Legge 1987; Frye et al 1966; Goyert et al 1981; Hyun and Kim 1988; Lipsitz and Macosko 1977; Lunardon et al 1980; Quiring et al 1981; Wal et al 1999; Zeitler et al 1986).

The morphology as well as the properties of the resulting polymer is not only dictated by the method of synthesis but also by the reactants and their reactivity. Side reactions which lead to the formation of allophanate and biuret causing chain branching and an increase in molecular weight (Woods 1990) could be minimized if the reaction is conducted in solution or maintaining the stoichiometric ratio of NCO/OH as 1. Reaction conditions also influence structural heterogeneity and molecular weight of the product. Polyurethanes prepared by prepolymer method results in highly ordered segments where the sequences are found to be more regular in comparison to that of one-step method. Thus, the properties exhibited by polyurethanes synthesized by prepolymer method are superior to that of one-step method since the hard segments are packed in ordered fashion resulting in structural regularity.

Scheme 2.9: Synthesis of polyurethane by one shot and prepolymer methods (Lamba et al 1997).
2.1.6 LITERATURE SURVEY

Kinetics of polyurethane has been studied by two different ways, indirect and direct methods. Indirect methods measure a physical property that can be functionally related to the extent of reaction e.g. rheometry and thermal techniques, whereas direct methods measure the concentration of reactant or product species e.g. titration and spectroscopy. Indirect methods such as DSC (Hager et al 1981; Sanchez and Graziano 1992) follows slow polyurethane reactions while adiabatic temperature rise (ATR) (Lipshitz and Macosko 1977; Richter and Macosko 1978; Steinle et al 1980) that follows fast polyurethane reactions are simplest methods used to monitor the kinetics of polyurethane reactions. Extent of reaction can be obtained by correlating the heat evolution by making many assumptions in ATR method. Spectroscopic techniques are also one of the most popular methods in monitoring the kinetics of polyurethane reactions by noticing the changes in the specific bands (either isocyanate or urethane) and then again furnish an idea about the extent of reaction.

Using aromatic diisocyanates, kinetics of polyurethane reaction has been extensively investigated (Majukdar et al 2000; Rand et al 1965; Willeboordse 1970; Turri et al 2000; Yilgor and McGrath 1985). Generally, the kinetics of polyurethane with or without catalyst between isocyanate and an alcohol follows a second order reaction as indicated by linearity of $1/[\text{NCO}]$ against time plot (Majukdar et al 2000; Rand et al 1965; Saunders and Frisch 1962; Willeboordse 1970; Turri et al 2000). There are many parameters in kinetics studies such as temperature, catalyst types and concentration, stoichiometric ratio of monomers and the types of isocyanate i.e. aromatic versus aliphatic have been well analyzed.

Kinetics of the isocyanate/alcohol reaction has been traditionally monitored by analysis of aliquots taken from the reaction at a regular time intervals. The instantaneous isocyanate concentration was determined by quenching the aliquot with a known excess of amine and then back-titrating the unreacted amine with an acid to determine the concentration of isocyanate within the aliquot (Majumdar et al 2000; Rand et al 1965; Turri et al 2000; Yilgor and McGrath 1985; Bialas et al 1990; Schwetlick et al 1994).
The progress of the reaction for polyurethane formation is widely monitored by the aforesaid two methods such as standard dibutylamine back-titration and FTIR spectroscopy such as transmission, reflection and ATR (attenuated total reflection). Both methods provide an idea of concentration of reactant or product and can be used to obtain kinetic data for the reaction concerned (Burel et al 2005; Ajithkumar et al 1997; Yilgor et al 2004; Keskin and Ozkar 2001). Though, spectroscopic techniques often demand extensive data processing, it can provide a detailed understanding of the polymerization by noticing the changes of specific bands during the reaction process. The knowledge of reaction intermediates could be obtained from in-situ reaction kinetics data by acquiring a series of spectra as a function of time (Yang and Lee 1988). Vibrational spectroscopic techniques are also more sensitive at high conversion than such conventional techniques as differential scanning calorimetry (DSC), densitometry and dilatometry (Gulari et al 1984). In the FTIR spectrum, urethane and isocyanate could be easily differentiated by the appearance of their characteristic absorption peaks.

According to the literature, the reaction of an isocyanate with an alcohol is globally described as second order model until isocyanate conversions that vary between 70% and 80%, after which a positive or negative deviation is observed. Positive deviations due to (i) catalytic effect of hydroxyl groups, (ii) autocatalysis of the formed urethane groups and (iii) the formation of allophanate groups (Sato 1962; Boufi et al 1993; Arlas et al 2007), are favored at high temperatures. On the other hand, with increase of viscosity during polymerization course when the reaction is carried out in bulk, negative deviations could also be justified. The cause of variations can alternatively be assigned to reactivity differences among functional groups (Pavier and Gandini 2000).

In the updated literature review, only one research group has been credited to carry out the kinetics of polyurethane formation using hyperbranched polyester as a crosslinker. Maji and Bhowmick studied the curing kinetics of polyurethane formation by using prepolymer with three different generations of hyperbranched polyol (Boltorn synthesized using pentaerythritol as a core and dimethylol propionic acid as a monomer) by using in-situ FTIR spectroscopy. The disappearance of the strong isocyanate
absorption peak was followed with time and temperature to determine the reaction kinetics. It was shown that all the hyperbranched polyols followed the second order kinetic equation and the reaction rate enhanced with increase in the number of the functional groups of the hyperbranched polyol (Maji and Bhowmick 2009).

2.1.7 OBJECTIVE OF THE CHAPTER

So far in the literature, curing kinetics of polyurethane (PU) formation by hyperbranched polyester (HBP) by one shot synthesis has not been reported at all. The objective of this chapter is,

(a) To synthesize different generations of hyperbranched polyesters (HBP-G1, HBP-G2 and HBP-G3) using phenyldichlorophosphate as a core and dimethylol propionic acid as a monomer by one-step synthesis and their characterization using different techniques.

(b) To ascertain the order of PU curing reaction for two different NCO/OH ratios using HBP-G3 as a crosslinker by in-situ FTIR technique.

(c) To determine quantitatively the percentage content of PU formed for lower NCO/OH ratio and to extract the pure urethane content as a function of curing temperature from non-isothermal curing kinetics using Factor Analysis program.

(d) To derive the thermodynamic parameters like activation energy, $E_a$; activation enthalpy, $\Delta H^\ddagger$; and activation entropy, $\Delta S^\ddagger$ from Arrhenius and Eyring plots for lower NCO/OH ratio.

2.2 EXPERIMENTAL

2.2.1 MATERIALS

All the required chemicals such as phenyldichlorophosphate (PDCP), dimethylol propionic acid (DMPA), polyethylene glycol (PEG, molecular weight 600), $p$-toluenesulphonic acid ($p$-TSA) and hexamethylene diisocyanate (HMDA) were procured from Aldrich Chemicals.
2.2.2 ONE STEP SYNTHESIS OF HYPERBRANCHED POLYESTERS (HBPs)

HBp polyol of generations 1 to 3 (HBp-G1 to G3) were synthesized separately by melt polycondensation method. For the synthesis of HBp-G3, calculated amount of PDCP (used as A₂ type core), DMPA (used as AB₂ type monomer) and p-TSA (0.05 wt.-% of DMPA) were taken in a three-necked flat-bottomed flask equipped with nitrogen inlet, guard tube, mechanical stirrer and placed in an oil bath. The reaction temperature was slowly raised to 140 °C and maintained at that condition for about 21 h to ensure the complete removal of HCl gas which is evolved as a by-product of the esterification reaction. Further reaction was carried out under reduced pressure for about 0.5 h to aid the removal of moisture and also to increase its molecular weight. The aforementioned procedure is adopted for synthesizing HBp-G1 (15 h at 140 °C) and HBp-G2 (17 h at 140 °C). The molar ratios for different generations of HBPs and its reaction schemes are shown in Table 2.3 and Scheme 2.10, respectively.

Table 2.3: Molar ratios used for the preparation of HBPs (HBp-G1 to HBp-G3)

<table>
<thead>
<tr>
<th>HBP</th>
<th>moles</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PDCP</td>
<td>DMPA</td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>G2</td>
<td>1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>1</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Reactions scheme:} \quad \text{PDCP} + \text{2DMPA} \xrightarrow{p\text{-TSA}} \text{HBp-G1} \quad \text{at} \quad 140 \degree C, N_2 \text{atm} \]
Scheme 2.10: Synthesis of HBPs (HBP-G1 to HBP-G3) in its idealized structure.

2.2.3 KINETICS OF POLYURETHANE

Among the three generations of HBPs synthesized in the present study, HBP-G3 was chosen as a crosslinker to analyze the curing kinetics of PU formation. One-shot PU formation limited to the reaction between PEG, HMDI and HBP-G3 (as a crosslinker) is shown in Scheme 2.11. The weight of reactants used and the NCO/OH ratios are given in Table 2.4. Prior to the reaction, PEG was subjected to vacuum at 60 °C for 3 h to remove the moisture, if any. At first, curing kinetic studies were performed for both lower and
higher NCO/OH ratios under isothermal condition (60 °C) to predict the reaction rate law and to confirm if the products formed are either primary (urethane) or secondary (allophanate, urea and biuret). In the second part, non-isothermal curing kinetic study was carried out from 40 to 160 °C (1 °C/min.) for the reactant composition pertaining to the NCO/OH ratio of 1.2316. Based on the data obtained from non-isothermal curing kinetics, the sample composition (NCO/OH = 1.2316) was finally subjected to isothermal curing kinetics at 70, 90 and 110 °C as a function of curing time. Calculated amount of PEG and HBP-G3 were homogenized by stirring at room temperature. Further, it is divided into equal portions and kept in a vacuum oven at 80 °C to remove the moisture. Later, a calculated amount of HMDI was added to the above reaction mixture, stirred vigorously and pasted on KBr pellet to study the kinetics of polyurethane reaction. The crosslinking of polyurethane is shown in Scheme 2.11. The relevant parameter for the kinetic analysis is the decrease in absorption intensity of -NCO band at ca. 2273 cm⁻¹. Factor analysis was performed for non-isothermal reaction from 40 to 160 °C to extract the pure-component spectra and polyurethane content formed.

<table>
<thead>
<tr>
<th>Polyo1 (mole)</th>
<th>HBP (mole)</th>
<th>HMDI (mole)</th>
<th>NCO/OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00185</td>
<td>0.00074</td>
<td>0.00319</td>
<td>1.2316</td>
</tr>
<tr>
<td>0.00185</td>
<td>0.00074</td>
<td>0.00545</td>
<td>2.1042</td>
</tr>
</tbody>
</table>

Scheme 2.11: Reaction scheme for the formation of crosslinked polyurethane.
2.2.4 CHARACTERIZATION TECHNIQUES

2.2.4.1 NMR

The structure of HBPs were confirmed from the $^1$H, $^{13}$C and $^{31}$P NMR spectra recorded by using Ascend™ (Brucker, Germany) 400-MHz spectrometer in hexadeuterated dimethyl sulfoxide (DMSO-d6) solvent. The internal standard used for $^1$H and $^{13}$C NMR spectra was trimethylsilane while H$_3$PO$_4$ for $^{31}$P NMR spectra.

2.2.4.2 MALDI-TOF MS

Mass spectra of the HBP-G3 was recorded on Voyager DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA, USA) MALDI-TOF (time of flight) MS instrument in IITM, India. A pulsed nitrogen laser of 337 nm was used for desorption ionization and TOF was operated in the delayed extraction mode. For the mass spectrometric study, HBP-G3 was dissolved in DMF and directly spotted on the target plate. The sample was made to dry in air and then got inserted into the spectrometer. The linear mode was chosen over the reflector mode. The matrix used was α-cyano-4-hydroxycinnamic acid. The ions were accelerated into the analyzer at a voltage of 25 kV. The mass spectra were collected in both the negative and positive ion modes and were averaged for 100 shots.

2.2.4.3 THERMAL ANALYSIS

The thermogravimetric analysis (TGA) of HBP-G3 was carried out on SDT Q600 V8.3 Build 101 (Korea) at a heating rate of 10 °C/min. under nitrogen (100 ml/min.) atmosphere upto 400 °C. A small amount of sample (around 5 mg) was used for TGA study. Differential scanning calorimetric (DSC) study was carried out on DSC Q1000 V9.9 Build 303 (Korea) at a heating rate of 10 °C/min. under nitrogen atmosphere (50ml/min.) in the temperature range, -80 °C to 200 °C. The glass transition temperature was measured from second heating cycle.
2.2.4.4 FTIR

Fourier transform infrared (FTIR) spectrum of HBP-G3 was recorded using a Bruker 66V FTIR spectrophotometer at a resolution of 4 cm\(^{-1}\) with 32 scans at room temperature. The homogeneous mixture of PEG, HMDI and HBP-G3 as a crosslinker was quickly poured into a transparent KBr pellet and thereafter, spectra were recorded on Bruker-IFS66V spectrometer for non-isothermal curing study in the temperature range from 40 to 160 °C at 1 °C/min. and isothermal curing study at the interval of 1 min. scan within a range of 4000-400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\).

2.2.4.5 INTRINSIC VISCOSITY

The viscosity of a solution is a measure of its resistance to flow. Viscosity measurements of synthetic polymer solutions have been used to deduce their molecular weights and degree of branching. By measuring viscosities of polymer solutions at varying concentrations, the intrinsic viscosity of the macromolecule which reflects the shape and volume of the macromolecule itself, can be deduced. This technique can be used to measure solution viscosities in the range of 0.35 to 30,000 centipoises for a solution density of ~1 g/mL.

For viscosity measurement in our study, the initial polymer solution was prepared by dissolving 0.5058 g of HBP-G3 in 25 ml of NMP solvent (2.0232 g/dL) in a standard measuring flask and kept stirring at 40 °C overnight. The efflux time for the NMP solvent \((t_s)\) was measured using Ubbelohde viscometer (AVS 260 Schott–Gerate GmbH) immersed in a water bath thermostated at 25 °C. The stirred polymer solution was filtered using a 25 micrometer PTFE filter and 20 ml of this polymer solution was transferred to the viscometer. The solution was allowed to equilibrate at 25 °C inside the viscometer before starting the experiment. After measuring the efflux time for initial polymer concentration, the apparatus automatically makes 3 more dilutions (1.4451, 1.1240 and 0.9196 g/dL) by taking neat solvent from the reservoir using a differential pressure. Two photocells detect the change of the refractive index of the solution as it passes through the two marks into the capillary. The signal is sent to a quartz clock that measures the flow time of each solution. For a particular dilution, the flow times agreed within 0.1 s. From
the time of flow, the specific viscosity $[\eta_{sp}]$ and the relative viscosity $[\eta_r]$ of the four solutions (initial solution and three dilutions) were determined. Each experiment was performed four times (The efflux time for each concentration was calculated from an average of four measurements).

The intrinsic viscosity $[\eta]$ (dL/g) was determined as usual as the common intercept of the Huggins and Kramer relationships (eqns. 1 and 2, respectively) using $[\eta_{sp}]$ and $[\eta_r]$ values obtained with the Ubbelohde viscometer. The concentration of solute, $c$ is expressed in g/dL:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2c$$  \hspace{1cm} (1)

$$\frac{\ln \eta_r}{c} = [\eta] + k_H[\eta]^2c$$  \hspace{1cm} (2)

From both equations, the intercept gives the intrinsic viscosity and the slopes (which are of opposite sign) are proportional to $[\eta]^2$. The constant $k_H$ is termed the Huggins constant and has values ranging from 0.3 in good solvents to 0.5 in poor solvents. Equations (1) and (2) are fitted from the minimum squared method and the mean value of the intercepts is taken as the intrinsic viscosity (Bustamant et al 2005).

2.2.4.6 HYDROXYL NUMBER DETERMINATION

1 g of the newly synthesized HBP-G3 sample was dissolved in a solution (15 cm$^3$) of acetic anhydride and pyridine (1:9 by volume) in a 250 cm$^3$ Erlenmeyer flask and the reaction mixture was refluxed for 1 h and then it was allowed to get the room temperature. Afterwards, a 50 cm$^3$ of distilled water was added slowly to the flask through the drying tube and again 50 cm$^3$ of distilled water was added into the same when the Erlenmeyer flask was disconnected from the drying tube. The solution was then titrated with 0.50 M KOH using phenolphthalein as an indicator. Blank titrations were also carried out. (Pyridine used was dried over solid KOH for several days.)

Finally, $N_{HN}$ was calculated as follows:
\[ N_{HN} = \frac{56.1 \times C_{KOH} \times (V_{BT} - V_{KOH})}{m_{sample}} \text{ mg of KOH} \]  \hspace{1cm} (3)

where \( C_{KOH} = \) concentration of KOH

\( V_{BT} = \) volume of KOH used for blank test

\( V_{KOH} = \) volume of KOH used for sample test

\( m_{sample} = \) mass of the sample

### 2.2.4.7 THERMODYNAMIC PARAMETERS

The following equations, Arrhenius (eqn. 4) and Eyring (eqn. 5) equations were used to determine activation energy \( (E_a) \), activation enthalpy \( (\Delta H^\dagger) \), and activation entropy \( (\Delta S^\dagger) \).

\[ \ln k = -\frac{E_a}{RT} + \ln A \]  \hspace{1cm} (4)

\[ \frac{k}{T} = -\frac{\Delta H^\dagger}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\dagger}{R} \]  \hspace{1cm} (5)

where \( T \) is the temperature in absolute scale (K); \( R \) is the Universal gas constant \( (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \); \( A \), the frequency factor; \( E_a \), the activation energy; \( k \), the kinetic rate constant; \( k_B \) is the Boltzmann’s constant \( (1.381 \times 10^{-23} \text{ JK}^{-1}) \); and \( h \), the Plank’s constant \( (6.6262 \times 10^{-34} \text{ Js}) \).

### 2.3 RESULTS AND DISCUSSIONS

#### 2.3.1 SPECTRAL CHARACTERIZATION OF HYPERBRANCHED POLYESTERS

The FTIR spectrum of HBP-G3 is shown in Fig. 2.1. The ester group of HBP-G3 can be confirmed from FTIR spectrum: at 1732 cm\(^{-1}\) as carbonyl band, the frequency at 1228 cm\(^{-1}\) for C-O-C=O stretching of ester and 1130 cm\(^{-1}\) indicates C-O-C stretching of ester group. The broad band at around 3200- 3600 cm\(^{-1}\) corresponds to hydrogen bonded OH group, while peaks at 2979, 2943 and 2889 cm\(^{-1}\) are the signatures of –CH\(_2\) and –CH\(_3\) groups. The peak which appears at 1473 cm\(^{-1}\) is due to CH\(_2\) bending deformation.
vibration while 1375 cm\(^{-1}\) reveals bending deformation vibration of CH\(_3\) group. The band at 1310 cm\(^{-1}\) confirms the stretching frequency of P=O in IR spectrum and it could also be verified by the following equation (Vien et al 1991),

\[
\tilde{\nu}(\text{P=O}) = 930 + 40 \sum \Pi
\]

(6)

where, \(\Pi\) represents phosphorus inductive constants and the P=O stretching frequency is calculated to be 1322 cm\(^{-1}\). The band at 915 cm\(^{-1}\) represents P-O stretching band. Aromatic C-H in-plane bending band is buried in the O-C stretching of ester band and its out-of-plane bending band appears in the region 915-670 cm\(^{-1}\). However, the existence of the COOH groups in the sample (1689 cm\(^{-1}\)) is invisible in the IR spectrum of the HBP-G3.

![FTIR spectrum of HBP-G3](image)

Fig. 2.1: FTIR spectrum of HBP-G3.

Figs. 2.2, 2.5 and 2.8 show the \(^1\)H NMR spectrum of HBP-G1, HBP-G2 and HBP-G3, respectively. The peaks at 0.99-1.15, 3.4-3.5 and 4.1-4.2 ppm correspond to -CH\(_3\), -CH\(_2\)OH, and -CH\(_2\)OR- groups, respectively. The terminal (-OH\(_T\)) as well as linear (-OH\(_L\)) hydroxyl groups appear at \(\approx 4.6\) and \(\approx 4.8\) ppm, respectively. The presence of
phenyl group is confirmed from the resonance signals from 6.5-7.5 ppm. The expanded form and the degree of branching of methyl group protons calculated by using Frechet and Frey equations (eqns. 7 and 8), (Hawker et al 1991; Holter et al 1997) are shown in Figs. 2.2, 2.5 and 2.8. The $^{13}$C NMR spectrum of HBP-G1, HBP-G2 and HBP-G3 as shown in Figs. 2.3, 2.6 and 2.9, respectively, represent peaks at 17-18 ppm for methyl carbons, 45-51 ppm for quaternary carbons, 63-68 ppm for methylene groups, 119-131 ppm for phenyl group and 173-178 ppm for carbonyl groups and the expansion of quaternary carbon region is also shown therein. The structural units (Zagar and Zigon 2011) found in HBPs as shown in Scheme 2.12 could also be noticed from the expanded plots of $^{13}$C NMR spectra (Figs. 2.3, 2.6 and 2.9). The signal at 72-73 ppm corresponding to oxyalkylene methylene carbons (-CH$_2$-O-CH$_2$-) formed from the etherification reaction as well as the presence of linear ether unit (E$_L$) in the quaternary carbon region at 49.4 (HBP-G1) and 49.2 (HBP-G2) ppm as shown in Figs. 2.3 and 2.6, respectively indicate the occurrence of side reaction leading to the formation of ether linkages along with the desired esterification reaction during the synthesis of HBP-G1 and HBP-G2. Such type of etherification has not occurred while synthesis of HBP-G3 as shown in Fig. 2.9, by the absence of peaks representing ether moiety. The degree of branching values of HBPs were computed by using Frechet and Frey equations, (Hawker et al 199; Holter et al 1997) as shown below and the data were reported in the figures itself (Figs. 2.3, 2.6 and 2.9). Figs. 2.4, 2.7 and 2.10 are representing the $^{31}$P NMR spectra of HBP-G1, HBP-G2 and HBP-G3, respectively. The three peaks in $^{31}$P NMR spectra may indicate the presence of Terminal ($\delta = \sim -1$ppm), Linear ($\delta = \sim -7$ppm) and Dendritic units ($\delta = \sim -13$ppm). Presence of the aforementioned peaks indicates that isomers of the HBPs may be formed during the synthesis of HBPs. The characterization of HBPs from $^{31}$P NMR spectral datum is very complicated due to more number of geometrical isomers formation during hyperbranched polymer synthesis (Zagar and Zigon 2011).

$$DB_{\text{Frechet}} = \frac{D+T}{D+L+T}$$  (7)

$$DB_{\text{Frey}} = \frac{2D}{2D+L}$$  (8)
Fig. 2.2: $^1$H NMR spectrum of HBP-G1.

Fig. 2.3: $^{13}$C NMR spectrum of HBP-G1.
Fig. 2.4. $^{31}\text{P}$ NMR spectrum of HBP-G1.

Fig. 2.5. $^1\text{H}$ NMR spectrum of HBP-G2.
Fig. 2.6: $^{13}$C NMR spectrum of HBP-G2.

Fig. 2.7: $^{31}$P NMR spectrum of HBP-G2.
Fig. 2.8: $^1$H NMR spectrum of HBP-G3.

Fig. 2.9: $^{13}$C NMR spectrum of HBP-G3.
Fig. 2.10: $^{31}$P NMR spectrum of HBP-G3.

Scheme 2.12: Structural units present in HBPs (HBP-G1 to HBP-G3).
2.3.2 PHYSICAL PROPERTIES OF HBP-G3

The HBP-G3 appears to be stable up to 210 °C as shown in Fig. 2.11(a) and its second order transition, $T_g$ is found to be 35 °C from second heating cycle as portrayed in Fig. 2.11(b). From MALDI-TOF analysis, the number average molecular weight, $M_n$ and the weight average molecular weight, $M_w$ of HBP-G3 are found to be 3430 and 5139 g/mol, respectively and the polydispersity calculated is found to be 1.50. Hydroxyl number of HBP-G3 is found to be 504 mg KOH/g and the intrinsic viscosity is 0.1352 dL/g.

Fig. 2.11: (a) TGA and (b) DSC plots of HBP-G3.

2.3.3 KINETICS STUDIES

Before utilizing any new material for applications such as composites, coatings, foams, etc, at first, we have to recognize the reaction pathway or to identify the reaction products. In PU-HBP case, primary reaction results in the formation of urethane linkages, whereas the secondary reactions produce allophanate or biuret linkages. The preferential formation of the reaction products dictates the end-user application of PU-HBP combination used in this study. 

*Isothermal Curing Kinetics - Effect of Varying NCO/OH ratios:* Fig. 2.12 shows the FTIR spectra of PU formed at 60 °C using HBP-G3 as a crosslinker for two different NCO/OH ratios. The diisocyanate, free urethane CO, hydrogen bonded urethane CO and
the NH stretching vibration bands appear at 2273, 1727, 1718 and 1527 cm\(^{-1}\), respectively. Absence of peaks at 1650-1708, 1640 and 1783-1776 cm\(^{-1}\) corresponding to

![Graph](image)

Fig. 2.12: FTIR spectra for (a) NCO/OH = 1.2316 and (b) NCO/OH = 2.1042 ratios in the region 2500-500 cm\(^{-1}\) for the formation of PU using HBP-G3 as a crosslinker.
allophanate, urea and dimer of NCO groups, respectively (Semsarzadeh and Navarchain 2003) indicate the negligible presence of side products and the exclusive formation of urethane as the primary product is corroborated from the presence of peak at 1727 cm\(^{-1}\) during PU formation for both lower and higher NCO/OH ratios as shown in Fig. 2.12. The decrease in isocyanate absorption intensity is considered for isocyanate conversion. The Lambert-Beer’s law is obeyed. The C-H stretching absorption band at 2964 cm\(^{-1}\) was considered as the internal standard for correcting the thickness during the curing of polyurethane. The FTIR spectra were base-line corrected and used for further work. The isocyanate conversion can be used as the degree of curing reaction as follows by the eqn. (9).

\[
\text{Isocyanate conversion, } p = 1 - \frac{A_t - A_\infty}{A_0 - A_\infty}
\]

where, \(A_0\) is the normalized absorbance peak intensity at the initial time, \(A_t\) is the normalized peak intensity of absorbance at specified time during curing and \(A_\infty\) is the final normalized absorbance peak intensity at infinite time. Fig. 2.13 depicts the conversion of isocyanate for different NCO/OH ratios at 60 \(^\circ\)C. Both ratios follow the similar trend and took almost the same time for the whole conversion. Around 615 min. were taken for converting whole of the isocyanate into polyurethane formation. It will be noteworthy to mention here that 80% conversion was observed within 100 minutes.

![Graph](image)

**Fig. 2.13:** Isocyanate conversion vs curing time of PUs formed using HBP-G3 as a crosslinker at 60 \(^\circ\)C for different NCO/OH ratios.
Crosslinking kinetics: Understanding the kinetics and mechanism of the curing reaction is very much essential to comprehend the structure-morphology-property relationship of a polymeric material. The polymer morphology which plays a vital role in dictating the properties of the cured thermoset is determined by chemical reaction taking place during crosslinking reaction. The degree of crosslinking, \( p \) can be expressed as

\[
p(t) = \int_0^t dp
\]  

(10)

A variety of kinetic models (Yi and Hilton 1998) can be adopted to describe the curing process of thermosetting polymers based on the above empirical rate law. The rate of the curing degree can be expressed as a function of the curing degree and temperature (Lisardo et al 1997).

The basic kinetic equation is

\[
\frac{dp}{dt} = k(T)f(p)
\]  

(11)

and under isothermal conditions,

\[
\frac{dp}{dt} = k \exp(-E_a/RT)f(p)
\]  

(12)

In non-isothermal condition (\( \beta = dT/dt \)), and

\[
\frac{dp}{dt} = \frac{A}{\beta} \{\exp(-E_a/RT)\} f(p)
\]  

(13)

The above two empirical equations, nth-order and autoaccelerated models, are widely used for modeling the cure kinetics for thermosetting materials (Mecan et al 2004; Chen and Chen 1999). The nth-order kinetics can be expressed as

\[
\frac{dp}{dt} = k_0(1-p)^n
\]  

(14)

and the autoaccelerated model as

\[
\frac{dp}{dt} = (k_1 + k_2p_m) (1-p)^n
\]  

(15)
where, $k$, $k_0$, $k_1$ and $k_2$ are rate constants which depend on temperature. Activation energy ($E_a$), the universal constant (R), the temperature (T) in absolute scale and parameters, $m$ and $n$ are related to the reaction order. In order to obtain a linear relationship between experimental and theoretical data, parameters, $m$ and $n$ are being sought by this method. In this study, nth-order approach is used for modeling the curing kinetics of polyurethanes.

If $n = 1$, \[ \ln(1-p) = -k_0 t + C \] (16)

If $n = 2$, \[ \frac{1}{1-p} = k_0 t + C \] (17)

If $n = 3$, \[ \frac{1}{(1-p)^2} = k_0 t + C \] (18)

where $C$ is the integration constant. Here, the above equations have been applied for polyurethane studies to find out the order of the reaction.

Figs. 2.14, 2.15 and 2.16 represent the first, second and third order rate plots of PU formed using HBP-G3 as a crosslinker at 60 °C for different NCO/OH ratios, respectively. For NCO/OH = 1.2316, the order of the reaction is found to be second.

Fig. 2.14: The first order rate plots for the formation of PU using HBP-G3 as a crosslinker at 60 °C for (a) NCO/OH = 1.2316 and (b) NCO/OH = 2.1042.
Fig. 2.15: The second order rate plots for the formation of PU using HBP-G3 as a crosslinker at 60 °C for (a) NCO/OH = 1.2316 and (b) NCO/OH = 2.1042.

Fig. 2.16: The third order rate plots for the formation of PU using HBP-G3 as a crosslinker at 60 °C for (a) NCO/OH = 1.2316 and (b) NCO/OH = 2.1042.

Scheme 2.13: Schematic representation of auto-catalytic effect of urethane reaction.
order, indicating that the primary reaction between -OH and –NCO groups has occurred, while, for the NCO/OH = 2.1042, the polyurethane formed follows third order reaction. Third order for higher NCO/OH ratio is due to auto-catalytic effect of urethane (Eceiza et al 1999) formed in the reaction which means that the urethane formed reacts with excess isocyanate. The auto-catalytic effect of urethane is shown in Scheme 2.13. Hence, further studies were carried out using the lower NCO/OH ratio of 1.2316.

Non-isothermal Curing Kinetics: Qualitative and Quantitative Analysis: In the second part of the study, qualitative analysis of PU reaction for NCO/OH = 1.2316 measured under non-isothermal (40→160 °C) by in-situ FTIR is shown in Fig. 2.17. From Fig. 2.17(a), it is evident that the decay of isocyanate peak at 2273 cm\(^{-1}\) could be noticed whereas the increase in absorption intensity of PU formed could be observed at 1721 cm\(^{-1}\) with increasing curing temperature. The isocyanate peak was completely disappeared after 120 °C.

![Fig. 2.17: FTIR spectra of PU formed using HBP-G3 as a crosslinker measured at 40 – 160 °C (a) in the region of 2400-1600 cm\(^{-1}\) and (b) absorption values of -NCO band and urethane band for NCO/OH = 1.2316.](image)

For quantitative studies, FA can be effectively applied for ‘binary’ or ‘ternary’ mixtures (Prabu et al 2009) and a detailed literature search revealed the absence of any previous reports involving FA to extract the pure components from a series of mixture spectra collected during non-isothermal curing of PU using in-situ FTIR.
In the present study, 18 spectra showing major changes in their absorption intensity with respect to isocyanate and urethane content were chosen among a series of FTIR spectra collected from the above qualitative study involving non-isothermal curing of PU between 40→160 °C. Since the reactants react immediately upon mixing together and their first FTIR spectrum is recorded after a few minutes into the start of the reaction, each spectrum used in this study is understood to be a mixture of both isocyanate and urethane phases as major components, though their contents may vary depending upon the actual curing temperature. From raw IR data, due to the overlapping of isocyanate and urethane bands, it is very difficult to identify non-overlapping bands of each component and hence, becomes more difficult to extract the pure spectrum of each component and their relative concentrations in each sample.

The frequency range of 2400–1645 cm\(^{-1}\) containing 588 data points was chosen for FA studies. FA data obtained using the normalized mixture absorbance spectra from non-isothermal curing studies are shown in Table 2.5 from which the magnitude of each independent component and their corresponding eigenvalues are known. Malinowski’s indicator function (IND)\(_k\) is employed to identify the non-zero eigenvalues between first maxima and minima and in our study, six pure and independent components are present in the mixture spectra. Higher magnitude of eigenvalue indicates a larger probability of its corresponding component to be present in the mixture spectra and from Table 2.5, the first two components have the highest magnitude of non-zero eigenvalue among all the components present in the mixture spectra followed by other components with much lesser non-zero eigenvalues.

Since FA can be effectively applied for ‘binary mixtures’, only the first two components having the highest non-zero eigenvalues corresponding to the amount of isocyanate and urethane as their major components were considered. The third and other following component factors may be related to changes in surface scattering, other insignificant side products, etc. and their magnitude is assumed to be much less when compared to that of isocyanate and urethane components. Hence, among the six abstract spectra as shown in Fig. 2.18(a), the eigenspectra 1 and 2 and their corresponding eigenvalues were used for further analysis to get the product spectrum as shown in Fig. 2.18(b). The bands at 2270 and 1722 cm\(^{-1}\) from the product spectrum were considered as
maximum and minimum characteristic bands for extracting pure isocyanate and urethane components. The extracted pure-component spectra, PuS-1 and PuS-2 and the percentage content of urethane as a function of curing temperature are depicted in Fig. 2.19.

Table 2.5: FA (18 samples) data for the formation of PU using HBP-G3 as a crosslinker by non-isothermal curing process from 40 – 160 °C for NCO/OH = 1.2316

<table>
<thead>
<tr>
<th>Components</th>
<th>Eigenvalue</th>
<th>$10^4 \times$ IND</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.1459</td>
<td>0.4712</td>
</tr>
<tr>
<td>2</td>
<td>1.8254</td>
<td>0.0680</td>
</tr>
<tr>
<td>3</td>
<td>0.0260</td>
<td>0.0238</td>
</tr>
<tr>
<td>4</td>
<td>0.0019</td>
<td>0.0136</td>
</tr>
<tr>
<td>5</td>
<td>0.0003</td>
<td>0.0108</td>
</tr>
<tr>
<td>6</td>
<td>0.0001</td>
<td>0.0092</td>
</tr>
<tr>
<td>7</td>
<td>0.0000</td>
<td>0.0100</td>
</tr>
<tr>
<td>8</td>
<td>0.0000</td>
<td>0.0114</td>
</tr>
<tr>
<td>9</td>
<td>0.0000</td>
<td>0.0130</td>
</tr>
<tr>
<td>10</td>
<td>0.0000</td>
<td>0.0151</td>
</tr>
<tr>
<td>11</td>
<td>0.0000</td>
<td>0.0181</td>
</tr>
<tr>
<td>12</td>
<td>0.0000</td>
<td>0.0230</td>
</tr>
<tr>
<td>13</td>
<td>0.0000</td>
<td>0.0305</td>
</tr>
<tr>
<td>14</td>
<td>0.0000</td>
<td>0.0446</td>
</tr>
<tr>
<td>15</td>
<td>0.0000</td>
<td>0.0741</td>
</tr>
<tr>
<td>16</td>
<td>0.0000</td>
<td>0.1564</td>
</tr>
<tr>
<td>17</td>
<td>0.0000</td>
<td>0.5587</td>
</tr>
<tr>
<td>18</td>
<td>0.0000</td>
<td>-</td>
</tr>
</tbody>
</table>
In Fig. 2.19 (a), the bands at 2271, 1742 and 1713 cm\(^{-1}\) correspond to isocyanate, ester and hydrogen bonded urethane peaks, respectively, as shown in PuS-1 spectrum and the absorption intensity of peaks represent the concentration of each components, whereas in PuS-2, there is no isocyanate peak and the band at 1721 cm\(^{-1}\) represents free hydrogen bonded urethane peak where the ester and the hydrogen bonded urethane peaks are buried in it. The percentage content of urethane is increased from 40 to around 120 °C and it remains plateau after 120 °C onwards [Fig. 2.19(b)].
Isothermal Curing Kinetics for Lower NCO/OH Ratio: In the third and final step, the data obtained from non-isothermal studies were used to decide three different isothermal curing temperatures, viz. 70, 90 and 110 °C. Fig. 2.20 represents the FTIR spectra of the PU formed at 70 °C. Free –OH and hydrogen bonded OH bands appear at around 3562 and 3490 cm⁻¹, respectively. The shoulder at 3432 and 3340 cm⁻¹ could be attributed to free –NH and hydrogen bonded –NH bands, respectively. The hydrogen bonded –NH band is emerging clearly as a peak with increasing reaction time. The isocyanate, -NCO band appears at 2267 cm⁻¹ whereas the formation of urethane band could be noticed at 1727 cm⁻¹ corresponding to free C=O band and 1718 cm⁻¹ band for hydrogen bonded C=O group. The bands at 1527 cm⁻¹ and 1247 cm⁻¹ correspond to δ(N-H) + υ(C-N) and δ(N-H) + γ(C-N), respectively. The absence of peaks at 1650-1708, 1640 and 1783~1776 cm⁻¹ corresponding to allophanate groups, urea linkages and dimer of NCO, respectively, (Semsarzadeh and Navarchian 2003) indicate the negligible or complete absence of secondary products during PU formation.

During polymerization, the decay of the absorption intensity of isocyanate band appeared at 2267 cm⁻¹ can be used to monitor the isocyanate group conversion. The Lambert – Beer law is utilized for quantification. For the correct thickness during curing, the C-H stretching absorbance (2966 cm⁻¹) was taken as the internal standard. Baseline corrected spectra were considered for kinetic studies. Since there is no significant side reaction taking place (Yilgor et al 2006), the decrease of the absorption intensity of the isocyanate band can be monitored for conversion during the reaction. The isocyanate conversion can be used as the degree of curing reaction by using the eqn. (9). The results are shown in Fig. 2.21(a) for different curing temperatures. Fig. 2.21(a) and (b) show the changes in isocyanate concentration as a function of curing times during curing of PU formation and isocyanate conversion vs curing time of PUs at 70, 90 and 110 °C, respectively. The reduction in concentration of isocyanate is more at higher curing temperature, 110 °C in comparison to that of at 70 °C by at around 3 times. The isocyanate conversion increases with increasing curing temperature as shown in Fig. 2.21(b).
Fig. 2.20: FTIR spectra of PU using HBP-G3 as a crosslinker as a function of curing time at 70 °C in the region (a) 4000-3000, (b) 2500-1600 and (c) 1600-1200 cm\(^{-1}\) for NCO/OH = 1.2316.
Fig. 2.21: (a) Changes in isocyanate concentration at different curing times during curing of polyurethane and (b) Isocyanate conversion vs curing time of PUs at 70, 90 and 110 °C for NCO/OH = 1.2316 using HBP-G3 as a crosslinker.

Fig. 2.22: (a) Second and (b) Third order plots of PU for NCO/OH = 1.2316 using HBP-G3 as a crosslinker.
Table 2.6: Rate constants and fitting results for the curing process of PU at 70, 90 and 100 °C ($k$, rate constants (min); $E_r$, the standard error of rate constants; SD, standard deviation of the fit)

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Parameter</th>
<th>70 °C</th>
<th>90 °C</th>
<th>110 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second Order</td>
<td>$k$</td>
<td>0.0483</td>
<td>0.1382</td>
<td>0.4187</td>
</tr>
<tr>
<td></td>
<td>$E_r$</td>
<td>0.006</td>
<td>0.0037</td>
<td>0.0286</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.0718</td>
<td>0.0874</td>
<td>0.3105</td>
</tr>
<tr>
<td>Third Order</td>
<td>$k$</td>
<td>4.0118</td>
<td>27.5914</td>
<td>250.6395</td>
</tr>
<tr>
<td></td>
<td>$E_r$</td>
<td>0.6814</td>
<td>4.0907</td>
<td>48.1095</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>259.3718</td>
<td>554.0577</td>
<td>2383.4307</td>
</tr>
</tbody>
</table>

From second and third order plots of PU using HBP-G3 as a crosslinker for NCO/OH=1.2316 as depicted in Fig. 2.22 and from the above data, the order of reaction for polyurethane formed by using HBP-G3 as a crosslinker by one shot synthesis follows second order kinetics indicating that there is no autocatalysis of urethane at specified higher curing temperature and it is not only good agreement with that of the literature mentioned (Maji and Bhowmick 2009) but also with that of linear polyurethanes (Kincal and Ozkar 1997; Madra et al 2009; Coutinho and Rezende 1986; Schpman et al 2002; Boufi et al 1993; Li et 2000). Generally, the larger part of the reaction can be described by kinetics equations but not towards the end because of diffusion controlled. Rate constants and fitting results are shown in Table 2.6.

Fig. 2.23 shows Arrhenius and Eyring plots of polyurethane which is used to compute the kinetic parameters based on the equations described earlier by eqns. (4) & (5) and are shown below:

1. Activation energy, $E_a = 58.93 \text{ KJ/mol}$
2. Frequency factor, $A = 4.4 \times 10^7 \text{ min}^{-1}$
3. Activation enthalpy, $\Delta H^\ddagger = 55.92 \text{ KJ/mol}$
4. Activation entropy, $\Delta S^\ddagger = -108.539 \text{ Jmol}^{-1}$
The values of kinetic parameters such as $E_a$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of polyurethane formation by using HBP-G3 as a crosslinker is in good agreement with the literature values already reported (Maji and Bhowmick 2009). Based on the values of $E_a$ and $\Delta H^\ddagger$, it can be confirmed that low value of these parameters indicate that the reaction is comparatively faster than that of by PU20 as mentioned in the literature (Maji and Bhowmick 2009). The values of activation enthalpy and entropy can be used to understand the mechanism (Espenson 1995). The large negative value obtained for the activation entropy is indicative of an associative mechanism in the transition states (Connors 1990) which is in accordance with the second order rate law for polyurethane formation.

![Graph](image)

Fig. 2.23: (a) Arrhenius and (b) Eyring plots of PU using HBP-G3 as a crosslinker for NCO/OH = 1.2316.

2.4 CONCLUSIONS

Hyperbranched polyesters of varying generation (HB-G1 to HBP-G3) were synthesized by the calculated amount of DMPA as a monomer and PDCP as a core. Their structures were proved by NMR spectroscopy and the degree of branching calculated by both Frechet and Frey indicated that the polymer formed is a highly branched polymer. The $M_n$, $M_w$, and polydispersity of HBP-G3 were computed from MALDI-TOF analysis. Physical properties like thermal stability (stable upto 210 °C) and second order transition
behavior (35 °C) from thermal analysis methods, the hydroxyl number (504 mg KOH/g) and the intrinsic viscosity (0.1352 dL/g) were determined for HBP-G3. The kinetics of polyurethane formation by one shot method between PEG, HMDI and HBP-G3 as a crosslinker was studied by in-situ FTIR for both the ratios at 60 °C and found that lower NCO/OH ratio follows second order, while the higher NCO/OH ratio follows third order rate laws due to auto-catalytic effect of urethane. Non-isothermal curing study was carried out for lower NCO/OH ratio and the percentage of urethane content as a function of curing temperature were done by FA and found that it reached at around 100% below 130 °C. The kinetics of polyurethane formation by one shot method between PEG, HMDI and HBP-G3 as a crosslinker was carried out by in-situ FTIR for lower NCO/OH ratio at different isothermal curing temperatures (70, 90 and 110 °C) and it was observed that it obeys second order rate law and their thermodynamic parameters were derived from Arrhenius and Eyring plots.