

**KINETIC STUDIES ON POLYURETHANE FORMATION REACTIONS WITH
INFRARED AND RAMAN SPECTROSCOPY: EFFECT OF REACTION
SOLVENT AND REACTION CONDITIONS ON PREPOLYMER FORMATION**

by

Armen Yıldırım

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This is to certify that I have examined this copy of a master's thesis by

Armen Yıldırım

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Committee members:

İskender Yılgör, Ph.D. (Advisor)

Ersin Yurtsever, Ph.D.

Yusuf Z. Menceloğlu, Ph.D.

Date: _____

ABSTRACT

Segmented Thermoplastic Polyurethanes (TPUs) are an important class of high performance polymeric materials. According to a recent report titled: “Polyurethanes (PU) Market: Global Industry Analysis, Size, Share and Forecast (2012-2018)”, by Transparency Market Research, global PU product market revenue reached USD 43.2 billion in 2012 and is expected to reach USD 66.4 billion by 2018, growing at a compounded annual growth rate of 7.4 % from 2012 to 2018. Looking at these figures it is not surprising that there is significant interest by both academic and industrial researchers on TPUs, especially on controlling the critical factors that influence the chemical structure, microphase morphology and properties of polyurethanes. One of the critical points in TPU synthesis is the control of the primary reaction between isocyanate and urethane groups and minimize the side reactions, in order to obtain linear polymers with controlled structures. Unfortunately, this point is usually overlooked, most probably since the majority of the fundamental studies on polyurethane formation reaction kinetics and mechanisms were performed more than half a century ago.

Therefore, in this research, our major goal was to investigate the effects of various reaction parameters such as; (i) the reaction solvent, (ii) diisocyanate and polyol structure, (iii) temperature and, (iv) catalyst type and (v) concentration on the reaction rate, extent of side reactions and isocyanate consumption in prepolymer formation reactions. For this purpose, a systematic investigation of the reactions between bis(4-isocyanatophenyl)methane (MDI) and various polyol oligomers (PTMO, PEO and PPO oligomers with $\langle M_n \rangle = 1000$ g/mol) have been performed. Concentrations of polymer solutions were about 25% by weight and the reaction temperatures employed were room temperature (22-25 °C) and 50 °C. Reactions were followed by monitoring the change in the strong isocyanate absorption peaks by using Fourier-Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy, which were centered at 2270 cm^{-1} and 1530 cm^{-1} , respectively.

As it is well documented in the literature, the reactions between isocyanate and alcohols follow second-order kinetics. Thus, results obtained were analyzed according to second-order kinetics in order to obtain the rate constant values and to understand the extent of side reactions, which resulted in deviations from the second-order kinetics. The results obtained clearly indicated the effect of solvent (especially DMF, which is a widely used solvent for the synthesis of polyurethanes in solution) on the extent of side reactions along with other parameters (concentration, temperature and catalyst). When DMF was used as the reaction solvent, the reaction rate and the observed excess isocyanate consumption levels were much higher than that of bulk or solution reactions carried out in other solvents. Moreover, in the case of DMF containing systems, a strong deviation from initial second-order linearity was also observed, indicating the presence of side reactions.

Comparative reactions using MDI and HMDI clearly demonstrated that the reactivities of aromatic diisocyanate towards alcohols are significantly higher than their aliphatic counterparts (due to electron withdrawing ability of phenylene rings in MDI). On the other hand, in the case of polyol structures, no significant change is observed upon changing the oligomer structure.

Reactions carried out at different temperatures also showed the effect of temperature on the polyurethane formation reactions. As expected, values of the rate constants increased with temperature. The dramatic difference between the catalytic activities of DMF and triethylamine (TEA) (a widely used catalyst in polyurethane formation reactions) were also presented in the last chapter. When compared with DMF, no significant amounts of side reactions were recorded in TEA containing systems.

To conclude, the frequently utilized techniques from published studies, which significantly promoted the side reactions, were also listed in the final chapter.

ÖZET

Çok kısımlı termoplastik poliüretanlar (TPU) yüksek performanslı malzemeler içerisinde önemli bir yere sahiptirler. Yakın zamanda *Transparency Market Research* tarafından yayınlanan “*Polyurethanes (PU) Market: Global Industry analysis, Size, Share and Forecast (2012-2018)*” adlı raporda belirtilen rakamlara göre poliüretan (PU) ürünlerinden elde edilen toplam küresel gelir miktarı 2012 yılı sonunda 43.2 milyar dolara ulaşırken, bu rakamın 2018 yılı itibariyle ise yıllık ortalama % 7.4 büyüme oranıyla 66.4 milyar dolar seviyesine çıkması öngörülmektedir. Bu rakamlar göz önüne alındığında hem akademik hem de sanayideki birçok araştırmacının çalışmalarını TPU alanında, özellikle de poliüretanların kimyasal yapısını, mikrofaz morfolojisini ve özelliklerini etkileyen faktörler üzerine yoğunlaştırması çok da şaşırtıcı değildir. TPU sentezinde kontrollü olarak lineer bir polimer yapısı elde etmek için dikkat edilmesi gereken en kritik ve önemli noktalardan birisi ise izosiyanat ve üretan grupları arasında gerçekleşen yan reaksiyonları minimize etmektir. Ancak, ne yazık ki günümüzde bu nokta çoğunlukla göz ardı edilmektedir. Bunun başlıca sebebi olarak da bu alanda yapılmış temel kinetik çalışmaların neredeyse tamamının 1960’lı yıllarda yayınlanmış olması gösterilebilir.

Bu nedenle, bu çalışmadaki temel amaç poliüretan sentezi esnasında uygulanan çeşitli reaksiyon parametrelerinin, örneğin; (i) çözücü, (ii) diizosiyanat ve poliol kimyasal yapısı, (iii) sıcaklık, (iv) katalizör ve (v) konsantrasyon gibi etkenlerin reaksiyon hızı ve sentez sırasında meydana gelen ve teorik miktardan daha fazla izosiyanat harcanmasına yol açan yan reaksiyonlar üzerindeki etkisi sistematik olarak incelenmiştir. Reaksiyonlarda aromatik *bis(4-izosiyanatofenil) metan (MDI)* ve alifatik *bis(4izosiyanatosikloheksil)metan (HMDI)* ile ortalama molekül ağırlığı 1000 g/mol olan çeşitli poliol oligomerler (*poli(tetrametilen oksit) glikol (PTMO1k)*, *poli(propilen oksit) glikol (PPG1k)*, *poli(etilen oksit) glikol (PEO1k)*) kullanılmıştır. Hazırlanan polimer çözeltilerinin konsantrasyonları ağırlıkça % 25 civarında olup reaksiyonlar oda

sıcaklığı (22-25°C) ve 50°C olmak üzere iki farklı sıcaklıkta gerçekleştirilmiştir. Reaksiyonların takibi IR (kızıl ötesi) spektroskopisinde 2270 cm⁻¹, Raman spektroskopisinde ise 1530.7 cm⁻¹'de bulunan izosiyanat pikindeki değişim gözlemlenerek takip edilmiştir.

Daha önce yapılan kapsamlı kinetik çalışmalarla izosiyanat-alkol reaksiyonlarının ikinci dereceden oldukları literatürde kesin bir şekilde belgelenmiştir. Bu nedenle, bu çalışma esnasında elde edilen veriler ikinci-dereceden reaksiyon kinetiğine göre analiz edilerek her bir reaksiyon için hız sabitleri hesaplanmıştır. Bunun yanı sıra, reaksiyonların ikinci-derece reaksiyon kinetiğinden daha yüksek derecelere doğru sapma eğilimine bağlı olarak sentez sırasında meydana gelen yan reaksiyonların boyutları anlaşılmaya çalışılmıştır. Elde edilen sonuçlar kullanılan çözücünün (özellikle çözücü olarak poliüretan sentezinde sıkça kullanılan DMF tercih edildiğinde) yan reaksiyonlar üzerindeki etkisini açıkça göstermektedir. DMF içeren reaksiyonlarda, reaksiyon hızının ve teorik miktara oranla fazladan harcanan izosiyanat miktarının diğer çözücü sistemlerine kıyasla daha fazla olduğu belirlenmiştir. Buna ek olarak, DMF içeren sistemlerde, yan reaksiyonların varlığına kanıt olarak yüksek oranlarda ikinci-derece reaksiyon kinetiğinden sapmalar gözlemlenmiştir.

Aromatik ve alifatik olmak üzere iki farklı izosiyanat türü (sırasıyla MDI ve HMDI) kullanılarak gerçekleştirilen reaksiyonlarda elde edilen sonuçlarda ise aromatik yapıya sahip olan diizosiyanatların alifatik diizosiyanatlara oranla alkol moleküllerine karşı daha reaktif oldukları tespit edilmiştir. Bunun başlıca sebebi olarak MDI molekülünde yer alan fenil gruplarının elektron çekme özelliği gösterilebilir. Öte yandan, farkı poliol oligomerleri kullanılarak gerçekleştirilen reaksiyonlarda ise poliol kimyasal yapısındaki değişikliklerin reaksiyon üzerinde önemli derecede bir değişime yol açmadığı belirlenmiştir.

Farklı sıcaklıklarda gerçekleştirilen reaksiyonlarda ise sıcaklığın poliüretan oluşum reaksiyonları üzerindeki etkisi incelenmiştir. Beklenildiği üzere, reaksiyon sıcaklığındaki artışa bağlı olarak hız sabiti değerlerinde de artışlar gözlemlenmiştir. Son

olarak, poliüretan reaksiyonlarındaki katalitik etkilerinin kıyaslanması amacıyla DMF ve trietilamin (TEA) katalizörü (poliüretan sentezinde sıkça kullanılan bir katalizördür) içeren sistemlere ait sonuçlar da son bölümde sunulmuştur. DMF ile kıyaslandığında, TEA içeren sistemlerde kayda değer bir yan reaksiyon oluşumu gözlemlenmemiştir.

Son bölümde ayrıca birçok saygın bültende yayınlanmış olan makalelerdeki poliüretan sentez teknikleri listelenmiştir. Bu teknikler dikkatlice incelendiğinde, uygulanan reaksiyon koşullarının yan reaksiyon oluşumuna ve dolayısıyla fazla miktarda izosiyanat tüketimine ne kadar yatkın oldukları açıkça görülmektedir.

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NOMENCLATURE

<Mn>	Number average molecular weight
DABCO	1,4-diazabicyclo-[2.2.2]-octane
DBTDL	Dibutyltindilaurate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DN	Donor Number
EPD	Electron Pair Donor
FTIR	Fourier Transform Infrared Spectroscopy
HMDI	Bis(4-isocyanatocyclohexyl)methane
HS	Hard Segment
MDI	Bis(4-isocyanatophenyl)methane
NMP	N-Methyl-2-pyrrolidone
PEO	Poly(ethylene oxide)
PPO	Poly(propylene oxide)
PTMO	Poly(tetramethylene oxide)

PU	Polyurethane
SAXS	Small Angle X-ray Scattering
SS	Soft Segment
TDI	Toluene diisocyanate
TEA	Triethylamine
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Melting temperature
TOL	Toluene
TPU	Segmented thermoplastic polyurethane
UV	Ultraviolet

CHAPTER-1

INTRODUCTION

1.1 Polyurethanes

The history of the polyurethanes dates back to 1937, when it was discovered by the German scientist Otto Bayer and his co-workers at Germany's I.G. Farbenindustrie (the predecessor of Bayer AG). [1] In contrast to many great inventions, the discovery and development of polyurethanes was not a coincidence. The main impetus for this project was to give a competitive response to the commercial success of the polyamides and polyesters developed by Carothers at Du Pont, USA. [2] Bayer utilized the known addition reactions of the isocyanate group with alcohols and amines, which has been discovered in 1848 by Wurtz and investigated well by Hoffman and others. [3] His studies on the reactions of diisocyanates with diols or diamines led to the discovery of new polymeric materials, which are called polyurethanes and polyureas respectively. The first polyurethane, Perlon U, was obtained through the stoichiometric reaction of 1,6-diisocyanatohexane and 1,4-butanediol. [4]

Upon their introduction, polyurethane products quickly gained a strong position in the market in late 1940s, mostly as elastomers and foamed materials. [5] Although they were used at modest tonnages (due to their high cost) until the mid-1970s by industry, polyurethane elastomer use has shown a substantial increase throughout the 1980s, in various diverse applications, including textiles, medical devices, automotive, synthetic leather and elastomeric foams. Now because of their superior dynamic mechanical properties and abrasion resistance, they even dominate certain niche markets such as in-line skate wheels and high-performance bowling balls. [2, 4] As a strong evidence to the success of PUs, their worldwide consumption reached to 16.4 million tons in 2013

(data from Bayer Corporation, Germany), clearly showing their significance in the polymer marketplace. [4] According to a recent report by Transparency Market Research titled, “Polyurethanes (PU) Market: Global Industry analysis, Size, Share and Forecast (2012-2018)”, global PU product market revenue reached USD 43.2 billion in 2012 and is expected to reach USD 66.4 billion by 2018, growing at a compounded annual growth rate of 7.4 % from 2012 to 2018. This commercial success of polyurethanes can be attributed to their wide range of properties, which are mainly controlled by their composition dependent microphase morphologies, moderate-cost and ease of production. [6]

1.2 Segmented Thermoplastic Polyurethane Elastomers (TPUs)

The first research program on the development of elastic polyurethanes started during World War II, in an effort to find an alternative material for natural rubber, which at the time was expensive and hard to obtain. In 1950, Bayer and his co-workers who have been working systematically on polyurethane science and technology, developed a new material called “Vulkollan rubbers”. Besides having good flexibility and elasticity, these polyurethane elastomers showed many advantages over natural rubber in terms of abrasion resistance, tear strength and resistance to oxygen ageing. However, the major drawbacks of these materials were the rapid breakdown in the presence of water and heat. [7]

As shown in Figure 1.1, a thermoplastic polyurethane elastomer (TPU) can be regarded as a block or segmented copolymer, which is usually composed of chemically immiscible segments (hard and soft segment) or blocks that are linked together by covalent bonds along a linear macromolecular backbone. Since the hard and soft segments are chemically immiscible, they are usually separated into micro-domains. [8] Thus, thermoplastic polyurethane elastomers are often referred to as *microphase-separated* (or segregated) polymers. [4] The segmented polymer structure is formed

typically by reacting together three fundamental building blocks: a long-chain diol (macrodiol or polyol), a diisocyanate (aromatic or aliphatic), and a small molecule chain-extender, which is usually a diol or diamine. [8] By altering the nature and chemical composition of these blocks, TPUs with a wide range of properties in terms of strength or stiffness can be produced.

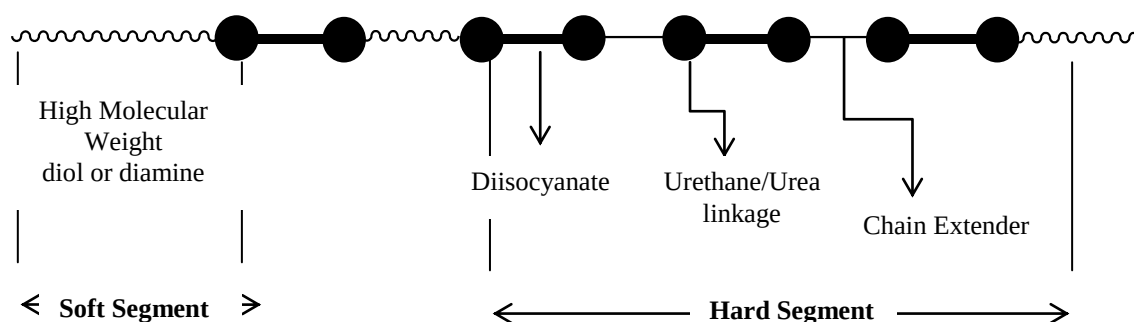


Figure-1.1: Primary structure in polyurethanes: backbone microstructure [4]

Soft segments (SS), which usually consist of aliphatic polyether, polyester or polycarbonate oligomers with number average molecular weights in 1000 – 3000 g/mol range, have glass transition temperatures (T_g) well below room temperature, generally in -50 to -100 °C range. This leads to the formation of TPUs with very high elasticity at room temperature. [9] On the other hand, the hard segments (HS), which have T_g , or if crystalline, T_m values well above room temperature (generally in 100 – 200 °C range), are obtained by the reaction of diisocyanates with low molecular weight diol or diamine chain extenders. It is well established in the literature that “these strongly hydrogen bonded hard domains serve as rigid reinforcements or physical crosslinks within the rubbery network and prevent macroscopic flow behavior; however the domains can be melted or softened at high temperatures, so that the polymer may be melt processed as an ordinary thermoplastic.” [8]

Figure 1.2 illustrates a simplistic view of microphase separation in segmented thermoplastic polyurethane elastomers. As a supporting evidence, the results obtained from small angle X-ray scattering (SAXS), thermal analysis measurements and other complementary techniques also show that elastomeric urethane polymers can be regarded as chains that are composed of long (1000-2000 nm) flexible segments and much shorter (150 nm) rigid units. For example, modulus-temperature data usually shows two distinct transitions: one below room temperature and one above 100 °C. These transitions are related to the segmental flexibility of the polyol and the dissociation of the intermolecular interactions (i.e. hydrogen bonding) between the hard segments, respectively. [2]

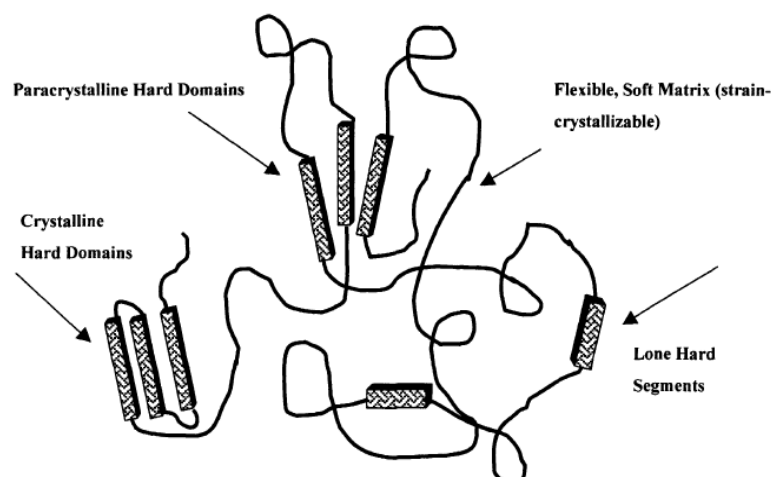


Figure 1.2: Schematic representation of microphase separation in segmented thermoplastic polyurethanes [10]

Preparation of segmented thermoplastic polyurethane elastomers were first reported by Schollenberger in 1958, in an effort to find a replacement for their chemically crosslinked counterparts. This report provided a new impetus for the field and numerous investigations took place on investigation of the morphological features and mechanical properties of polyurethane elastomers as a function of the chemical structure and composition of the hard and soft segments. [8] In 1966, pioneering and now classical

study published by Cooper and Tobolsky *et al.*, for the first time demonstrated the microphase separated morphology of TPUs, which was followed by the report of Bonart and Clough *et al.*, in 1968. Bonart and Clough confirmed the effect of hydrogen bonding during the self-association of hard segments into hard domains. [11, 12] Unlike the chemical crosslinks, these hard domain based physical crosslinks are reversible upon heat treatment and/or in polar solvents. [10]

As shown in Figure 1.1, the linkage between the soft and the hard segment is either a urethane or urea bond, both of which are very polar and capable of hydrogen bonding. The formation reactions and the chemical structures of urethane and urea linkages are illustrated in Figure 1.3. The reactions of isocyanates with alcohols and amines yield urethane and urea groups respectively. Since many types of polyurethane polymers contain both urethane and urea linkages, it is appropriate to use the term polyurethaneurea for these types of materials. However, as it can be seen in the literature, the blanket term “polyurethanes” or “TPU” are more common to refer to such polymers. [4] Detailed discussions on the structural design and synthesis of segmented polyurethanes (*one-shot* and *prepolymer* techniques) are presented in Chapter 1.3.

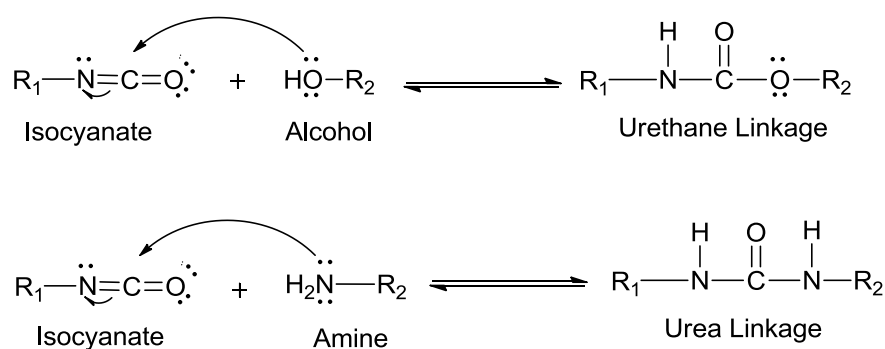
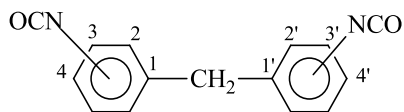


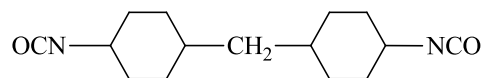
Figure 1.3: Formation of urethane and urea linkages through the reactions of isocyanates with alcohols and amines

As mentioned earlier, aromatic and aliphatic diisocyanates along with diol or diamine chain extenders constitute the hard segments in polyurethane elastomers. Two of the

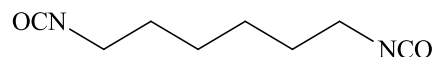
commercially most important aromatic diisocyanates are toluene diisocyanate (TDI) (usually a mixture of 2,4- and 2,6- isomers) and 4,4'-diphenylmethane diisocyanate (MDI). Although these aromatic diisocyanates are susceptible to ultraviolet (UV) degradation, their aromatic units provide the rigidity to create polyurethanes with high modulus and tensile strengths. On the other hand, aliphatic diisocyanates, such as 4,4'-diisocyanatodicyclohexylmethane (HMDI) and 1,6-hexamethylene diisocyanate (HDI) exhibit greater UV stability and resistance to hydrolytic degradation, but are less reactive than their aromatic counterparts. [7] Symmetrical diisocyanates such as HDI or para-phenylene diisocyanate (PPDI) leads to a high degree of microphase segregation. [12] Table 1.1 shows the chemical structures of some of the commonly used aromatic and aliphatic diisocyanates.



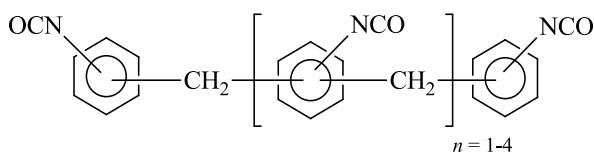
4,4' , 2,4' and 2,2'- Methylene diphenyl diisocyanate (MDI)



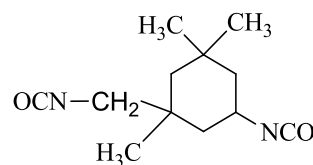
4,4'-Diisocyanato dicyclohexylmethane (HMDI)



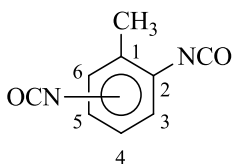
Hexamethylene diisocyanate (HDI)



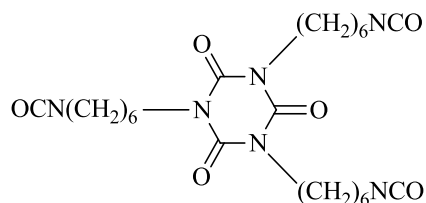
Polymeric MDI (PMDI)



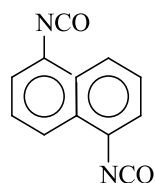
Isophorone diisocyanate (IPDI)



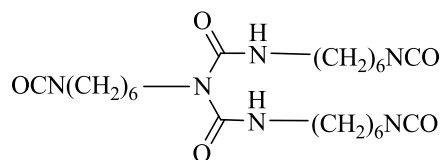
2,4 and 2,6-Toluene diisocyanate (TDI)



Isocyanate trimer of HDI (HDI trimer)



Naphtalene diisocyanate (NDI)



Biuret of HDI

Table 1.1- Commercially important aromatic and aliphatic diisocyanates [4]

Chain extenders are typically low molecular weight ($MW < 400$ g/mol) diols or diamines designed to react with the isocyanate group to increase the urethane and/or

urea hard segment content and the overall molecular weight of the final product. [4, 7, 9] Chain extenders also play an important role on the microphase segregation, thus on thermal and mechanical properties of TPUs. Without a chain extender, depending on the composition and various other factors, resulting polymer may exhibit poor degree of phase segregation and therefore may lead to the formation of TPUs with poor physical properties. On the other hand, utilization of a chain extender leads to an increase in the hard segment length, allowing improved microphase segregation and good thermo-mechanical properties in TPUs, which include an increase in the both the rubbery plateau modulus and HS glass transition temperature of the polymer. [7]

The soft segments commonly used in the preparation of polyurethane elastomers are aliphatic polyether or polyester based macrodiols, such as poly(tetramethylene oxide) (PTMO) and poly(ethylene adipate). [10] Due to their hydrogen bonding capability with the urethane linkages (NH-CO) in the hard domain, both the ether (C-O) and the ester (CO-O) bonds may have a dramatic influence on the degree of microphase segregation. [12] In the case of polyesters, ester carbonyl group (C=O) leads to a stronger hydrogen bonding between HS and SS than that of polyethers, thus rendering polymers more stiffer and with higher tensile strengths. SS molecular weight also plays a critical role on the extent of microphase separation and properties of the TPUs. [13] Table-1.2 presents some of the commonly used polyols in TPU synthesis. [7]

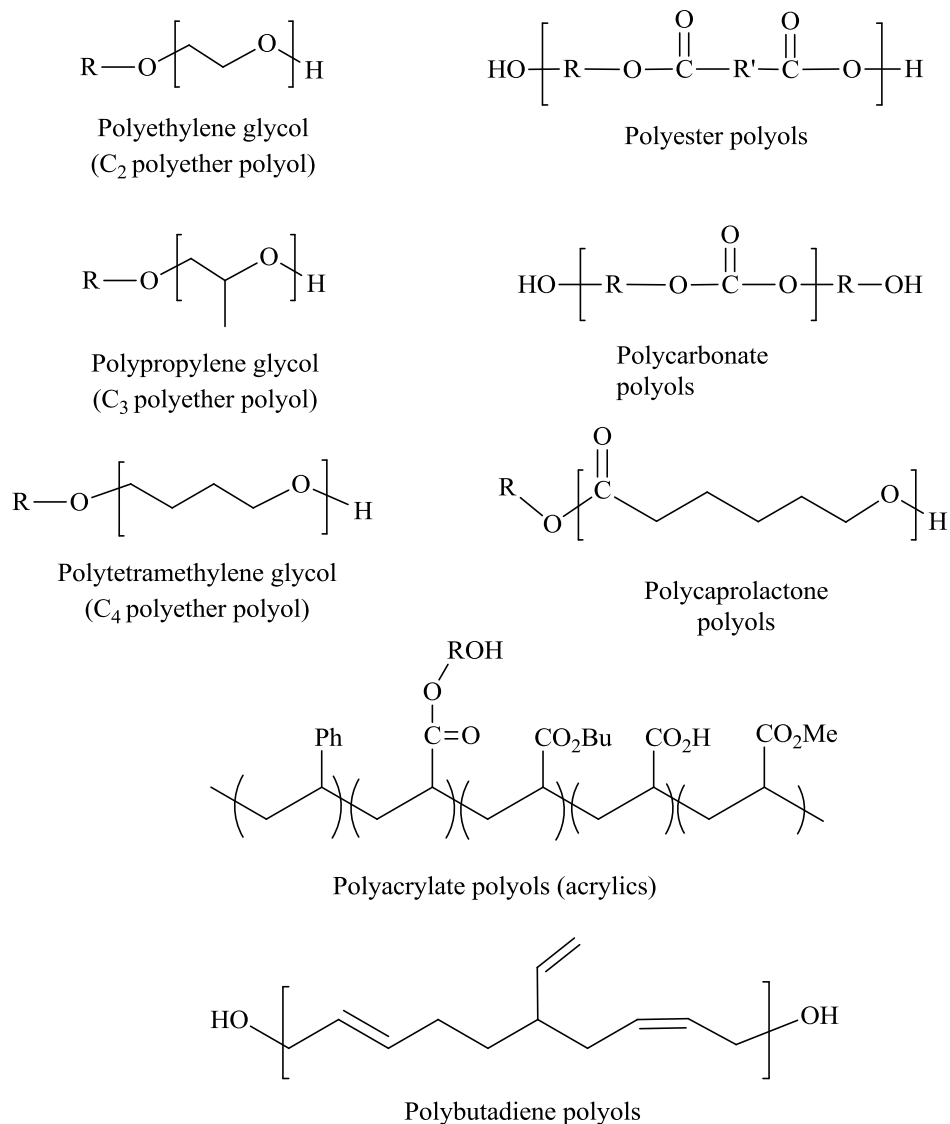


Table-1.2: Structures of commonly used polyol types in polyurethane synthesis [4]

1.3 Synthesis of Polyurethane Elastomers

Thermoplastic polyurethane elastomers are synthesized by two basic approaches, known as *one-shot* and *prepolymer* techniques. These techniques differ from one another in terms of chain build-up and structural regularity, which can dramatically affect the microstructure and thus the overall properties of the polymers. [7]

In the *one-shot procedure* (Fig.-1.4a) all reactants (diisocyanate, polyol, chain extender and other additives) are introduced into the reactor at the same time. Although this technique is faster and easier than the recipe utilized in prepolymer method, there is no control over the hard segment chain length and its distribution in the polymer backbone. As a result, hard segment domain sizes are highly dispersed in one-shot technique. [4, 7]

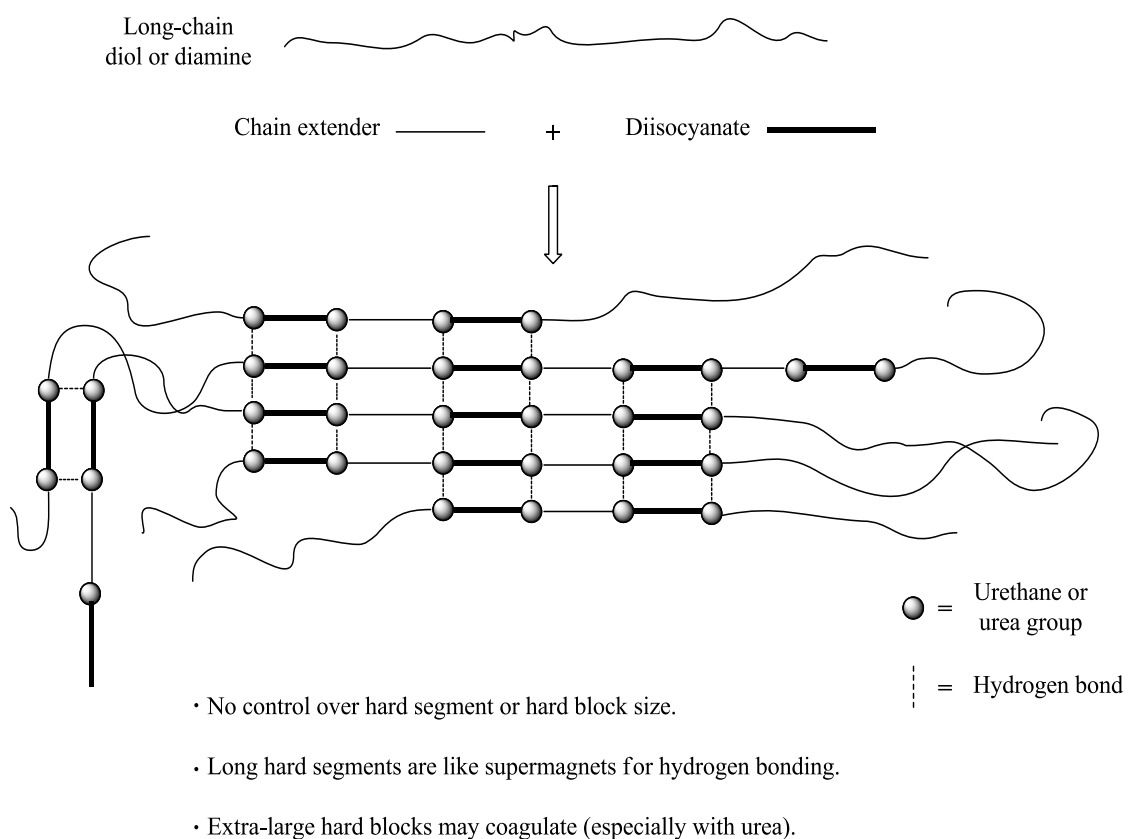


Figure-1.4 (a): Microstructure formation in polyurethane elastomers: *One-shot technique* and molecular structure [4]

On the contrary, the prepolymer technique is composed of two steps, which are; (i) the prepolymer formation and (ii) chain extension. In the first step, a diisocyanate

terminated prepolymer is produced through the reaction of a high-molecular weight diol with an excess of diisocyanate. The isocyanate terminated prepolymer is then reacted with a chain extender (low molecular weight diol or diamine) to controllably form the hard segments and also increase the overall molecular weight of the polyurethane. [4, 7] When compared with the one-shot method, polyurethane elastomer structures obtained by the prepolymer technique are more regular and the resulting hard segments are relatively well defined, which in turn results in better microphase separation and mechanical properties. [7] Figure-1.4b and Figure-1.5 illustrate the microstructure regularity and the polymer formation sequence in prepolymer technique, respectively.

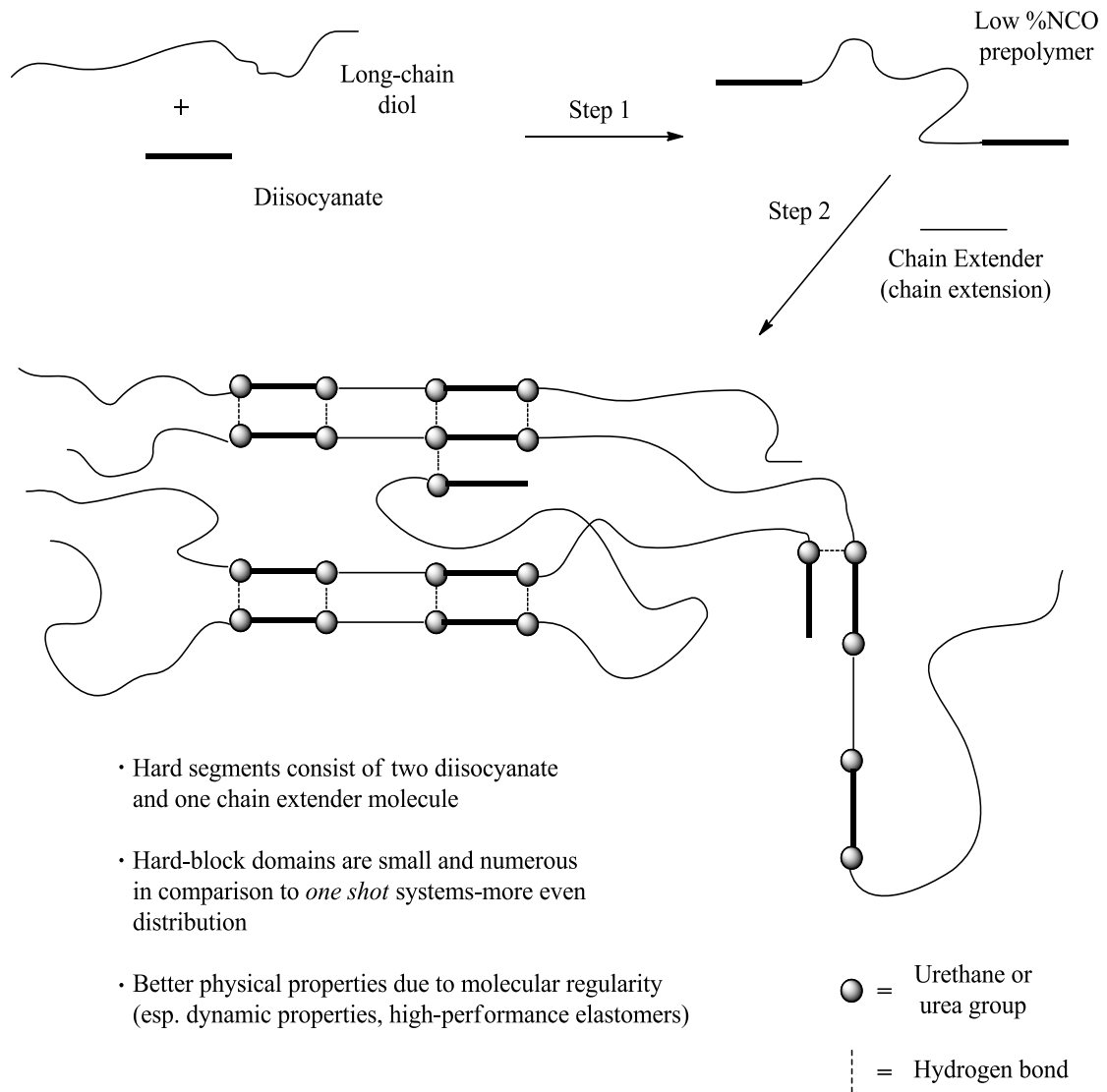


Figure-1.4 (b): Microstructure formation in polyurethane elastomers: *Prepolymer technique (two shot)* and molecular structure [4]

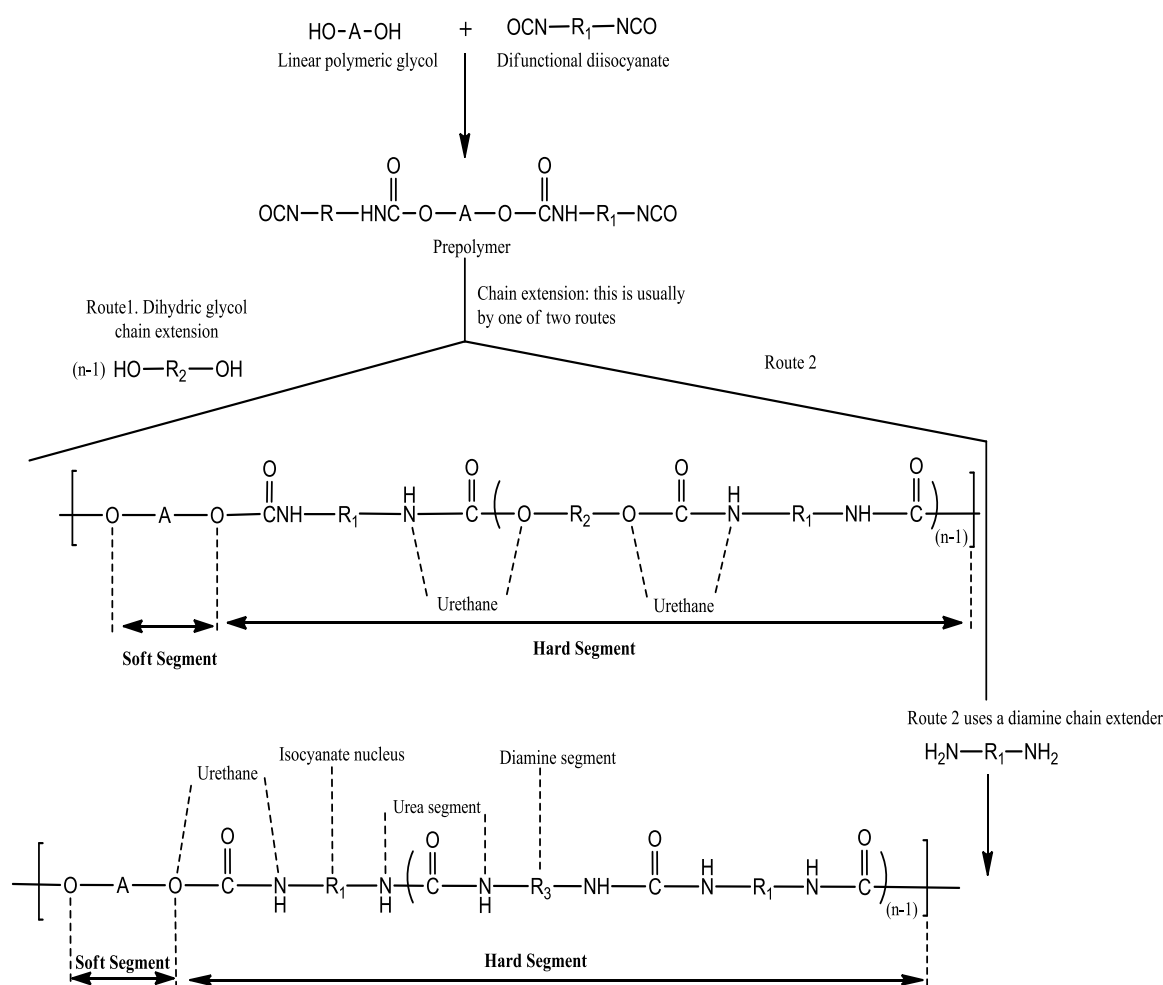


Figure-1.5: Prepolymer method for polyurethane elastomer synthesis [2]

1.4 Kinetics of Polyurethane Polymerization

The progress in polyurethane manufacturing technology and in their widespread applications attracted the attention of both academic and industrial researchers towards controlling the kinetics of the reactions between diisocyanates and polyols through selection of appropriate catalysts, solvents, reaction temperature and synthetic method used. [5] One of the most critical factors that influence the chemical structure, topology,

microphase morphology and properties of TPUs is the synthetic procedure followed and the reaction conditions employed. Unfortunately, this point is overlooked, most probably since the majority of the fundamental kinetic studies on polyurethane formation reactions were performed in 1960s. [14, 15] Recently, two excellent review articles providing a very broad overview of the kinetic analysis of polyurethane formation reactions were published, where the effect of the nature and type of the diisocyanate, reaction temperature, reaction time, solvent and catalysts on urethane formation reactions, especially on the extent of possible side reactions consuming excess isocyanate were discussed. [3, 5]

It is well established in the literature that “the analysis of kinetic research done for various reactants, with or without a catalyst, with and without a solvent, with solvents of various polarities, under equimolar conditions and with excess amount of one monomer, proved that the basic reaction, which produces urethanes, satisfies the second order kinetic equation. (Eq. (1))”: [3, 5, 14, 15]

$$\frac{-d[R_1NCO]}{dt} = k \cdot [R_1NCO] \cdot [R_2OH] \quad (1)$$

where (k) is the rate constant and $[R_1NCO]$ and $[R_2OH]$ represent concentrations of the isocyanate and the hydroxyl groups, respectively. However, this equation is appropriate only for low-to-medium degree conversions. [3] As the polymerization reaction proceeds and conversion increases, as a result of the side reactions (e.g. allophanate and biuret formation) shown in Fig.-1.6, the reaction kinetics may show deviations from the second-order to higher order kinetics.

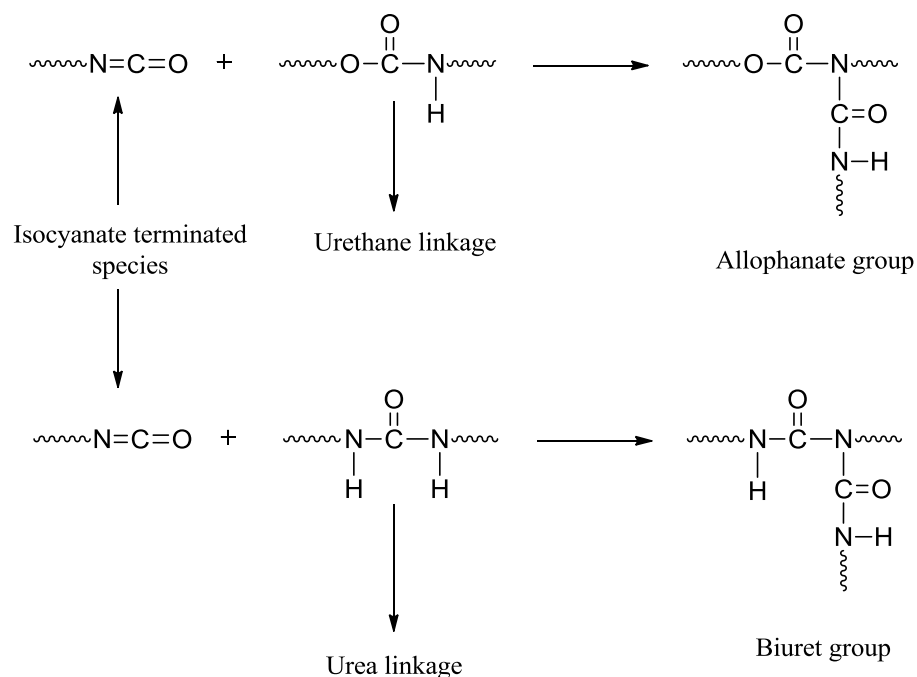


Figure-1.6: Reactions of the urethane and urea groups with isocyanates leading to allophanate and biuret formation.

The auto-catalytic effect of alcohol and urethane groups, which are illustrated in Figure-1.7, may also give rise to deviations from the second-order reaction kinetics. During these processes an active complex is formed in both cases and subsequently reacts with $-\text{OH}$ groups. This step is then followed by decomposition, which yields urethane groups and hydroxyl compounds, respectively. [5]

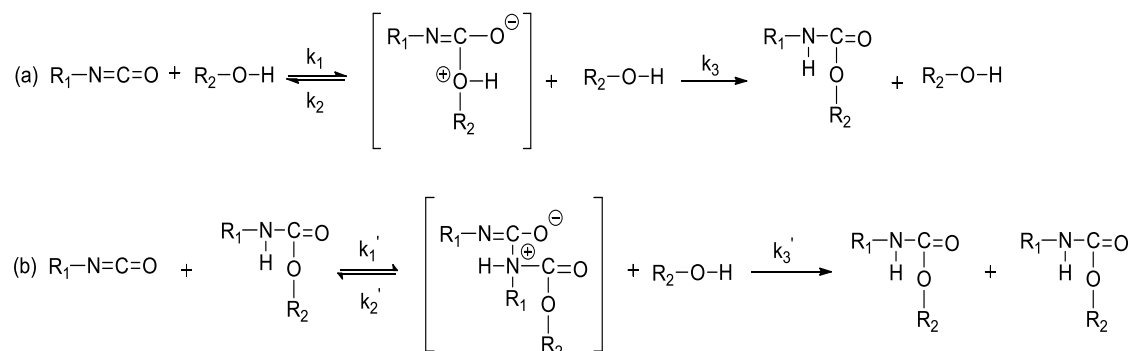


Figure-1.7: Autocatalytic mechanism (a) between isocyanate and ROH or (b) between isocyanate and urethane/urea [3, 5]

The rates of these autocatalytic reactions were first taken into account by Sato [15, 16] and described by the following kinetic equations, where k_1 , k_2 and k_3 represent the rate constants in isocyanate-alcohol reaction, whereas k_1' , k_2' , and k_3' represent the rate constants between isocyanate-urethane reactions as shown in Figure 1.7:

$$\frac{-d[R_1NCO]}{dt} = \frac{k_1 k_3 [R_1NCO][R_2OH]^2}{k_2 + k_3 [R_2OH]} \quad (2)$$

$$\frac{-d[R_1NCO]}{dt} = \frac{k_1' k_3' [R_1NCO][R_2OH][R_1NHCOOR_2]}{k_2' + k_3' [R_2OH]} \quad (3)$$

Since aromatic isocyanates are highly reactive, the values of k_2 and k_2' are much higher than $k_3[R_2OH]$ and $k_3'[R_1NHCOOR_2]$, respectively. Thus, the equations can be simplified as:

$$\frac{-d[R_1NCO]}{dt} = k_I[R_1NCO][R_2OH]^2 \quad (4)$$

$$\frac{-d[R_1NCO]}{dt} = k_{II}[R_1NCO][R_2OH][R_1NHCOOR_2] \quad (5)$$

where $k_I = \frac{k_1 k_3}{k_2}$ and $k_{II} = \frac{k'_1 k'_3}{k'_2}$

Despite the association effect, the auto-catalytic effect is more prevalent for the reactions which are carried out in solvents. On the contrary, the reactions which have been performed in bulk follow the second-order reaction given in equation (1). [5] Further details regarding the effect of reaction conditions on polyurethane formation kinetics (e.g., the nature of the reaction solvent, temperature, diisocyanate and polyol structures, and reaction stoichiometry etc.) will be discussed in Chapter-3.

1.5 Purpose of the Study

As mentioned previously in the introduction, due to the availability of very large selection of soft and hard segment constituents, thermoplastic polyurethanes offer a wide range of structure and composition dependent properties. As a consequence, in order to better control the progress of the polymer formation reactions and so the chemical structures and properties of the resulting TPUs, numerous studies (Baker [17-23], Saunders [14], and Sato [15, 16] etc.) have been focused on controlling the reactions between the diisocyanates and polyols; the building blocks of the thermoplastic polyurethanes. Today, most researchers do not seem to be very aware of

these studies, since the majority of the fundamental kinetic studies on polyurethane formation reactions were performed more than half a century ago. Therefore, the main aim of this research project is to understand the effects of the reaction conditions employed (e.g. solvent, concentration, temperature, etc.) on the extent of side reactions, which strongly affect the polymer topology and microphase morphology.

The two-step “pre-polymer method” was used as in this thesis to understand the significance of the effects of previously mentioned conditions on the prepolymer synthesis, which plays a critical role in determining the chemical structure, topology, and microphase morphology of TPUs.

To summarize, the main goals of this research are to investigate and optimize the effects of the following parameters such as;

- (i) the reaction solvent,
- (ii) diisocyanate and polyol structure,
- (iii) temperature,
- (iv) catalyst type and,
- (v) stoichiometry and concentration

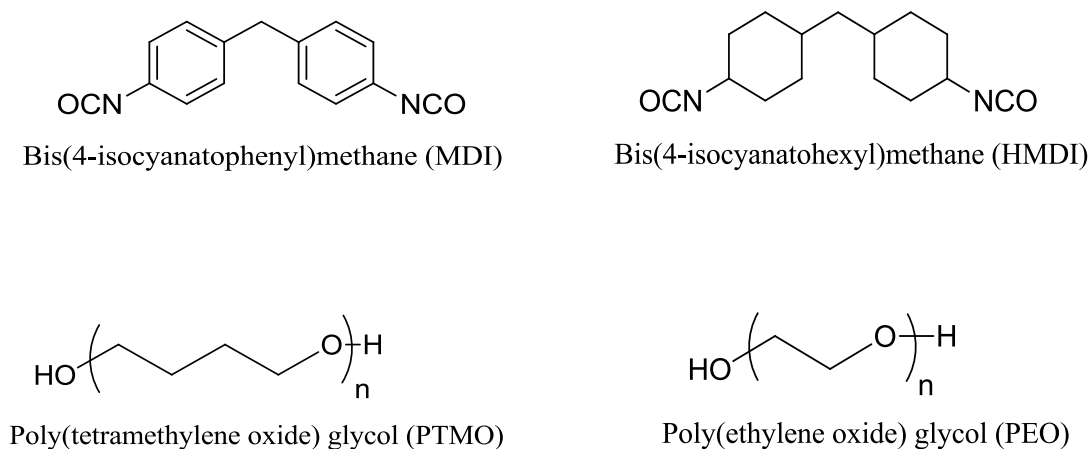
on the extent of side reactions and isocyanate consumption in prepolymer formation reactions. For this purpose, a systematic investigation of the reactions between Bis(4-isocyanatophenyl)-methane (MDI) and various polyol oligomers have been performed, which will be discussed in greater detail in Chapter-3.

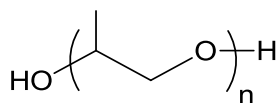
CHAPTER-2

EXPERIMENTAL

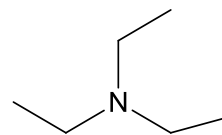
2.1 Materials

Bis(4-isocyanatophenyl)methane (MDI) and bis(4-isocyanatocyclohexyl)methane (HMDI) were kindly provided by Bayer AG, Germany and were used as received. Poly(tetramethylene oxide)glycol (PTMO) with $\langle M_n \rangle = 1000$ g/mol (DuPont), Poly(ethylene oxide)glycol (PEO) with $\langle M_n \rangle = 1000$ g/mol, and Poly(propylene oxide)glycol (PPO) with $\langle M_n \rangle = 1000$ g/mol (Bayer) were used as received. Triethylamine (TEA) was obtained from J.T. Baker and was used as a catalyst in the reactions of MDI with PTMO1k. Reagent grade dimethylformamide (DMF), tetrahydrofuran (THF) and toluene were purchased from Merck and used without further purification. Chemical structures of the reactants and the catalyst are provided in Table-2.1 along with those of the solvents that were utilized during the reactions.

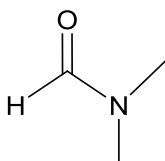
Table-2.1: Chemical structures of the reactants



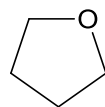
Poly(propylene oxide) glycol (PPO)



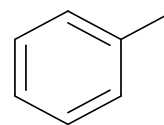
Triethylamine (TEA)



Dimethylformamide (DMF)



Tetrahydrofuran (THF)



Toluene

2.2 General Reaction Procedures and the Characterization Techniques Used for Monitoring Polymerization Reactions between MDI and Polyol Oligomers

Depending on the characterization method used, two different reaction procedures were followed. In the first case, where the kinetic data was collected by FTIR spectroscopy, reactions were carried out in a 100 mL, 3-neck round bottom Pyrex flask equipped with an overhead stirrer and a thermometer. Calculated amounts of MDI and PTMO1k (and solvent if desired) were weighed into the reaction flask and reactions were carried out under continuous stirring (130 rpm). Reactions were conducted either in bulk or in solution, where toluene, THF, DMF, THF/DMF, and toluene/DMF mixtures were used as the reaction solvent, at two different temperatures, room temperature (21-25 °C) and 50 °C. The solids content of the polymer solution was 25% by weight. Samples were taken at regular intervals from the reaction solution and thin films were cast onto KBr pellets. Reactions were followed by monitoring the change in the strong isocyanate absorption peak centered at 2270 cm^{-1} , as shown in Figure-2.1. Nicolet Impact 400-D spectrometer equipped with a DTGS-KBr detector was used for analysis. Reaction solvent was evaporated using a heat gun and 32 scans were taken for each spectrum with a resolution of 4 cm^{-1} .

Since the intensity of the peaks in infrared spectroscopy are highly dependent on the amount of sample used and because the amount of the sample withdrawn can never be controlled precisely, all infrared spectra were normalized with respect to an internal standard. For this purpose, intensity of the peak centered at 2850 cm^{-1} was used. This band was the result of aliphatic C-H stretching in polymer chain, whose concentration remains constant throughout the reaction.

As can clearly be seen in Figure-2.1, as the reaction proceeds and the concentration of urethane groups increase, the intensity of the -N=C=O absorption band centered at 2270 cm^{-1} decreases. As a result, the peak height was used as a measure of the isocyanate concentration in this study. The numbers from 1 to 5 in the figure above are assigned to the spectra taken during various stages of the reaction.

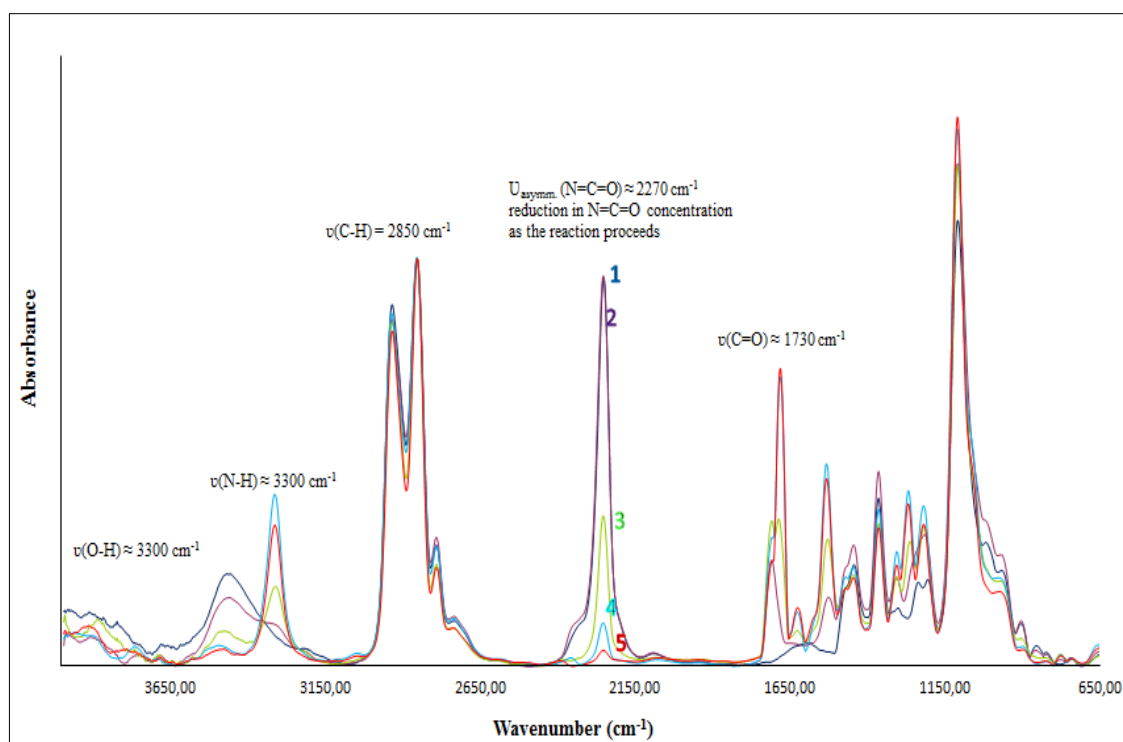


Figure-2.1: Infrared spectra of MDI-PTMO1k reaction in DMF

In the second case, where Raman spectroscopy was used, all reactions were carried out in standard Raman sample tubes, either in the presence of a solvent or in bulk. Concentrations of polymer solution were about 25% by weight and the temperatures were around room temperature (21°C). Calculated amounts of MDI and polyol (e.g., PTMO1k, PEO1k, PPG1k) were weighed into reaction flasks and after continuous stirring (130 rpm) for a minute they were injected into Raman sample tubes by syringes. A Renishaw Raman Spectrometer equipped with a 60 mW, 532 nm Cobolt CW DPSS laser was used to collect kinetic data of TPU polymerization every 2 minutes. Reactions were followed by monitoring the variation in 1530 cm^{-1} peak, which arises from (4,4'-isomer) disubstituted phenylene ring vibrations in MDI, as presented in Figure 2.2. On the other hand, although the band discernable at approximately 1445 cm^{-1} belongs directly to symmetric isocyanate vibrations, there is a significant overlap in the region with bands resulting from CH_2 bending vibrations. As a result, this band cannot be assigned to track the isocyanate consumption rate during prepolymer formation reactions. Furthermore, as it was the case in infrared spectroscopy, an internal standard was also utilized to normalize all spectra. For this purpose, the band at 1612 cm^{-1} (the band which is assigned to aromatic ring breathing/stretching vibrational modes present in the phenylene groups of MDI), was used. [24] The numbers 1 and 2 in the figure below are assigned to the two different spectra recorded at different reaction times.

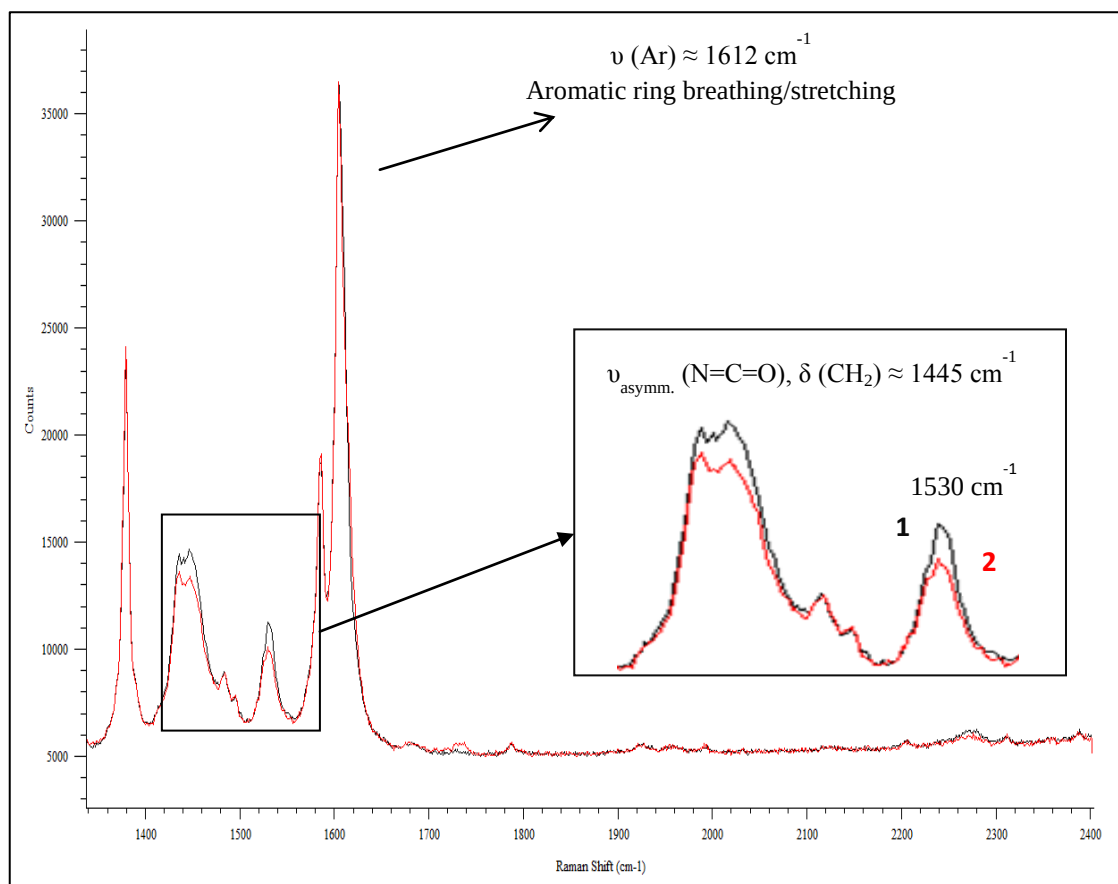


Figure-2.2: Raman spectra of MDI-PTMO1k reaction in toluene

CHAPTER-3

RESULTS AND DISCUSSION

3.1 Effect of the reaction solvent on isocyanate consumption and the extent of side reactions in MDI-PTMO1k reactions

3.1.1 Solvent effect on MDI-alcohol reactions: A literature survey

As briefly discussed in the previous section, during the synthesis of TPUs as the polymerization reaction proceeds and the concentration of urethane groups increase, the N-H groups in the polyurethane linkages can also react with the isocyanate groups, leading to side reactions and a deviation from the second-order to higher order kinetics. As a consequence, this also results in the consumption of considerably higher amounts of diisocyanate than expected. The extent of these side reactions not only depends on the temperature or the presence of catalysts, but is also determined by the nature and characteristics of the reaction solvent used, such as; the polarity, hydrogen bonding ability, and dielectric constant. [3] For instance, dimethylformamide (DMF), which is one of the key parameters investigated in this study, is a widely used solvent for the synthesis of TPUs in solution. However, as we have clearly demonstrated in this study, DMF also has a strong catalyzing effect on diisocyanate-polyol reactions, which dramatically increases the reaction rate but at the same time the side reactions.

The catalytic character of the DMF stems mainly from its solvating power or solvation capability, which can basically be defined as the ability of a solvent to form strong secondary interactions with the solute molecules. One of the most important types of these interactions is the typical acid-base interaction between an electron pair donor and an electron pair acceptor.[25] From this standpoint, coordination chemists usually categorize solvents on the basis of their capability to donate electron pairs to solutes.

The *donor number* (DN) scale (a quantitative measure of the solvent's ability to act as an electron pair donor), is developed by Gutmann in 1974 and is the best known system for classifying solvents as electron-pair donors. [26, 27] Donor number (DN) values of various electron-pair donor (EPD) solvents are provided along with their dielectric constants (ϵ) in Table-3.1. In general, the power of interaction between solvent and acceptor increases with an increase in solvent donor number. [25] As can be seen in Figure-3.1, in the case of polar aprotic solvents like dimethyl sulfoxide (DMSO), *N*-Methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) (whose DN values are relatively higher than other EPD solvents), the electron lone pairs located on the oxygen atom bonded to an sp^2 hybridized planar carbon are somewhat separated from the rest of the molecule. As a result of these electron pairs on well-exposed atoms, cations are solvated very strongly. [27]

Table-3.1: Donor numbers (DN) and dielectric constants (ϵ) of various electron-pair donor (EPD) solvents [26]

Solvent	Donor Number, DN	Dielectric Constant, ϵ
Benzene	0.1	2.3
Toluene	0.1	2.4
Nitrobenzene (NB)	4.4	34.8
Acetonitrile (AN)	14.1	38.0
Ethyl Acetate	17.1	6.0
Tetrahydrofuran (THF)	20.0	7.6
Dimethylformamide (DMF)	26.6	36.1
<i>N</i> -Methyl-2-pyrrolidone (NMP)	27.3	32.2 ^a
Dimethyl sulfoxide (DMSO)	29.8	45.0

^aHandbook of Organic Solvent Properties [28]

Numerous studies by Baker et al. [17-23, 29], Ephraim et al [29], Saunders and Frisch [14] on the mechanism of urethane formation reactions between isocyanates and alcohols revealed that the reactivity towards isocyanate (-NCO) groups mostly depends on the possible association state of the alcohol molecule. [3] By combining all these kinetic data and the donor number concept, a general ion-paired mechanism is proposed by Chang in 1987, which elucidates the catalytic activity of DMF in urethane formation reactions. [30] (see Figure-3.1)

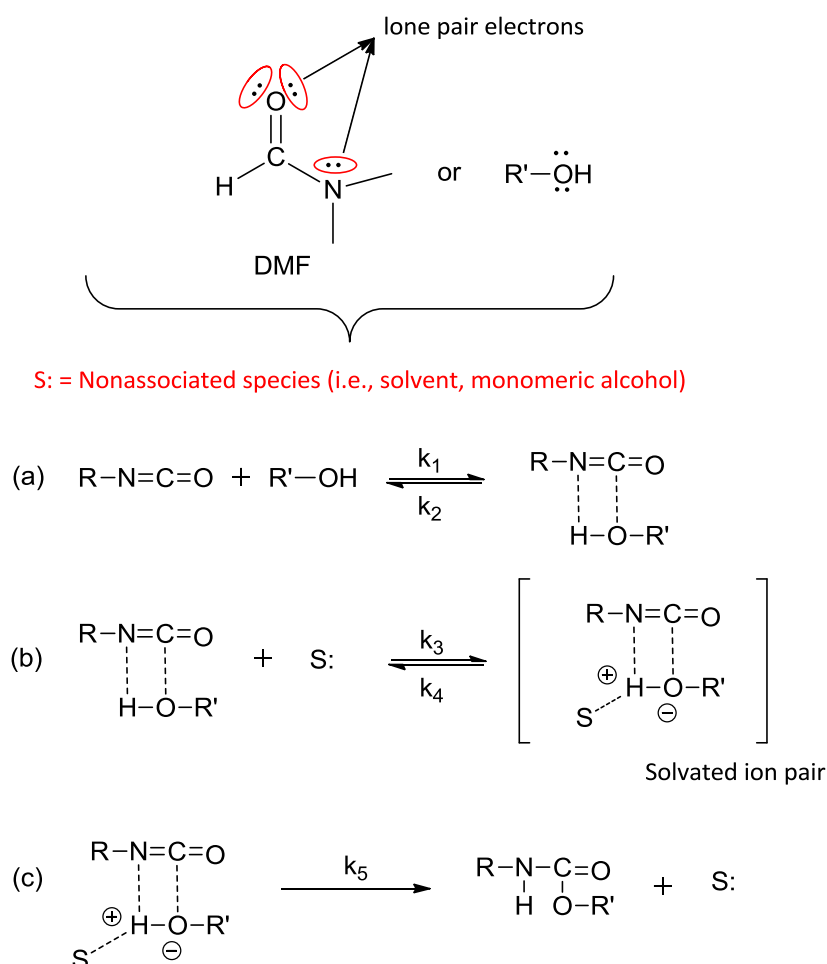


Figure-3.1: The proposed ion-pair mechanism [30]

According to the suggested mechanism by Chang, shown in Figure-3.1, the alcohol and the isocyanate firstly form a hydrogen bonding complex, which is then solvated by the non-associated species (i.e., S: solvent or alcohol) through the active hydrogen site of the complex to create an solvated ion pair (Figure-3.1b). As a result, the negatively charged oxygen atom of the alcohol now can readily attack to the electrophilic carbon of isocyanate and allows the urethane formation reaction to take place more easily. [30, 31] On the other hand, instead of solvating the isocyanate/alcohol complex, any S: molecule can also form a hydrogen bonding complex with the oxygen of monomeric alcohol, leading to a reduction in the concentration of key isocyanate/alcohol complex and of monomeric alcohol. This will inevitably cause a decrease in both catalytic activity and the reaction rate. However, as it is previously discussed, in the case of some aprotic solvents such as, DMSO, NMP and DMF, the solvated ion pair concentration in the reaction system will increase (due to their high DN values than alcohols), counteracting the lower alcohol/isocyanate complex concentration to produce an overall catalytic effect. [3]

In the last step (Figure-3.1c), the high dielectric constant (ϵ) of the solvent (which can be defined as the ability of solvent to separate charges) facilitates the dissociation of the O-H bond and thus the formation of the urethane group. [3, 25]

3.1.2 Effect of the reaction medium on the kinetics of the stoichiometric reactions between MDI and PTMO1k

In order to better understand the catalytic effect of DMF, we carried out a systematic study on the reaction between MDI and PTMO1k. Reactions were conducted at room temperature (22 to 25 °C) in bulk and in solution using three different solvents, which were DMF, toluene (TOL) and tetrahydrofuran (THF). Overall concentrations of the solutions were 25% solids by weight. Figure-3.2 presents the change in the isocyanate content of the reaction mixture (for the reactions with an initial ratio of

[MDI]/[PTMO1k]=1.0) throughout the reaction as a function of time, in bulk and in three different solvents.

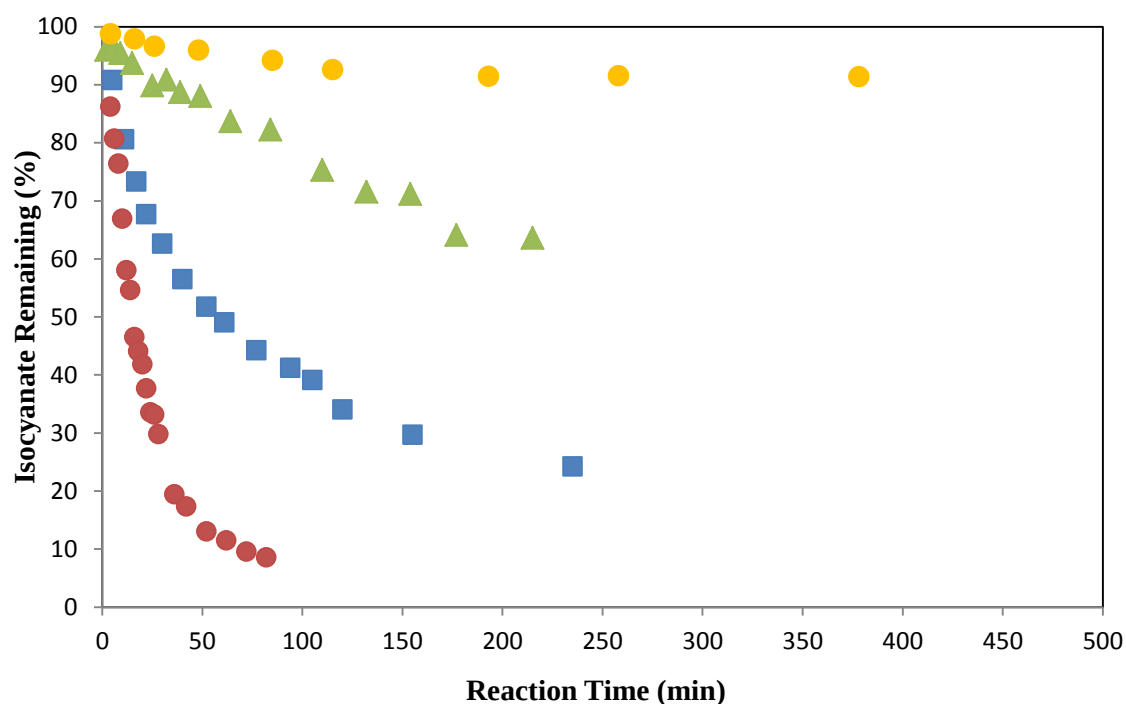


Figure-3.2: Isocyanate consumption as a function of time at room temperatures with an initial ratio of [MDI]/[PTMO1k] = 1.0 (●) in DMF at 22°C (■) Bulk at 22.5°C (▲) in toluene at 25°C, and (●) in THF at 25°C

As shown in Figure 3.2., the bulk reaction between stoichiometric amounts of MDI and PTMO1k at 22 °C is fairly rapid and reaches to about 80% conversion in 4 hours. When compared with the bulk system, the reactions carried out in TOL and THF solutions are much slower. This is expected since the rate of a second order reaction is concentration dependent and as explained before, the concentrations of the reaction medium carried out in TOL and THF solutions is 25% by weight, which is much lower than that of the bulk. (Molar concentrations are provided on the second column of Table-3.2) Interestingly, the nature and polarity of reaction solvent (THF and TOL) seem to have a

strong effect on the reaction rate. Urethane formation reaction in toluene proceeds much faster when compared to the reaction in THF, although DN number of THF is much larger than that of TOL (Table-3.1). As mentioned before, formation of isocyanate/alcohol complex is the first and critical step of the reaction. In the case of THF, which strongly hydrogen bonds to alcohol, formation of isocyanate/alcohol complex is significantly reduced and thus the rate of the isocyanate-alcohol reaction.

Very interestingly, as can clearly be seen from Figure-3.2, when compared with the bulk and solution reactions in THF and TOL, MDI-PTMO1k reactions carried out in DMF proceed significantly faster, reaching 90% conversion in less than 70 minutes. This clearly shows the dramatic catalytic activity of DMF in polyurethane formation reactions when an aromatic diisocyanate, such as MDI is used.

Kinetic analysis of the data presented in Figure 3.2 were carried out according to the second-order rate law, where;

$$\frac{-d[C]}{dt} = k \cdot [C]^2 \quad (6)$$

This equation can be rearranged, and integrated as shown below:

$$\frac{d[C]}{[C]^2} = -k dt \quad (7)$$

$$\int_{[A]_o}^{[A]_t} \frac{d[C]}{[C]^2} = -k \int_0^t dt \quad (8)$$

$$\frac{1}{[C]_t} - \frac{1}{[C]_o} = kt \quad (9)$$

Upon rearrangement of the integrated rate equation, we obtain a linear equation:

$$\frac{1}{[C]_t} = kt + \frac{1}{[C]_o} \quad (10)$$

As shown in Figure-3.3, when $1/[C]$ is plotted against time a line is obtained for second-order reactions. Slope of this line gives the rate constant (k), whereas the intercept gives $1/[C]_o$.

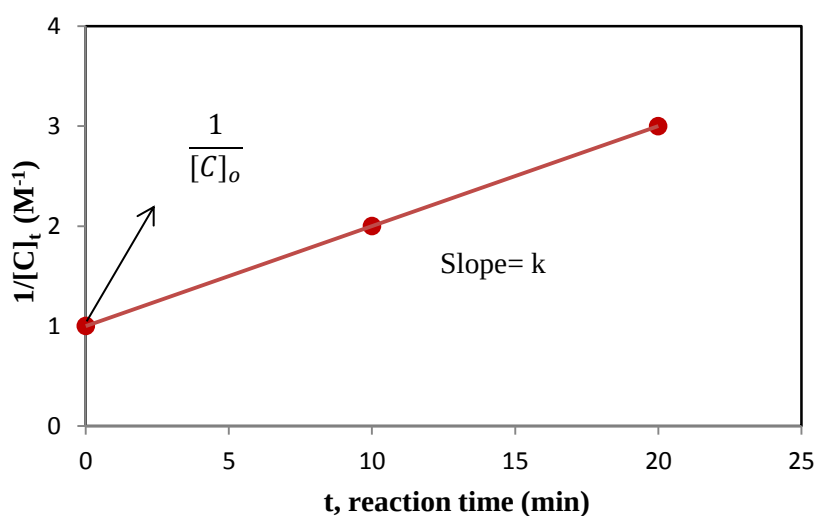


Figure-3.3: Relationship between the rate constants and the plot of $1/C$ vs time

Second-order plots for the stoichiometric reactions between MDI-PTMO1k in bulk, THF, TOL and DMF solutions are provided in Figure 3.4. Since the reaction in bulk, THF and TOL solutions are much slower than the reaction in DMF, an expanded view of the plots for these systems are provided in the inserted figure. It is interesting to note fairly linear second-order plots for bulk, THF and TOL reactions. On the other hand for the reaction in DMF, in addition to a very fast reaction rate compared to the others, a strong deviation from initial linearity is also observed. This clearly indicates the presence of side reactions, which is due to the reaction of the isocyanate groups with the hydrogens of the urethane groups formed, in this system. Interestingly, the isocyanate-urethane reaction also seems to be second order, since the plot is linear, and much faster

than the alcohol-isocyanate reaction. Therefore, for DMF reaction, two different second-order rate constants were determined from the slopes of each line and provided in Table-3.2.

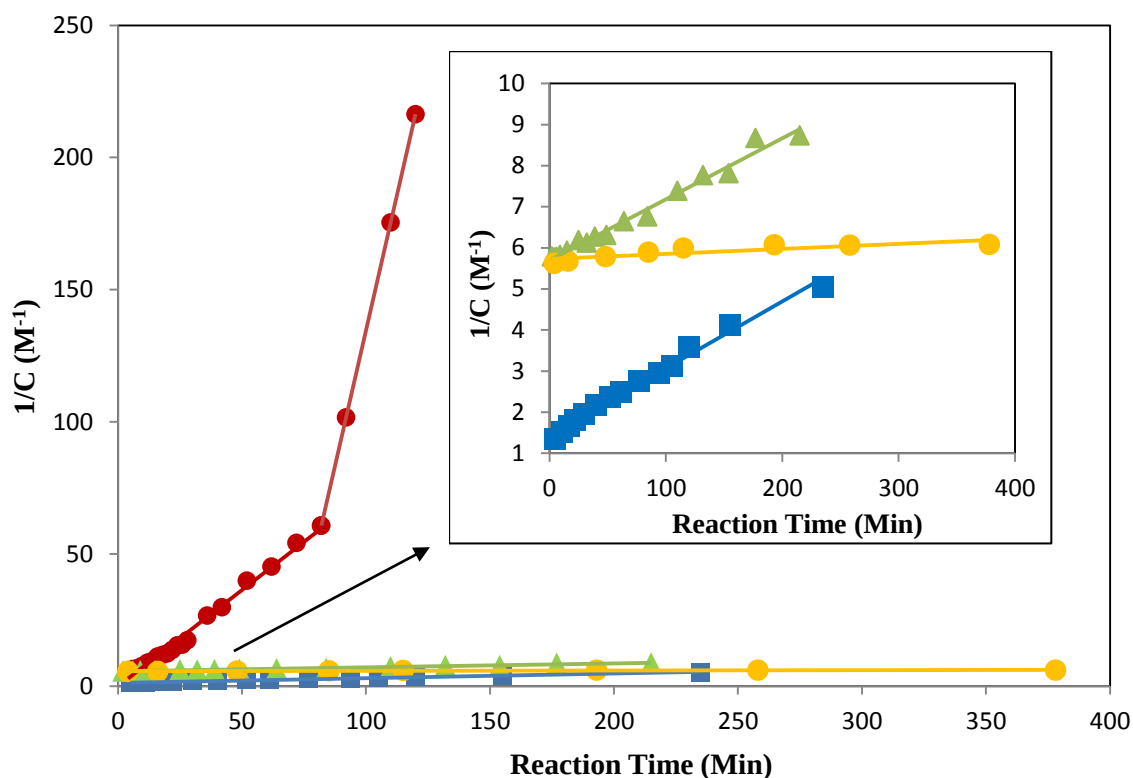


Figure-3.4: $1/C$ plots as a function of reaction time at room temperatures with an initial ratio of $[MDI]/[PTMO1k] = 1.0$ (●) in DMF at 22°C (■) Bulk at 22.5°C (▲) in toluene at 25°C , and (●) in THF at 25°C

Values of the second-order rate constants obtained from these plots are provided in Table-3.2. It is interesting to note that as expected, bulk reaction has a higher rate constant than both of the solution reactions in THF and TOL. The lowest rate is observed in THF, since THF can strongly hydrogen bond to alcohol, inhibiting the

formation of isocyanate/alcohol complex, which is a critical step in determining the rate of the isocyanate-alcohol reactions, as discussed before. For an easier comparison, relative magnitudes of the rate constants (k_1) are also provided on the last column of Table 3.2, assuming the rate constant of bulk reaction to be 1.00. It is interesting to note that the reaction in DMF is almost 40-fold faster than the bulk reaction and over 600-fold faster than the reaction in THF solution.

Table-3.2: Rate constant values of the reactions at room temperatures with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 1.0$

Solvent	$[\text{MDI}]_0$ (mol/L)	Temperature (°C)	$k_1 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)	$k_2 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)	Relative values of k_1
DMF	0.193	22	72.4	409.5	40
Bulk	0.833	22.5	1.8	-	1.00
Toluene	0.180	25	1.49	-	0.83
THF	0.182	25	0.12	-	0.07

3.1.3 Effect of the reaction medium on the kinetics of the reactions between PTMO1k and excess MDI

In order to better understand the effect of reaction stoichiometry and the catalytic effect of DMF on the extent of the side reactions, a series of reactions with two-fold molar excess of diisocyanate to polyol oligomer at room temperature (22-25 °C) were also performed. In fact this reaction is similar to the “prepolymer formation” step used in most TPU reactions. Since two-fold molar excess of MDI to PTMO1k is used, it is important to notice that without any significant side reactions all curves should level off around 50% isocyanate consumption.

Interestingly, as presented in Figure-3.5, the system where DMF is used as the reaction solvent, 50% consumption line is reached in about 20 minutes (even at room temperature) and almost all isocyanate was consumed within 3 hours, indicating very

extensive side reactions. However, in the case of the bulk reaction, 50% consumption line was reached in about 75 minutes, after which the reaction slowed down dramatically. The side reactions basically leveled off after two hours, where about 15% more than the stoichiometric amount of isocyanate was consumed. Reactions in THF and TOL were very slow when compared to bulk and DMF reactions and reached to 15 and 35 % isocyanate consumption levels after 6 h of reaction. Second-order plots for $[\text{MDI}]: [\text{PTMO1k}] = 2.0$ reactions are provided on Figure 3.6. All reactions, except the DMF system give fairly straight lines, indicating a second-order reaction. On the other hand reactions performed in DMF showed two consecutive second-order reactions as before, where the value of k_2 was tenfold higher than that of k_1 . Table-3.3 presents the rate constants obtained from $1/C$ versus time plots (using data from Figure-3.6).

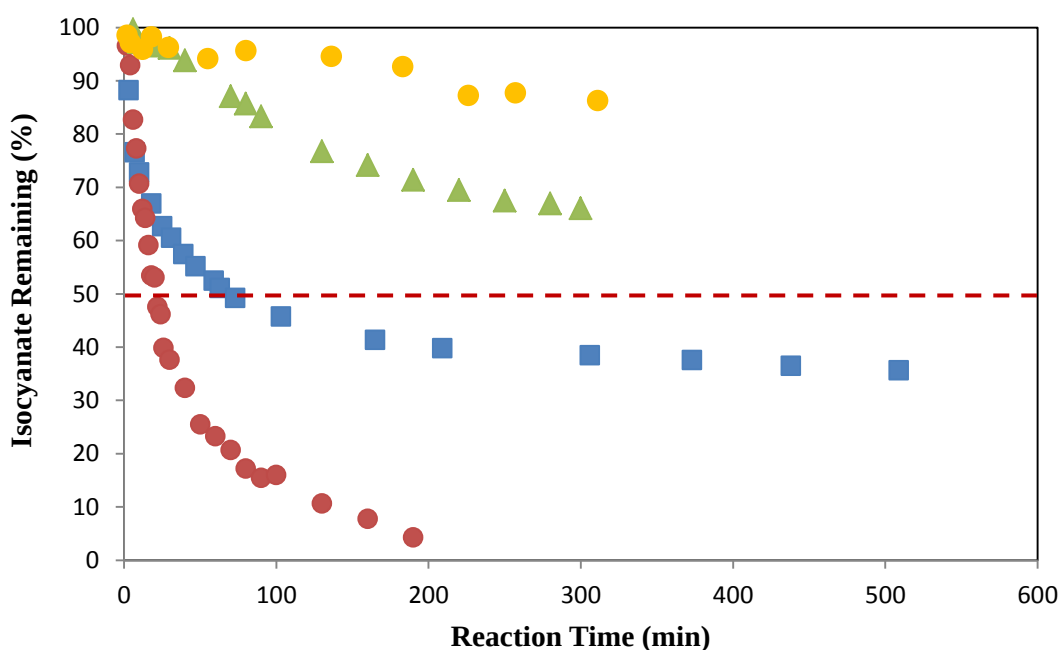


Figure-3.5: Isocyanate consumption as a function of time at room temperatures with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ (●) in DMF at 25°C (■) Bulk at 22.5°C (▲) in toluene at 22°C, and (●) in THF at 25°C

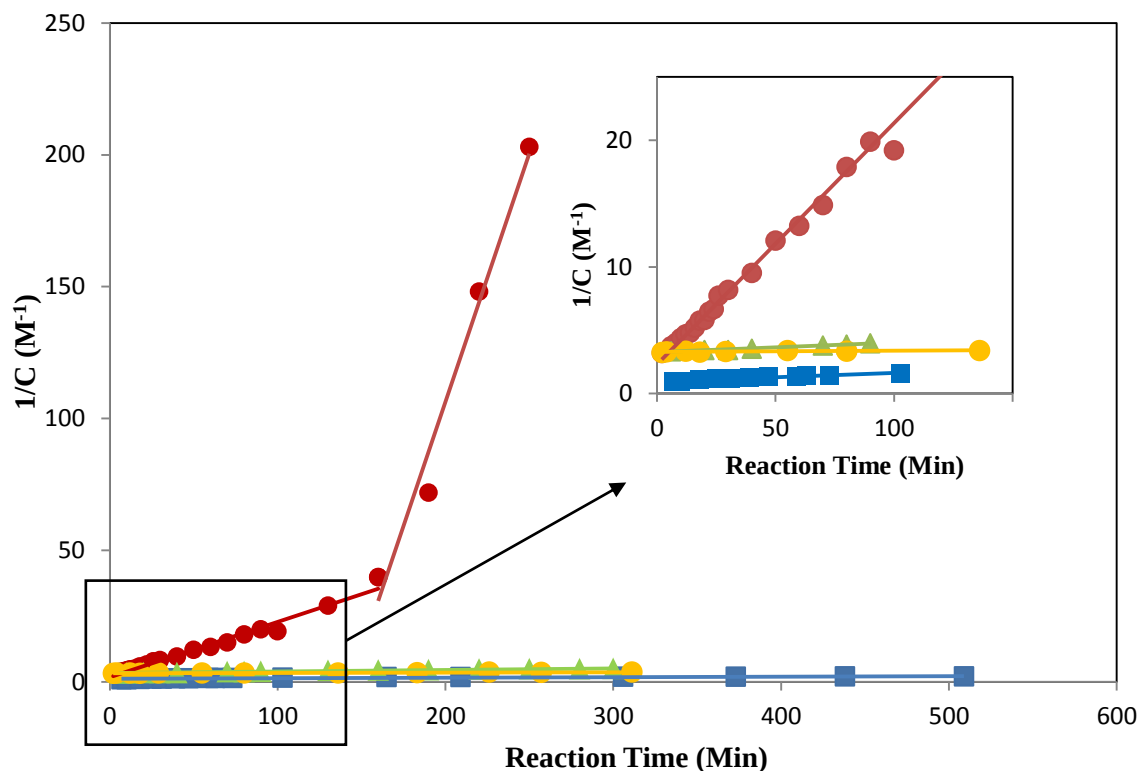


Figure-3.6: $1/C$ plots as a function of reaction time at room temperatures with an initial ratio of $[MDI]/[PTMO1k] = 2.0$ (■) Bulk at 22.5°C (●) in THF at 25°C (▲) in toluene at 22°C , and (●) in DMF at 25°C

Table-3.3: Rate constant values of the reactions at room temperatures with an initial ratio of $[MDI]/[PTMO1k] = 2.0$

Solvent	$[MDI]_0$ (mol/L)	Temperature ($^{\circ}\text{C}$)	$k_1 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)	$k_2 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)
DMF	0.325	21	17.9	188.7
Bulk	1.430	22.5	0.66	-
Toluene	0.303	22	0.61	-
THF	0.312	25	0.14	-

These results clearly prove the catalytic activity of DMF in urethane formation reaction between MDI and PTMO1k, even in the experiments carried out at a fairly low temperature of 25 °C. Effect of the reaction temperature (50°C) on the catalytic activity of DMF and the extent of the side reactions will also be discussed, shortly.

The reaction between the excess MDI and PTMO in DMF was also monitored by FT-IR spectroscopy and the plots obtained were quite similar to that of Raman, verifying the reliability of the techniques that has been used in this study. (see Fig-3.7)

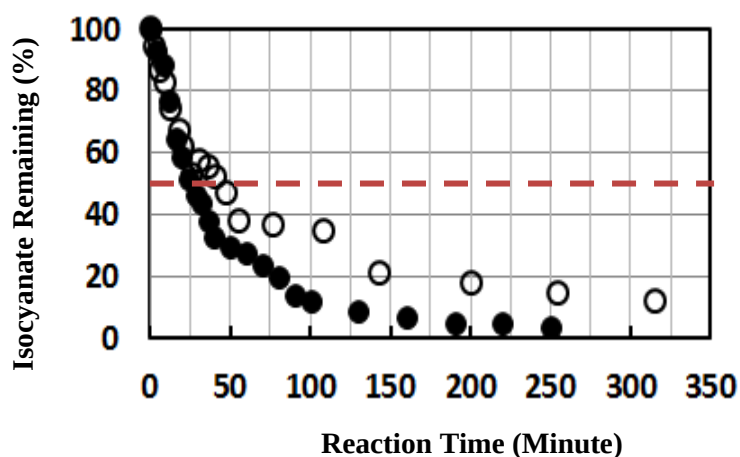


Figure-3.7: Isocyanate consumption as a function of time at 25 °C with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ in bulk. (o) FTIR spectroscopy, (●) Raman spectroscopy.

In order to see the effect of the chemical structure of the oligomer used, MDI was reacted with PEO1k and PPO1k, which are very commonly used for TPU synthesis. Reactions were conducted in DMF at 21 °C, at $[\text{MDI}]:[\text{Polyol}]=2.0$ ratio. Conversion-time curves for these reactions are provided in Figure 3.8. As can clearly be seen from these curves, there is no significant effect of the structure of the oligomer used on the isocyanate consumption rate.

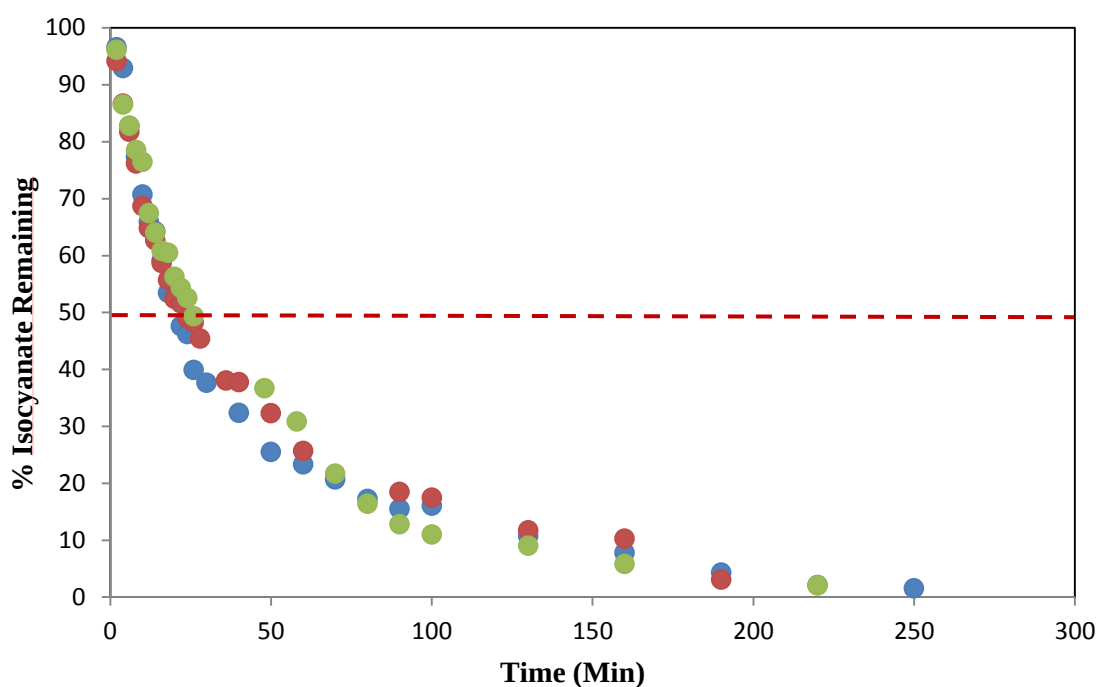


Figure-3.8: Isocyanate consumption as a function of time at 21°C in DMF (●) [MDI]/[PTMO1k] = 2.0 (●) [MDI]/[PEO1k] = 2.0 (●) [MDI]/[PPO1k] = 2.0

Second-order plots for these reactions are provided in Figure 3.9. As can be seen from these plots, all reactions seem to display two consecutive second-order plots. Values of the rate constants for the reactions between MDI and various polyols in DMF with an initial ratio of $[\text{MDI}]/[\text{Polyol}] = 2.0$ are provided in Table 3.4. The reaction of MDI with PTMO1k seems to be slightly faster than that of PEO1k, while PPO1k gives the slowest reaction. The rate constant for the second reactions (k_2) are much higher than (k_1) for all reaction systems.

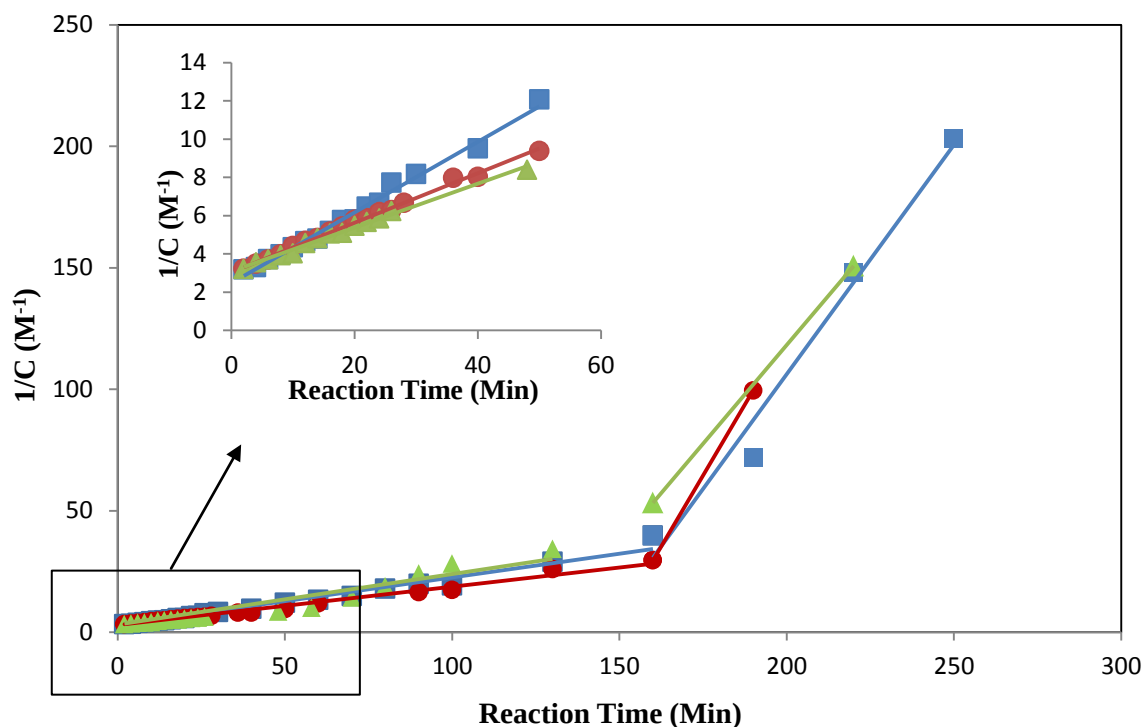


Figure-3.9: $1/C$ plots as a function of reaction time at 21°C with an initial ratio of $[\text{MDI}]/[\text{Polyol}] = 2.0$ in DMF (■) $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ (●) $[\text{MDI}]/[\text{PEO1k}] = 2.0$ (▲) $[\text{MDI}]/[\text{PPO1k}] = 2.0$

Table-3.4: Rate constant values of the reactions between MDI and various polyols in DMF with an initial ratio of $[\text{MDI}]/[\text{Polyol}] = 2.0$

Solvent	Reaction	$[\text{MDI}]_0$ (mol/L)	Temperature ($^{\circ}\text{C}$)	$k_1 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)	$k_2 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)
DMF	$[\text{MDI}]/[\text{PTMO}]=2$	0.325	21	17.9	188.7
DMF	$[\text{MDI}]/[\text{PEO}]=2$	0.330	21	15.3	232.9
DMF	$[\text{MDI}]/[\text{PPO}]=2$	0.325	21	11.5	163.2

In addition to the single-solvent systems, TOL/DMF mixtures with weight ratios of 99/1, 90/10 and 75/25 were also used as the reaction solvent in order to understand the

catalytic activity of DMF. Reactions were carried out at 50 °C using equimolar amounts of MDI and PTMO1k at a concentration of 25% by weight solids. Conversion-time curves for these reactions are provided in Figure 3.10, together with that of the bulk reaction and pure DMF as the solvent. It is interesting to note that the rate of the reaction in toluene solution containing 25% by weight of DMF was higher than the bulk reaction.

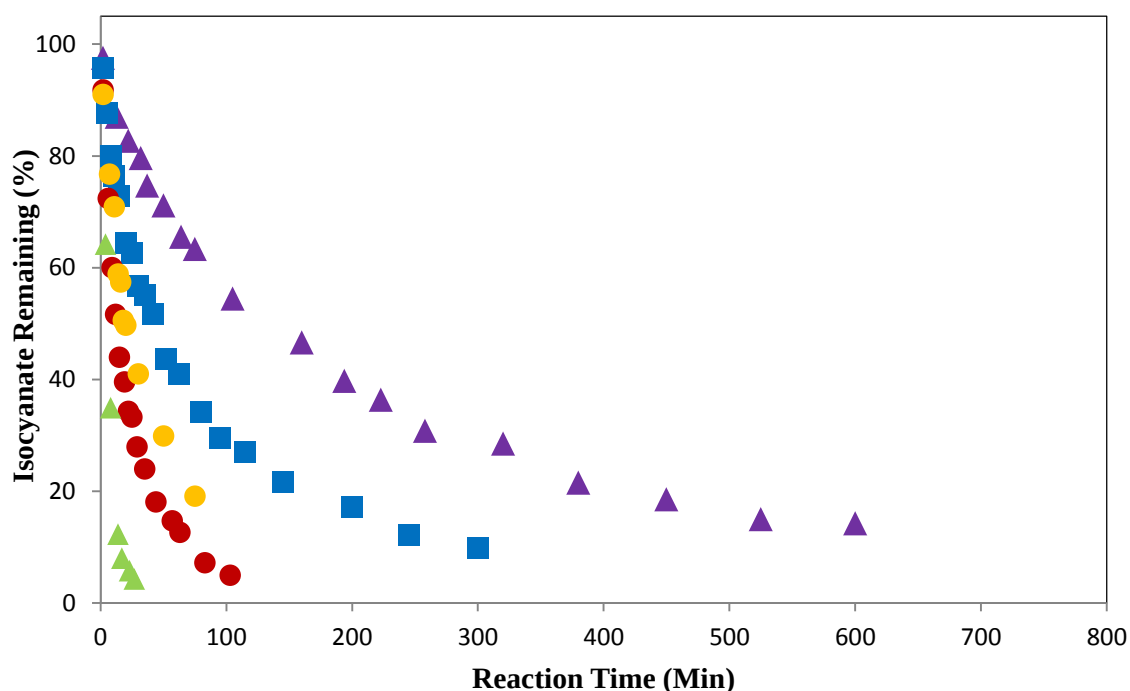


Figure-3.10: Isocyanate consumption as a function of time in $[\text{MDI}]/[\text{PTMO1k}] = 1.0$ reaction at 50°C in (▲) pure DMF, (●) 75/25 by weight (Toluene/DMF) (●) Bulk (■) 90/10 by weight (Toluene/DMF), and (▲) 99/1 by weight (Toluene/DMF)

Second-order plots for these reactions are provided in Figure 3.11. As can be seen from the results in Figure-3.11, all reactions, except the bulk reaction indicates the presence of two consecutive second-order reactions, similar to those observed earlier. The rates of the reactions were strongly correlated with the amount of DMF present as the co-

solvent, which clearly acted as a catalyst. As a result the higher the relative amount of DMF in the solvent system, the faster was the reaction. When the rate constants for the first (k_1) and the second (k_2) reactions are compared, in general second reactions were 2–5 times faster. (see Table- 3.5) Very interestingly the increase in the rate of the reactions are linearly correlated with the amount of DMF used as the co-solvent as shown in Figure 3.12.

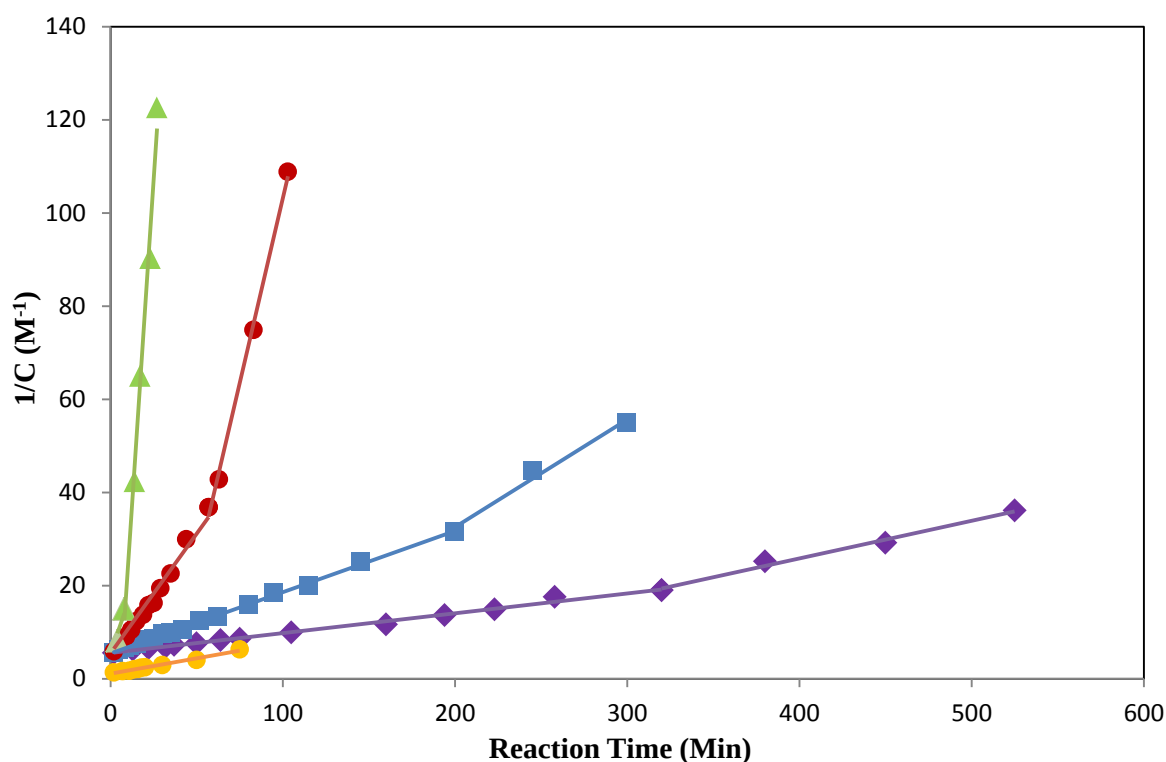


Figure-3.11: $1/C$ plots as a function of reaction time in $[MDI]/[PTMO1k] = 1.0$ reaction at 50°C in (▲) pure DMF (●) 75/25 (Toluene/DMF) by weight (●) Bulk at 50°C (■) 90/10 (Toluene/DMF) by weight, and (◆) 99/1 (Toluene/DMF) by weight

Table-3.5: Rate constant values of the reactions in various mixed solvent systems with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 1$

Solvent	$[\text{MDI}]_0$ (mol/L)	Temperature (°C)	$k_1 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)	$k_2 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)
DMF	0.192	49	111.7	583.9
75/25 (Toluene/DMF)	0.185	50	51.4	165.1
90/10 (Toluene/DMF)	0.185	50	13.2	23.1
Bulk	0.833	50	6.6	-
99/1 (Toluene/DMF)	0.185	50	4.3	7.6

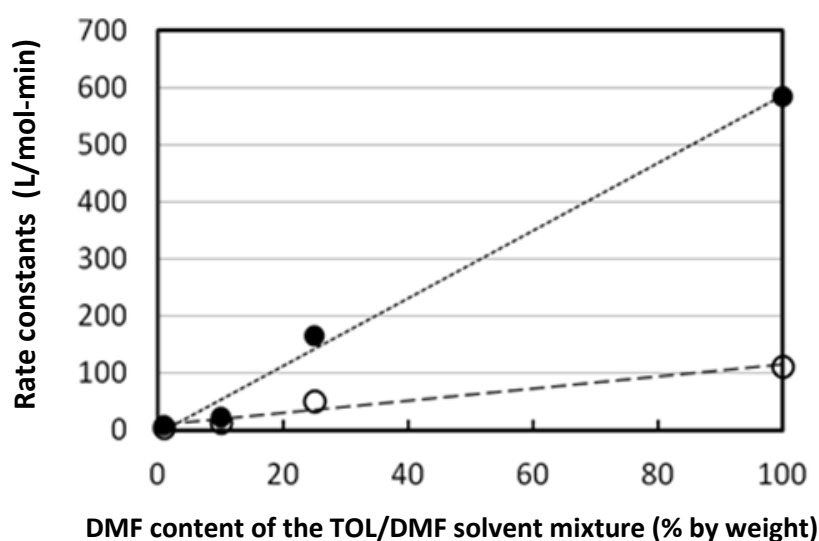


Figure 3.12 : Linear correlation between the DMF content of the reaction solvent and second-order rate constants for the equimolar reaction between MDI and PTMO1k at 50°C. (○) k_1 and (●) k_2

Effect of the composition of the reaction solvent (TOL/DMF) on the rate of MDI/PTMO1k reactions with an initial $[\text{NCO}]/[\text{OH}]$ stoichiometry of 2.0 at 50 °C was

also studied. We believe this is an important study, which resembles the prepolymer formation reaction, where it is critical to minimize the side reactions (e.g. allophanate formation), which consumes excess isocyanate and lead to branching and even crosslinking. Conversion-Time curves for these reactions are provided in Figure-3.13. When the reaction is carried out in DMF, isocyanate content is halved in nearly five minutes and almost all isocyanate is consumed in less than 35 minutes. These results clearly indicate that DMF is not a very good reaction solvent for this system, since significant amount of side reactions take place. For TOL/DMF solvent system with a ratio of (75/25), reaction is again considerably fast and 70% of the isocyanate is consumed in about 2 hours. In the case of TOL/DMF (90/10) system, the reaction slows down considerably and reaches 50% level within 4 hours, where the isocyanate consumption seems to level off. For comparison we also carried out a reaction in (90/10) (THF/DMF). The results obtained were very similar to that of TOL/DMF (90/10) solvent system. In general the results obtained in these $[MDI]/[PMO1k] = 2.0$ reaction correlates well with the results obtained in stoichiometric MDI-PTMO1k reactions.

Second-order plots for these reactions are provided in Figure 3.14 and the rate constants are listed in Table-3.6. Although it was expected for the DMF containing system (due to previously obtained results) to exhibit two consecutive lines, only one straight line is observed. This is most probably due to the combined effect of both high temperature (50 °C) and DMF, which increased the reaction rate dramatically and made it hard to track the isocyanate consumption precisely at the very beginning of the reaction.

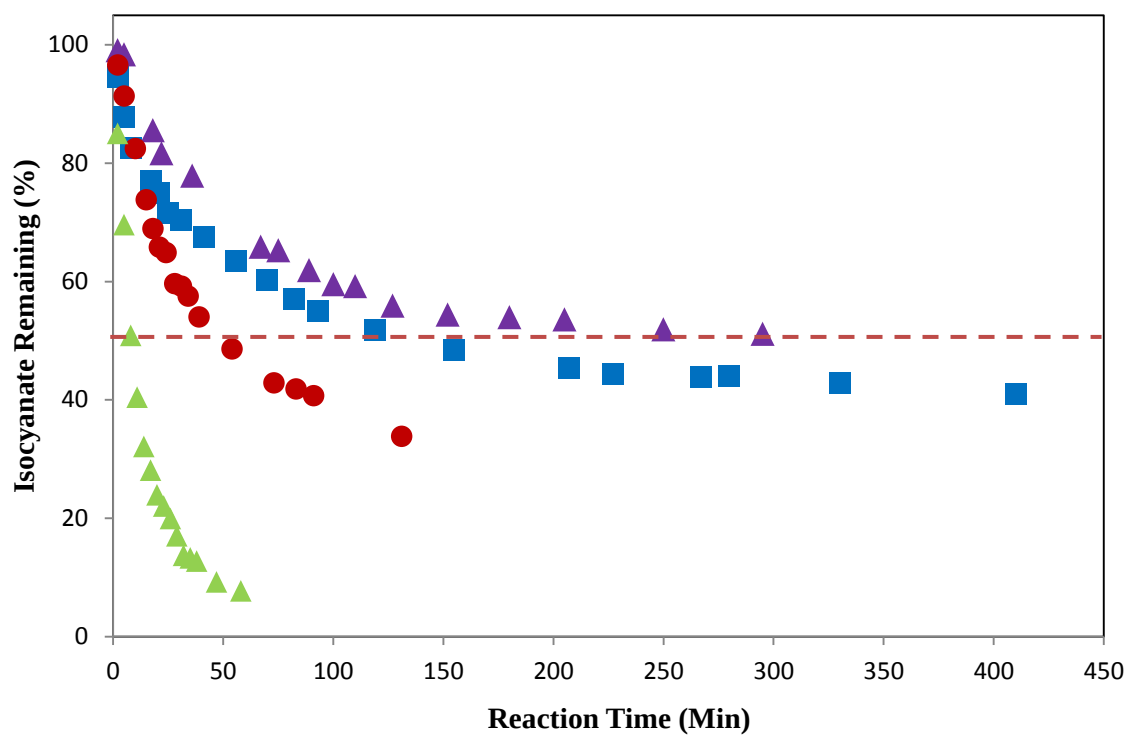


Figure-3.13: Isocyanate consumption as a function of time in $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ reaction at 50°C in (▲) pure DMF (●) 75/25 (Toluene/DMF) by weight (■) 90/10 (THF/DMF) by weight and (▲) 90/10 (Toluene/DMF) by weight

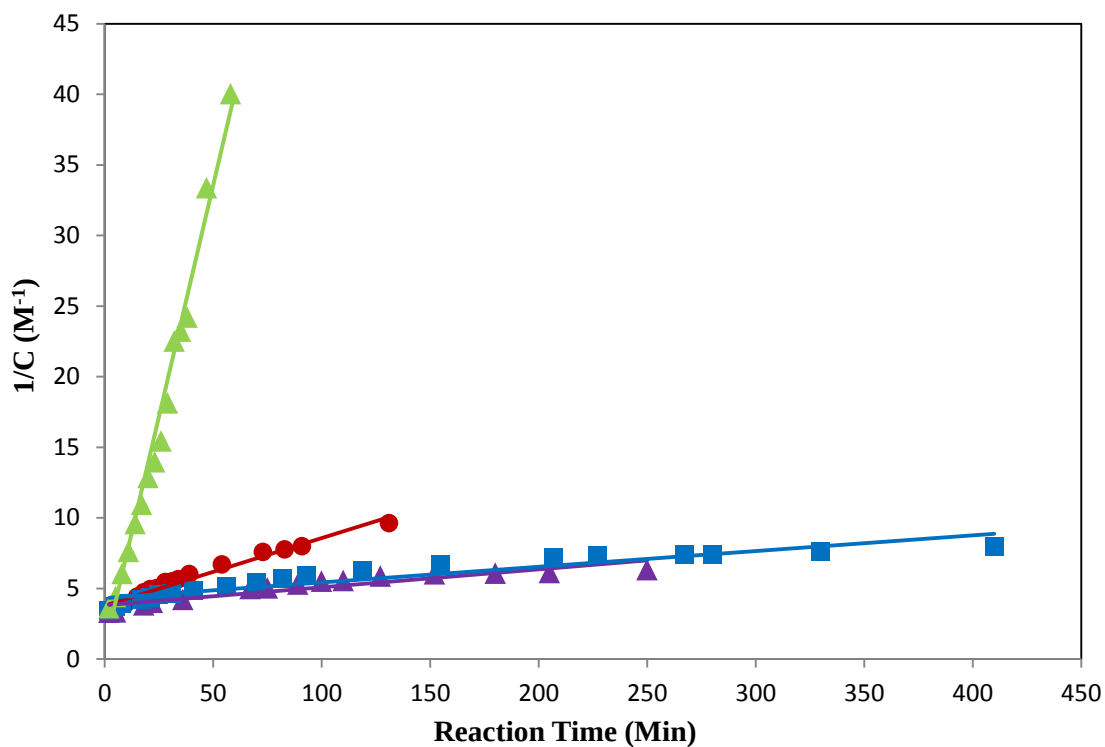


Figure-3.14: $1/C$ plots as a function of reaction time in $[MDI]/[PTMO1k] = 2.0$ reaction at 50°C in (▲) pure DMF (●) 75/25 (Toluene/DMF) by weight (■) 90/10 (THF/DMF) by weight and (▲) 90/10 (Toluene/DMF) by weight

Table-3.6: Rate constant values of the reactions in various mixed solvent systems with an initial ratio of $[MDI]/[PTMO1k] = 2.0$

Solvent	$[MDI]_0$ (mol/L)	Temperature ($^\circ\text{C}$)	$k_1 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)
DMF	0.325	50	66.5
75/25 (Toluene/DMF)	0.308	50	4.8
Bulk	1.430	50	0.1
90/10 (THF/DMF)	0.308	50	1.1
90/10 (Toluene/DMF)	0.305	50	1.2

The results presented above clearly show the importance of the solvent selection during MDI based prepolymer formation in order to reduce the undesired side reactions and keep the excess isocyanate consumption at a minimum level. Although it is suggested by many articles on polyurethane synthesis that using about 10% excess MDI would be enough to compensate the side reactions, it is clearly evident from our results that this amount is not sufficient, especially if the reactions are conducted in DMF at high temperatures (such as 50-80 °C range) for long periods. Therefore, in order to calculate the exact amount of the chain extender to be used, one should first precisely determine the isocyanate content of the prepolymer by back titration.

3.1.4 Effect of diisocyanate structure on isocyanate consumption in DMF

Type and nature of the diisocyanates, the essential constituents of the hard segments along with the chain extenders, have a dramatic effect on the rates of the urethane formation reactions. Before going into the detailed discussion on the structures of the diisocyanates it would be beneficial to examine the isocyanate functional group.

The isocyanate group is a strained linear structure with a cumulated double bond sequence of N=C=O. As presented in Figure 3.15, due to the high electronegativities of the oxygen and the nitrogen, an isocyanate displays several resonance structures and has a fairly electrophilic carbon atom, which is susceptible toward nucleophilic attacks, such as by an alcohol or amine. [3, 32, 33]

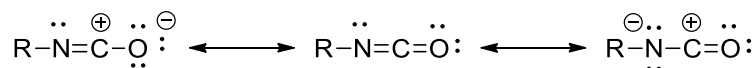


Figure-3.15: Resonance structures of the isocyanate functional group

In the case of aromatic diisocyanates, due to the electron withdrawing ability of the phenylene rings, which increases the electropositivity of the carbon on the —N=C=O group, aromatic diisocyanates are much more reactive towards alcohols when compared with their aliphatic homologs. In general, without taking the steric factors into account, any electron-withdrawing group attached on the molecule will increase the positive charge on the carbon atom and hence the reactivity. [3, 32] This difference in reactivities can also be utilized in the preparation of TPUs with distinct features. For example, while polyurethanes made from aliphatic isocyanates are light stable, materials that consist of aromatic isocyanates have a tendency to undergo photo degradation upon their exposure to light. [7]

Figure-3.16 shows the effect of isocyanate symmetry on the reaction rate calculations for aromatic diisocyanates. When two isocyanate groups align symmetrically in a molecule, both groups will exhibit the same reactivity at the beginning of their reactions with alcohols (or amines), which can be expressed as $k_1=k_2=k$. However, as the reaction proceeds, the reactivity of the unreacted isocyanate group becomes reduced (k') due to the electronic and steric effects of the formed urethane (or urea) group. On the other hand, in asymmetric diisocyanates, isocyanate groups already possess two different reactivities, which are again changed upon the consumption of the first isocyanate group. As a result, four different reaction rate constants (e.g., k_1 , k_2 , k_1' , k_2') are obtained. [3]

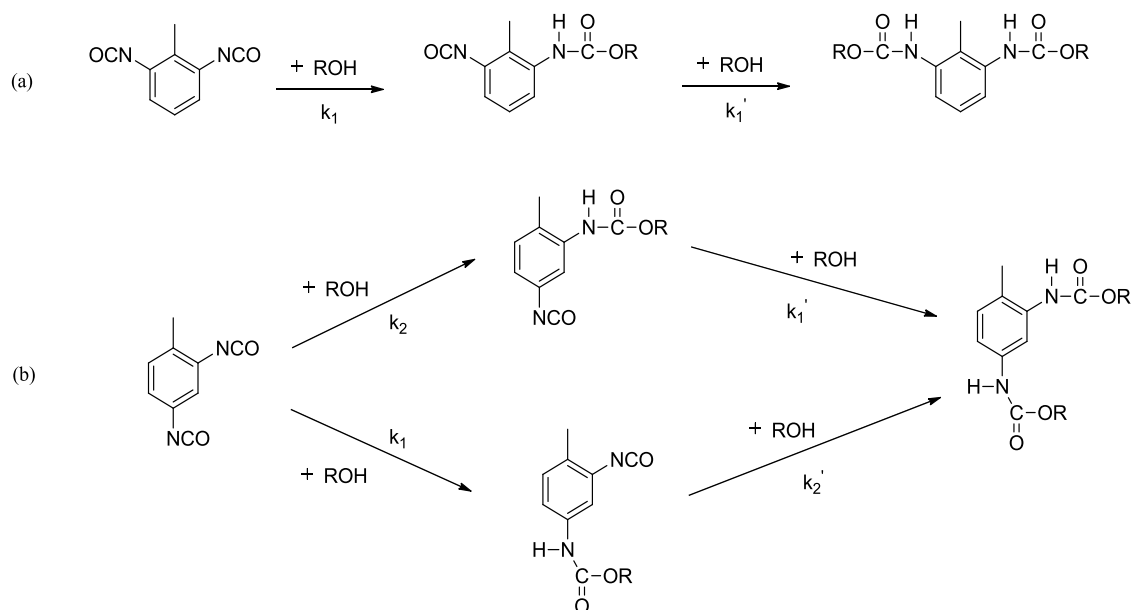


Figure-3.16: The relationship between the isocyanate symmetry and the reaction rate constants
(a) 2,6 TDI and (b) 2,4 TDI [3]

As a further evidence, reactivity ratios between isocyanate groups of 2,4- TDI reacted with two different types of alcohol are listed in Table 3.7

Table 3.7: Reactivity ratios of an asymmetric diisocyanate (2,4-TDI) against different alcohols.
(The lowest reaction rate (k_2') is taken as a reference)

diisocyanate	alcohol	$r_1 = k_1/k_2^a$	$r_2 = k_2/k_2'^b$	$r_1' = k_1'/k_2'$
2,4-TDI	n-butanol, 25°C	18.1	4.5	4.2
	Poly(propylene glycol), 60°C	15.8	2.6	2.1

^aNCO group in *para* position. ^bNCO group in *ortho* position

In this study, in order to demonstrate the dramatic difference between the reactivities of aliphatic and aromatic diisocyanates towards alcohols, reactions of PTMO1k with an aromatic and aromatic diisocyanate (bis(4-isocyanatophenyl)methane, MDI) and an aliphatic diisocyanate (bis(4-isocyanatocyclohexyl)methane, HMDI) were carried out in DMF at 25 °C. Isocyanate conversion versus time plots obtained by using FTIR and Raman spectroscopy are presented in Figure 3.17. As can clearly be seen from Figure 3.17, while the isocyanate groups in MDI are completely consumed in about 120 minutes, there is almost no noticeable change in the concentration of the isocyanate groups in HMDI. These results clearly indicate the dramatic influence of the electron withdrawing capacity of the phenylene rings in activating the isocyanate groups in MDI. These results also indicate that much higher reaction temperatures and/or a catalyst is needed in order to have reasonable reaction rates between HMDI and alcohols.

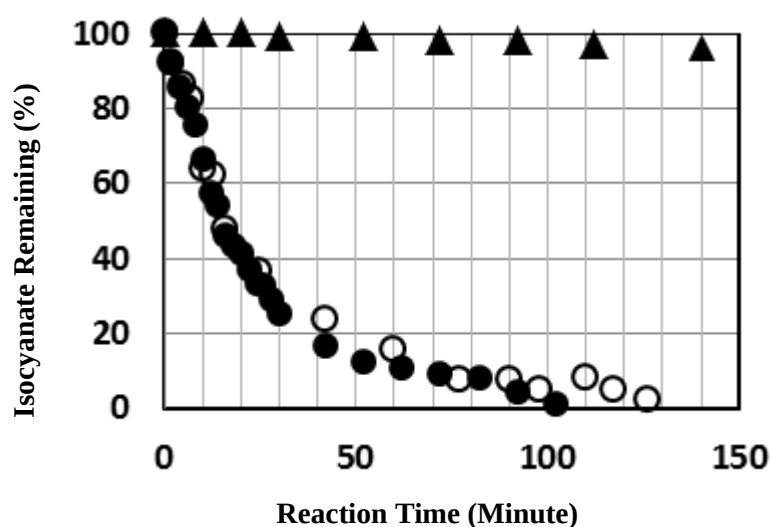


Figure-3.17: Isocyanate consumption as a function of time in stoichiometric reactions between PTMO-1000, MDI and HMDI in DMF at 25 °C; (○) MDI/PTMO by FTIR spectroscopy, (●) MDI/PTMO by Raman spectroscopy, and (▲) HMDI/PTMO by FTIR spectroscopy

3.2 Effect of reaction temperature on the extent of side reactions and isocyanate consumption in MDI-PTMO reactions

In addition to the previously discussed factors, as well known temperature also plays a critical role on both the reaction rate and also on the extent of side reactions in polyurethane synthesis. In general, for a reaction to occur, the reactants need to collide with each other. At this stage, increasing the temperature of the reactants will cause the average speed (and kinetic energy) of the molecules to increase, leading to an increase in the collision frequency. Therefore, the rates of the most chemical reactions increase as the temperature rises.

In this study, the reactions with an initial stoichiometric ratio of $[\text{MDI}]/[\text{PTMO1k}] = 1.0$ and $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ in bulk and in DMF solutions were investigated at two different temperatures, which are 22 and 50 °C. Figure 3.18 presents the results for the reactions in which the starting diisocyanate and polyol concentrations were equal. A close examination of the data provided reveals that, at temperature of 49 °C, 90% of the isocyanate was consumed in DMF within 15 minutes while this amount was only 50% at a fairly low temperature of 22°C, indicating the importance of temperature on the reaction rates. On the other hand, in the case of bulk reactions, which were also carried out at 50°C and 22.5°C, the 75% isocyanate consumptions are reached in about 70 minutes and 6 hours, respectively.

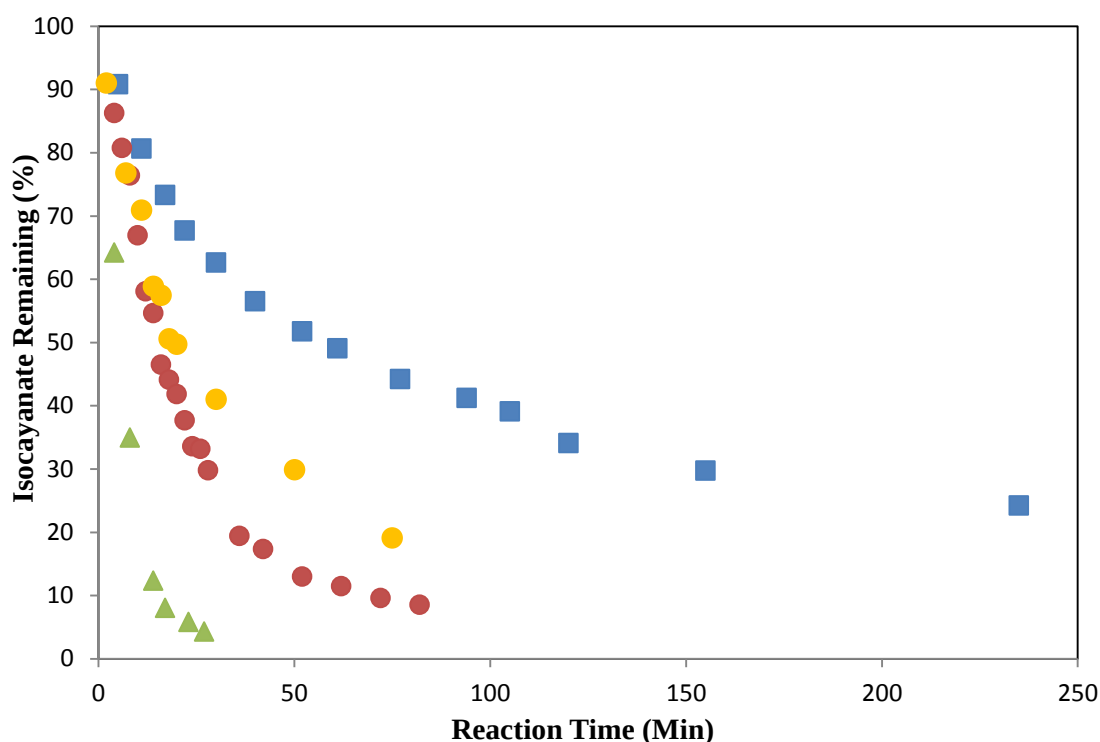


Figure-3.18: Isocyanate consumption as a function of time at different temperatures with an initial ratio of $[MDI]/[PTMO1k]=1$ (●) in DMF at 22°C (▲) in DMF at 49°C (■) Bulk at 22.5°C (●) Bulk at 50°C

Second-order plots for these reactions are provided in Figure-3.19. As previously discussed in detail in Chapter 3.1, only DMF containing systems show deviations from the second-order linearity, strongly indicating the presence of side reactions. Table 3.8 provides the rate constant values obtained from $1/C$ versus time plots. It is very interesting to note that the both k_1 and k_2 values for the reaction in DMF at 49 °C are about 1.5 times higher than that of k_1 and k_2 values at 22 °C.

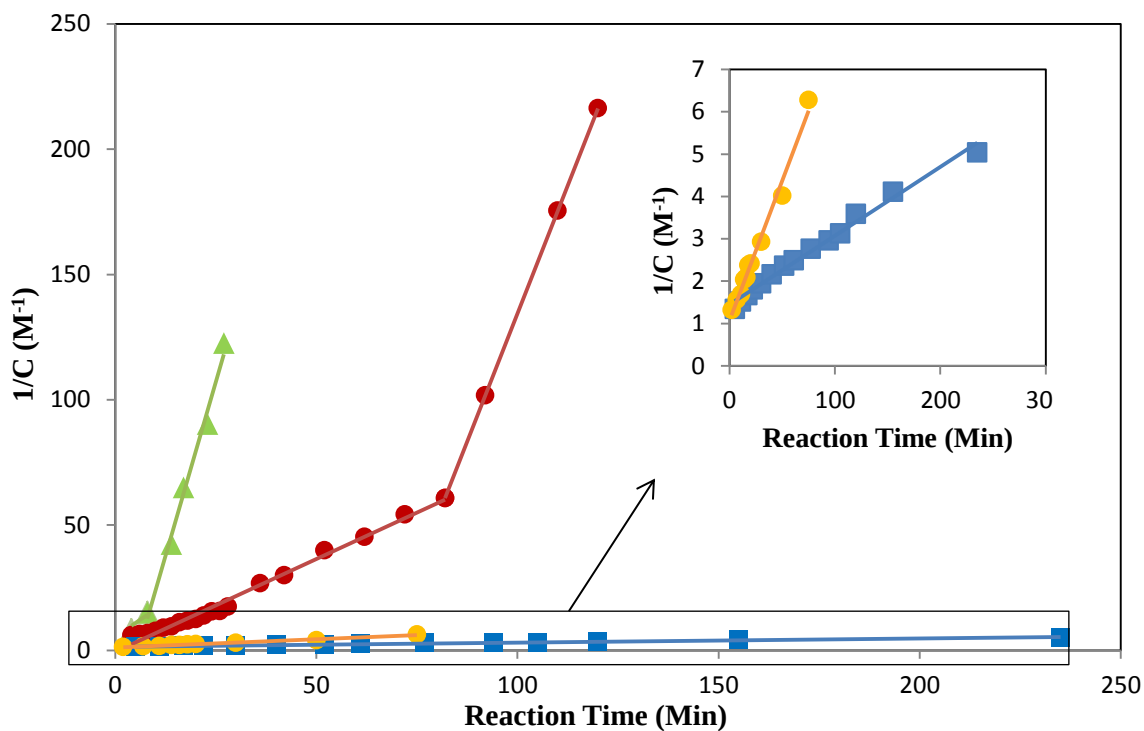


Figure-3.19: $1/C$ plots as a function of reaction time at different temperatures with an initial ratio of $[MDI]/[PTMO1k]=1$ (●) in DMF at 22°C (▲) in DMF at 49°C (■) Bulk at 22.5°C (●) Bulk at 50°C

Table-3.8: Rate constant values of the reactions at both room temperature and 50°C with an initial ratio of $[MDI]/[PTMO1k] = 1.0$

Solvent	$[MDI]_0$ (mol/L)	Temperature ($^{\circ}\text{C}$)	$k_1 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)	$k_2 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)
DMF	0.193	22	72.4	409.5
Bulk	0.833	22.5	1.8	-
DMF	0.192	49	111.7	583.9
Bulk	0.833	50	6.6	-

As shown in Figure 3.20, rates of the reactions with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ in DMF are again pretty fast. Furthermore, Figure-3.20 also shows that in DMF at 50°C , almost all excess isocyanate is consumed in about 60 minutes, whereas it takes approximately 3 hours for the reaction in DMF at 21°C to reach the complete consumption.

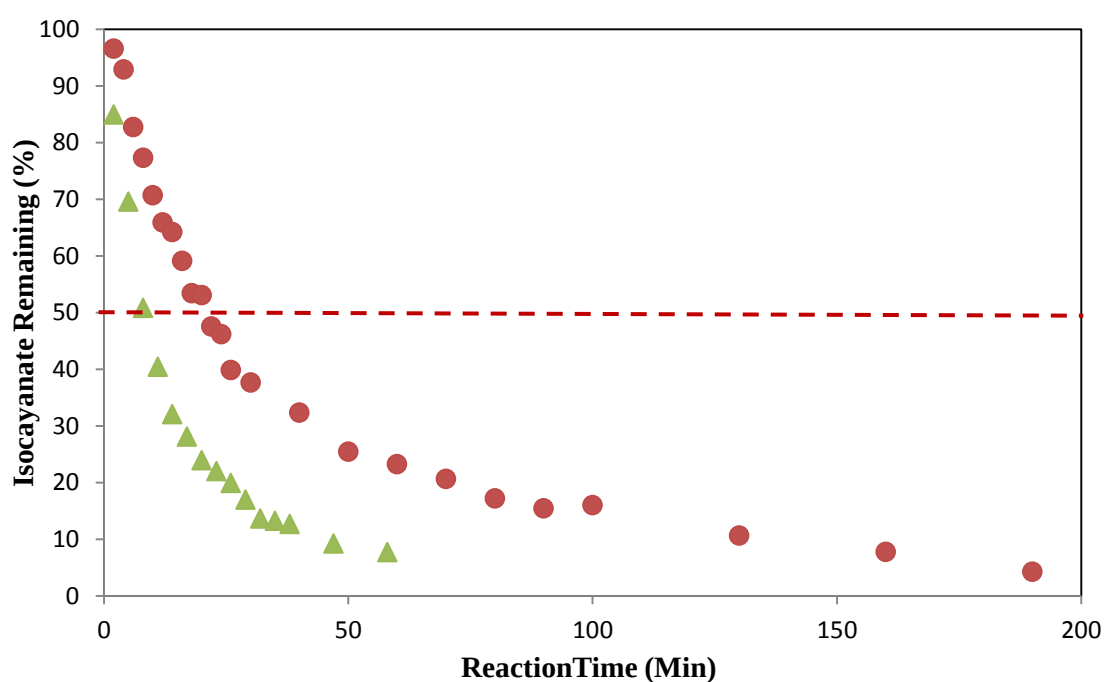


Figure-3.20: Isocyanate consumption as a function of time at different temperatures with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 2$ (●) in DMF at 21°C (▲) in DMF at 50°C

Second-order plots and the values of the rate constants are provided in Figure 3.21 and Table 3.9, respectively. As it can be seen from the table, increasing the temperature by 29°C caused the k_1 value to increase by almost 4 times.

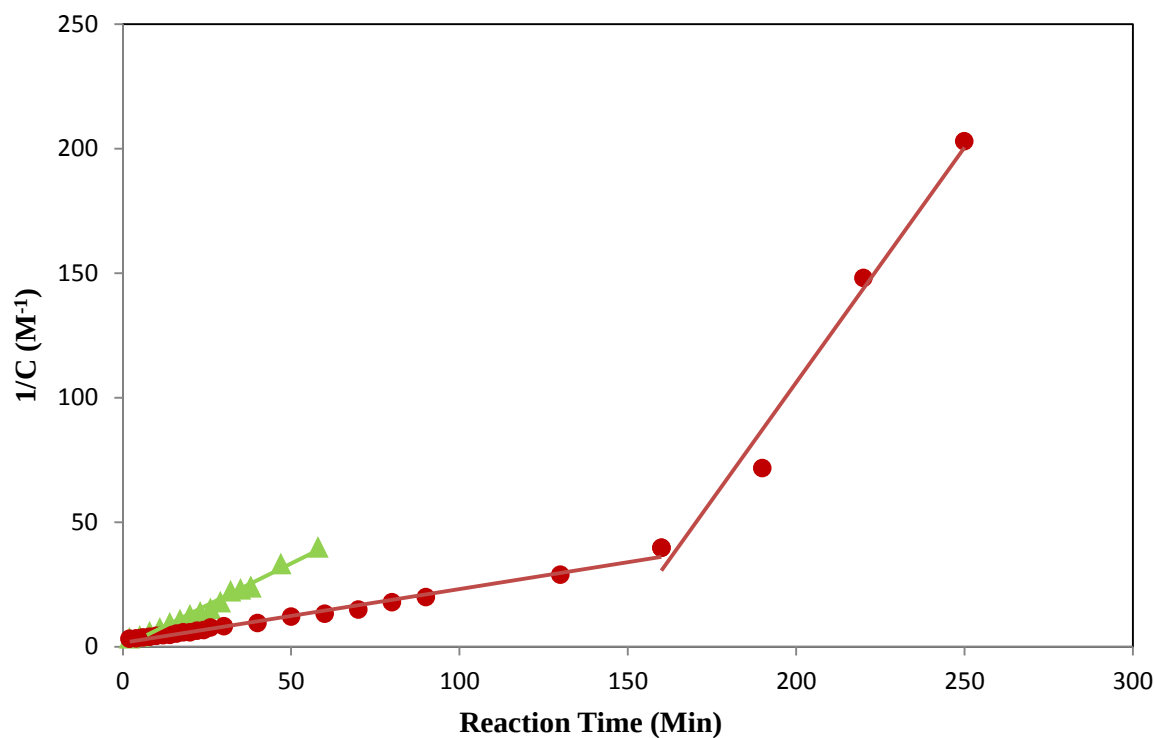


Figure-3.21: $1/C$ plots as a function of reaction time at two different temperatures with an initial ratio of $[MDI]/[PTMO1k] = 2$ (●) in DMF at 21°C (▲) in DMF at 50°C

Table-3.9: Rate constant values of the reactions at both room temperature and 50°C with an initial ratio of $[MDI]/[PTMO1k] = 2.0$

Solvent	$[MDI]_0$ (mol/L)	Temperature ($^{\circ}\text{C}$)	$k_1 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)	$k_2 \times 10^{-2}$ ($\text{L mol}^{-1}\text{min}^{-1}$)
DMF	0.325	21	17.9	188.7
DMF	0.325	50	66.5	-

Tables 3.10 and 3.11 present the literature values of the rate constant (k_1 and k_2) for the reaction between MDI and various diols and the effect of temperature. As expected, both rate constants increase with increasing temperature. These results correlate very well with our studies on the effect of temperature.

Table-3.10: Kinetic data on the reaction of MDI with 1,4-butanediol in DMF [34]

Alcohol	Temperature (°C)	Conc. OH eq/l	$k_1 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)	$k_2 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)
HO(CH ₂) ₄ OH	25.1	0.439	1.45	3.29
	40.0	0.439	3.92	6.65
	59.8	0.768	11.0	14.3

Table-3.11: Temperature effects on diisocyanate reaction rates (Reaction of 4,4'-diphenylmethane diisocyanate with glycol adipate polyester in chlorobenzene) [2]

Diisocyanate	Reaction rate constant, $10^4 k$ (liter mol ⁻¹ s ⁻¹)					
4,4'-Diphenylmethane both NCO s	30 °C	40 °C	50 °C	60 °C	70 °C	100 °C
	0.34	-	0.94	-	3.6	9.1

3.3 Effect of reaction catalyst on the extent of side reactions and isocyanate consumption in MDI-PTMO1k reactions

Polyurethane catalysts can be broadly classified into two categories; amine compounds and organometallic complexes, and among the latter the most important compounds are those of Sn, Pb and Fe. [5]

As it is well documented in the literature, the tertiary amines are the largest and most versatile class of polyurethane catalysts, among which the two of the most widely used in the industry are 1,4-diazabicyclo-[2.2.2]-octane (DABCO) and triethylamine (TEA).

[4, 5] Figure-3.22 presents the two proposed catalyzing mechanisms of tertiary amines in isocyanate-alcohol reactions. In 1947, Baker and Holdsworth [23] proposed the first of the two mechanisms (Fig-3.22a) by suggesting the formation of isocyanate-tertiary amine complex. According to their proposal, the isocyanate carbon atom is activated by Lewis acid-base coordination with the amine, and this step is then followed by a subsequent addition of O-H group across the C=N bond to form the urethane linkage and regenerate the catalyst.

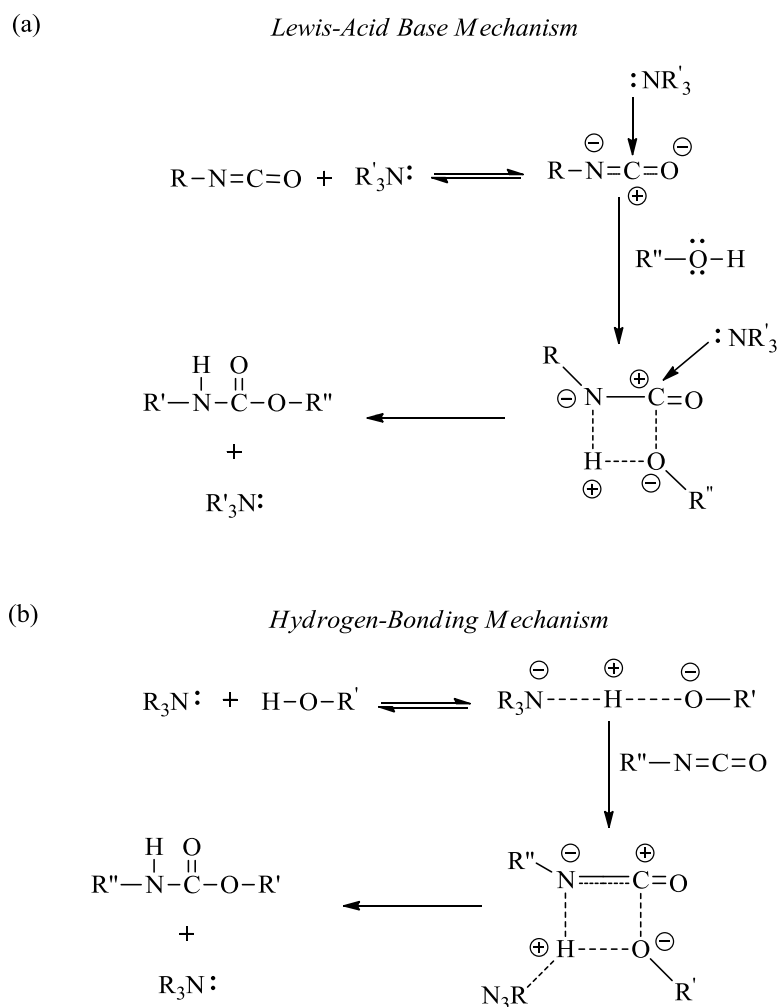


Figure-3.22: Proposed mechanisms for amine catalyzation of the NCO/OH reaction. [4]

The second mechanism (Fig-3.22b), which is proposed by Farkas and Strohm in 1965 [35], involves the formation of an amine-active hydrogen complex. In this complex, the O-H bond of the alcohol molecule is weakened and lengthened via its hydrogen bond interaction with an amine, making the oxygen atom more nucleophilic towards the N=C=O group. [4]

On the other hand, the organo-tin (Sn^{4+} and Sn^{2+}) compounds are the next largest category of urethane catalysts among all other organometallic complexes. And in terms of available commercial products, the Sn^{4+} compounds constitute the biggest class of tin catalysts, such as Dibutyltindilaurate (DBTDL, Figure-3.23), which is a very effective and extensively used catalyst in polyurethane industry. [4] The study published by Yilgor and McGrath in 1985 gives broad information on catalytic activity of dibutyltindilaurate along with other organometallic compounds used in polyurethane industry, such as $\text{Hg}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{CH}_3\text{COO})_2$. [36]

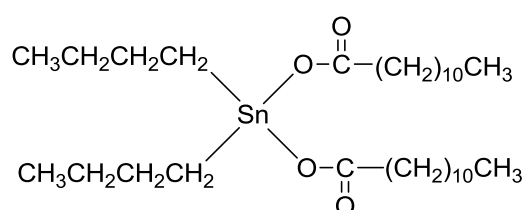
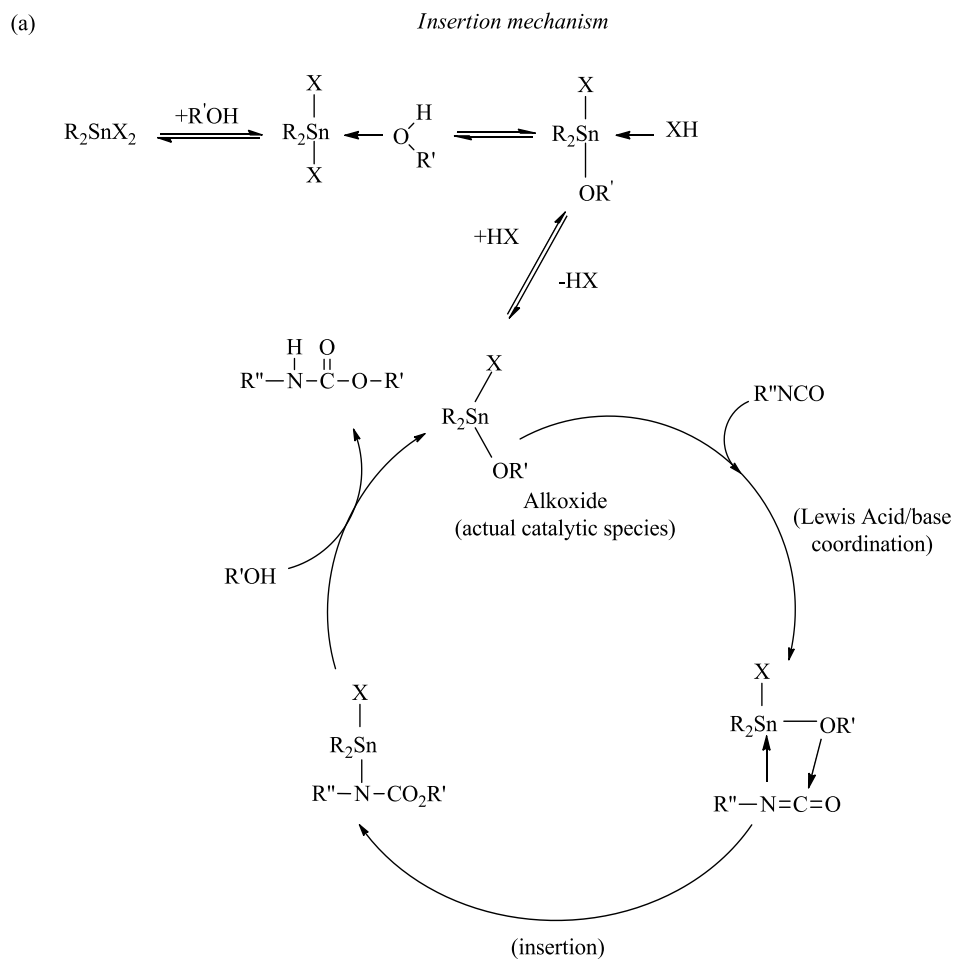


Figure-3.23: Chemical structure of Dibutyltindilaurate.

As in the case of amine catalysts, two possible mechanisms are also suggested concerning the catalyzing mechanisms of organo-tin compounds (see Figure-3.24), which are the insertion mechanism, which is proposed by Bloodworth and Davies [37] in 1963, and the Lewis Acid/Base mechanism. The first mechanism involves the formation of a tin alkoxide, $\text{R}_2\text{Sn}(\text{X})\text{OR}'$, the actual catalytic species, which are generated through the alcoholysis of the R_2SnX_2 compound. The isocyanate then coordinates to the Sn atom in $\text{R}_2\text{Sn}(\text{X})\text{OR}'$ and inserts into (as the name implies) the Sn-O bond, resulting in the carbamate formation. This step is then subsequently followed by the replacement of carbamate by incoming $\text{R}'\text{OH}$, forming and regenerating the

urethane group and alkoxide, respectively. The latter mechanism (Figure-3.24b) suggests Lewis acid-base coordination of the isocyanate group to the tin atom, which in turn polarizes the NCO group and renders the carbon atom (by creating a positive charge on the carbon atom) more susceptible towards nucleophilic attacks by alcohol.



(b) *Lewis Acid/Base Mechanism*

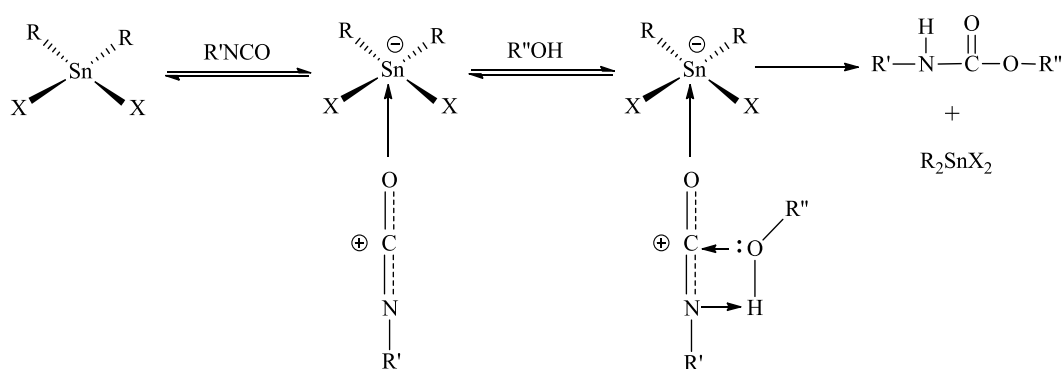


Figure-3.24: Proposed mechanisms for catalysis of isocyanate/ alcohol reactions by organo-tin compounds. [3, 4]

In our study, in order to see the effects of a reaction catalyst on the extent of side reactions, triethylamine (TEA) is used as a catalyst along with a solvent, such as THF, that has no catalyzing effect in isocyanate/alcohol reactions. The results are presented in Figure-3.25.

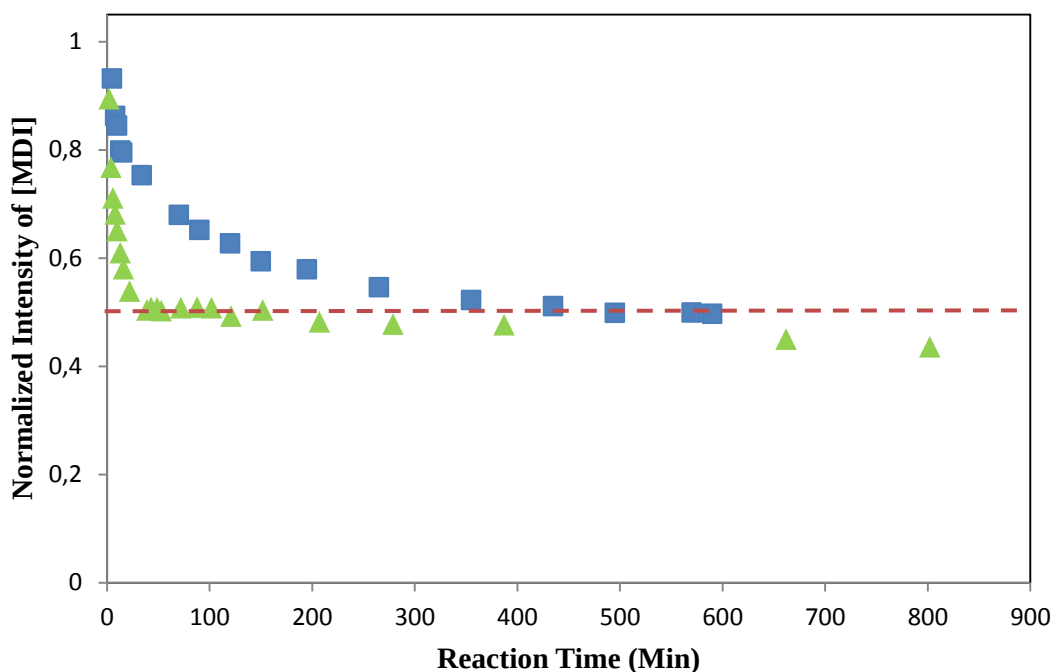


Figure-3.25: Isocyanate consumption as a function of time at 50°C in THF with an initial ratio of $[\text{MDI}]/[\text{PTMO1k}] = 2.0$ (■) $0.1/99.9 = \text{TEA/THF}$ (by weight) (▲) $1/99 = \text{TEA/THF}$ (by weight)

In these reactions TEA/THF mixtures with weight ratios of 0.1/99.9 and 1/99 were utilized and two-fold molar excess of isocyanate to PTMO1k were employed. Reactions were carried out at 50°C and overall concentrations of the solutions were 25% solids by weight. Fig-3.25 shows the change in the isocyanate content of the mixture throughout the reaction as a function of time and concentration of the catalyst. In contrast to the results that were presented previously, both plots level off around 50%, indicating no side reactions or excess isocyanate consumption.

In the case of low catalyst concentration, the isocyanate consumption reached to the theoretical complete reaction line of 50% conversion in about 6 hours and showed no change for the following 3 hours, indicating no excess isocyanate consumption. However, as the concentration of catalyst is increased by tenfold, the amount of time that is required for the plot to reach the theoretical 50% line is reduced dramatically and took only 40 minutes. There were no clear signs of side reactions for this system also for the following 6 hours.

Second-order plots for these reactions are provided in Figure 3.26 and the values of rate constants are listed in Table-3.12. As can be seen in Table-3.12, a 10 fold increase in TEA amount causes the reaction constant to increase by almost 8 times.

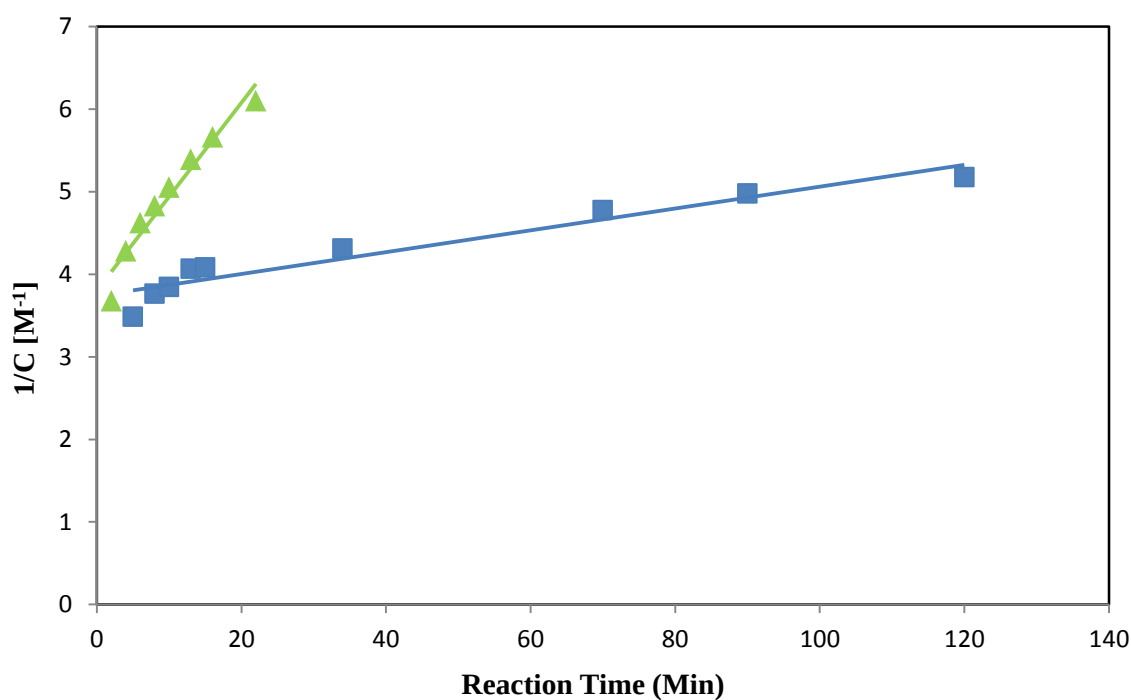


Figure-3.26: 1/C plots as a function of reaction time at 50°C in THF with an initial ratio of [MDI]/[PTMO1k] = 2.0 (■) 0.1/99.9 = TEA/THF (by weight) (▲) 1/99 = TEA/THF (by weight)

Table-3.12: Rate constant values of the reactions at 50°C in THF with an initial ratio of [MDI]/[PTMO1k] = 2.0

Solvent	TEA/THF ratio (by weight)	$k_1 \times 10^{-2}$ (L mol ⁻¹ min ⁻¹)
THF	0.1/99.9	1.9
THF	1/99	15.1

The catalytic activity of DMF and the way it promotes the side reactions were previously discussed in detail. As a further evidence, the comparison made in the Figure-3.27 clearly presents how the catalytic activity of DMF differs dramatically from a tertiary-amine catalyst. As presented in Figure-3.27, although the isocyanate consumption rates are found to be quite similar at the very beginning of both reactions, the isocyanate consumption rate increases tremendously in the case of DMF/THF mixture (in comparison to 0.1/ 99.9 = TEA/THF). However, this increase in the reaction rate led to excess isocyanate consumption, which was about 10%, while no significant side reaction is observed for the tertiary-amine catalyst.

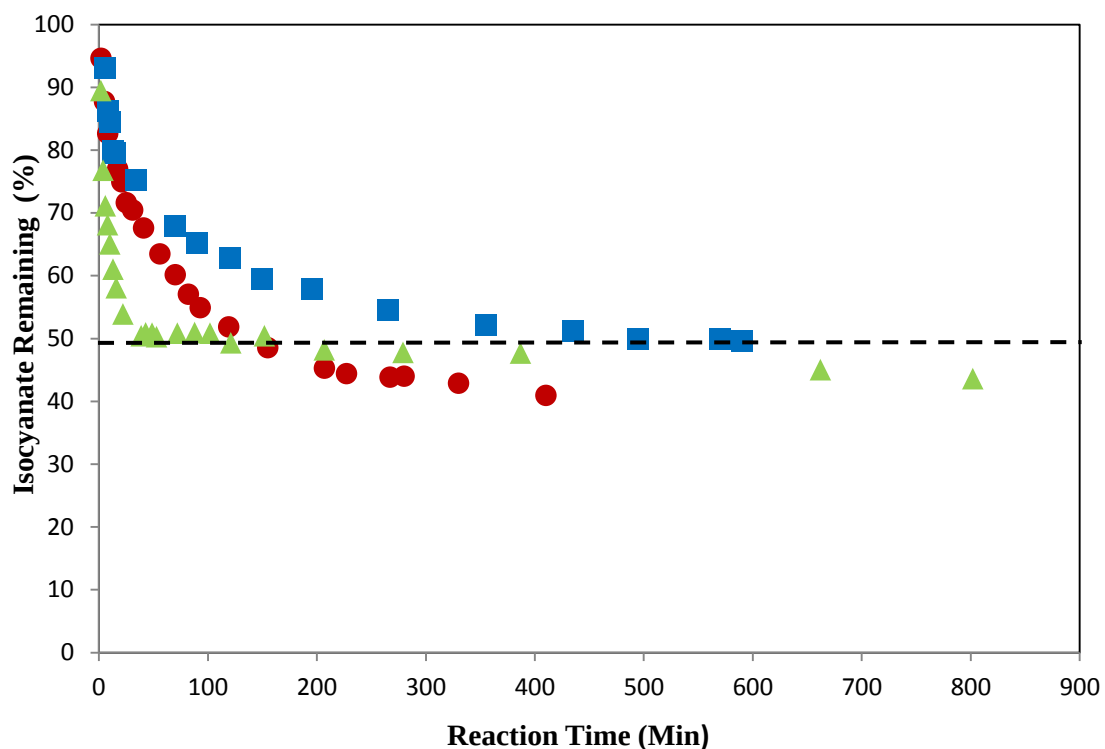


Figure-3.27: Isocyanate consumption as a function of time at 50°C in THF with an initial ratio of [MDI]/[PTMO1k] = 2 (■) 0.1/99.9 = TEA/THF (by weight) (▲) 1/99 = TEA/THF (by weight) (●) 10/90 = DMF/THF (by weight)

These results and the discussion above, in terms of both catalyst type and the amount used, clearly point out the importance of the catalyst selection on the extent of side reactions in polyurethane synthesis.

However, examples that are listed below taken from various journals clearly show how the previously discussed critical parameters (e.g., solvent, catalyst, temperature etc.) were overlooked in the preparation of MDI based polyurethanes. According to the results of our study, the polymer synthesis techniques shown below (and published in fairly prestigious journals) are likely to promote substantial side reactions, which

inevitably will effect the morphology of the resulting polymer and its thermal and mechanical properties as well. Here are some of those examples:

“The PUEs were prepared by a *bulk prepolymer method*. The PTMG were dried with dried nitrogen under a reduced pressure. Prepolymers were prepared from PTMG and MDI with the ratio of $[NCO]/[OH]=3.3$ and 5.3 at $80\text{ }^{\circ}\text{C}$ for 3 hours under nitrogen atmosphere.” [38]

“PTMO (3 wt %) was dissolved in *DMAc* and stirred in a flask while MDI was added to the solution. These two reactants were heated to $80\text{ }^{\circ}\text{C}$ and held there for 2 hours.” [39]

“Polyurethane was synthesized from its monomer, MDI and PTMO by a two-step process, using BD as a chain extender. First, the pre-polymer was prepared from a reaction of 5.005 g of MDI in 40 mL of DMF and 10 g of PTMO in 20 mL of DMF in a 500-mL four-neck cylindrical vessel heated to $60\text{ }^{\circ}\text{C}$ for 90 min with mechanical stirring under a nitrogen atmosphere. Subsequently, 0.92 g of BD in 10 mL DMF was added slowly to the prepolymer at $110\text{ }^{\circ}\text{C}$ over 240 min and the mixture allowed to react fully.” [40]

“PTMO dissolved in DMF was charged into a 250-mL dry four-neck round-bottom flask equipped with thermometer, reflux condenser, dropping funnel, and drying tube, followed by stoichiometric amounts of *MDI solution in DMF and a drop of stannous octoate* $[Sn(Oct)_2]$ as catalyst. The reaction system was stirred by magnetic stirring for 3 h in an oil bath at 70°C under dry N_2 atmosphere to obtain the –NCO-terminated prepolymers.” [41]

“PTMO (5 wt%) was dissolved in DMF and stirred in a flask while freshly distilled MDI was added to the solution. These two reactants were heated to $80\text{ }^{\circ}\text{C}$ and remained at this temperature for 2 h .” [42]

“TPU was prepared by a solution polymerization technique in N,N-dimethylformamide. Poly(tetramethylene ether glycol) was reacted with various amounts of 4,4'-diphenylmethane at 60 °C for 90 min to prepare prepolymer with terminal NCO groups. The prepolymer was chain-extended in DMF by adding 1,4-butanediol and *additional MDI* at 60 °C for 120 min. ” [43]

“Polyurethane was synthesised via a two-step, solution polymerization of PTMO, MDI and chain extended with BD. This was carried out in a three-neck flask equipped with a stirrer, a nitrogen inlet and a condenser guarded by a calcium chloride drying tube. The reaction was carried out at molar ratios of (PTMO: MDI: BD) 1:2:1. The temperature of the reaction in the first step was 50 °C whilst all soft segments were dissolved in the DMF. *MDI dissolved in DMF* was then added drop-wise to the reactor. *The temperature was increased to 80 °C and kept for 1 hour to form the prepolymer.* The prepolymer was then chain extended using BD at 120 °C for four hours.” [44]

“A three-step procedure was used. In the first step, isocyanate terminated prepolymers were synthesized by reacting *PTMO with an excess of MDI at 50 °C for 1.5 h* under nitrogen atmosphere. In the second step, dibutyltin dilaurate was added to the prepolymers as a catalyst. A chain extension reaction of the prepolymers was subsequently carried out by dropping BD and MDEA dissolved in DMF. The reaction temperature was slowly raised to 80 °C for 2 h with stirring.” [45]

“One mole of degassed PTMO and 2 moles of melted MDI were added to a four-necked flask equipped with a mechanical stirrer. *After 3–4 h under N₂ stirring at 65 – 70°C*, a white fluid PU prepolymer was obtained.” [46]

“A flask equipped with a mechanical stirrer and an inert gas bubbler was charged with dehydrated PTMO and MDI in a mole ratio of 1:2. *The mixture was stirred at 65 °C under N₂ for 4 h to yield the prepolymer 2, diisocyanate capped urethane.*” [47]

CHAPTER 4

CONCLUSIONS

In order to understand the effects of various reaction parameters on rate of isocyanate consumption and the extent of side reactions, a series of reactions between MDI and various polyol oligomers (i.e. PTMO, PEO and PPO) were carried out. Effects of the reaction solvent, diisocyanate and polyol structure, concentration, temperature and catalyst were investigated.

When compared with the bulk and as well as other solvent systems (e.g., Toluene, THF), the reactions carried out in DMF solutions were significantly faster. Moreover, very interestingly, this increase in the rate of the reactions was linearly correlated with the amount of DMF used as a co-solvent in multi-solvent systems. These results clearly indicate the dramatic catalytic activity of DMF in polyurethane formation reactions when an aromatic diisocyanate, such as MDI is used. Additionally, values of the rate constants obtained from the second-order plots were also used to calculate the rate constant values of the reactions. As expected, in the case of DMF containing systems, strong deviations from second-order linearity were observed, suggesting the consumption of excess isocyanate during side reactions. Furthermore, very similar results obtained from both FTIR and Raman spectrometers also demonstrated the reliability of the techniques utilized during the study.

In order to understand the effect of polyol structure on the extent of isocyanate consumption rates, reactions of MDI with PTMO, PEO and PPO (initial stoichiometric ratios of $[MDI]/[Polyol] = 1.0$) were performed. As expected, no effect of oligomer structure on the rate of the reactions was observed. On the other hand, in the case of different diisocyanate structures (i.e. MDI and HMDI), as expected, the rate of the

reaction of aromatic diisocyanate, MDI, was much greater than its aliphatic analogue, HMDI. This great difference in reactivity towards alcohol molecules mainly stems from the electron withdrawing capability of the phenylene rings present in MDI. These results clearly indicate the dramatic influence of isocyanate selection during polyurethane formation reactions. On the other hand, these results also suggest that much higher reaction temperatures and/or catalyst is needed in order to achieve noticeable reaction rates between HMDI and alcohols.

The results presented above clearly demonstrate the importance of optimizing the reaction conditions during MDI based prepolymer formation in order to reduce the undesired side reactions and keep the excess isocyanate consumption at a minimum level. Although it is suggested by many articles on polyurethane synthesis that using about 10% excess MDI would be enough to compensate the side reactions, it is clearly evident from our study that this amount is not sufficient, especially if the reactions are conducted in DMF at high temperatures (such as 50-80 °C range) for long periods.

In order to understand the difference between the catalytic activities of DMF and the TEA (a widely used catalyst in polyurethane formation reactions), a series of reactions involving THF solvent and DMF and TEA as catalyst were performed. From these results we observed that, when DMF (10%) is used as a co-solvent with THF, significant amount of side reaction was observed within 3 hours, whereas the mixture containing 0.1% TEA catalyst did not result in excess isocyanate consumption.

To conclude, in order to calculate the exact amount of excessively consumed isocyanate and thus to determine the amount of chain extender to be used, one should first precisely determine the isocyanate content of the prepolymer by back titration prior to chain extension step. However, examples provided from various published studies as discussed above clearly demonstrated that most researchers do not seem to be aware of these critical phenomena during polyurethane synthesis reactions.

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VITA

Armen Yıldırım was born in Istanbul, Turkey in 1989. He received his B.S. degree from Department of Chemistry, Marmara University in 2012. He received the Erasmus Programme scholarship and visited the Nottingham Trent University, UK as an exchange student for two semesters in his senior year. In Fall 2013, he started his M.S degree in Materials Science & Engineering Program at Koc University. He will continue his academic career in Polymer Engineering PhD program at University of Akron, USA.