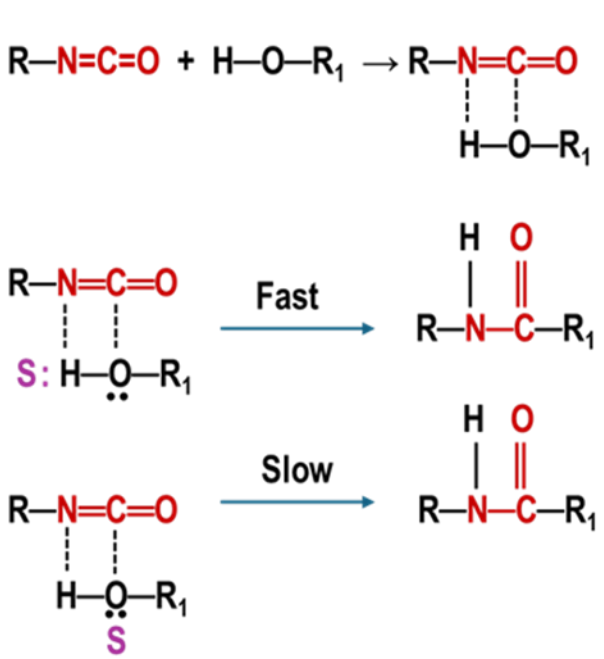
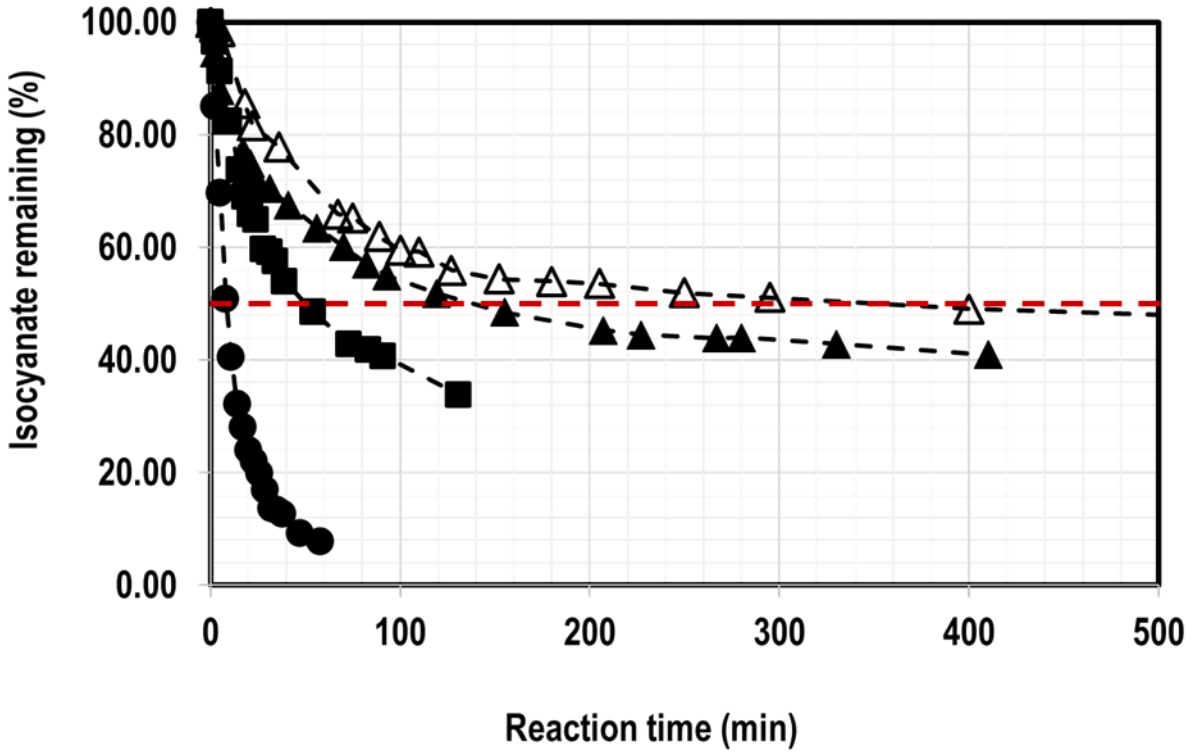
Graphical Abstract





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Polyurethane synthesis revisited: Effect of solvent, stoichiometry, and temperature on the reaction of MDI with polyether glycols

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Abstract

Thermoplastic polyurethanes (TPU) are one of the most widely investigated polymeric systems due to their interesting structure-morphology-property behavior. They also find broad range of applications in various fields. Global TPU market is projected to grow about 7.3% annually from $2.30 billion in 2021 to $3.80 billion in 2028. 4,4'-Diphenylmethane diisocyanate (MDI) is the most widely used diisocyanate for the preparation of TPUs both in academia and industry. When TPU synthesis is carried out in solution, a polar aprotic solvent is necessary to obtain high molecular weight polymers. Most preferred solvents for TPU synthesis are high boiling, polar, aprotic solvents, such as dimethylacetamide (DMAC), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP). When MDI is used as the diisocyanate, depending on the solvent used and reaction temperature, extensive side reactions may be observed, which consume excess diisocyanate and affect reaction stoichiometry. Side reactions strongly influence TPU structure, topology, microphase morphology, and properties. In this study influence of the solvent, initial [NCO]/[OH] stoichiometry and reaction temperature on the rate of isocyanate consumption and kinetics of the reactions between MDI and poly(tetramethylene oxide)glycol (PTMO) were investigated. Strong catalytic effect of DMF even at reactions conducted at room temperature were observed, resulting in significant excess MDI consumption due extensive side reactions. During prepolymer formation in [MDI]/[PTMO]=2.0 system at 50 °C, side reactions were minimized or eliminated by using THF/DMF or toluene/DMF (90/10) solvent mixtures.

Keywords: Polyurethane reaction kinetics; MDI; dimethylformamide; TPU; polyol

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1. Introduction

Thermoplastic segmented polyurethanes (TPU) are composed of alternating hard (HS) and soft (SS) segments covalently linked together by urethane bonds along a linear macromolecular backbone, as schematically shown in Figure 1. Depending on the type and nature of the HS and SS and polymer composition, TPUs display unique combination of microphase morphologies and bulk and surface properties [1-9]. As a result, TPUs are one of the most widely investigated multiphase polymeric systems by both academic and industrial scientists since their discovery of about 60 years ago [1]. Furthermore, availability of a very large selection of commercially available raw materials makes TPUs one of the most widely produced polymeric materials globally [2-9].

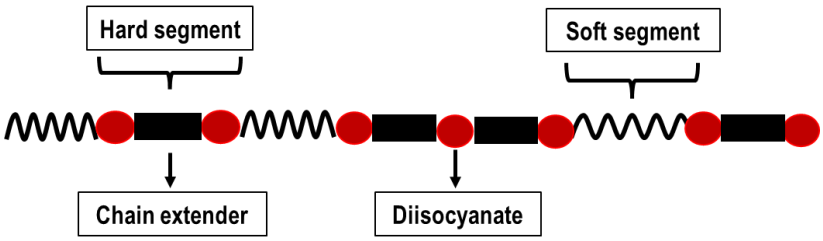


Figure 1. Schematic representation of the chemical structure of a linear, segmented TPU.

Urethane linkages are formed by the addition of alcohols to isocyanates through a mechanism suggested in Figure 2 for bulk reaction [6], where nucleophilic oxygen on alcohol attacks to the electrophilic carbon on the isocyanate group, leading to the formation of an ionic intermediate, which has a resonance structure shown in the brackets. (N-) group on the resonance structure abstracts the proton from the alcohol and generates the urethane group.

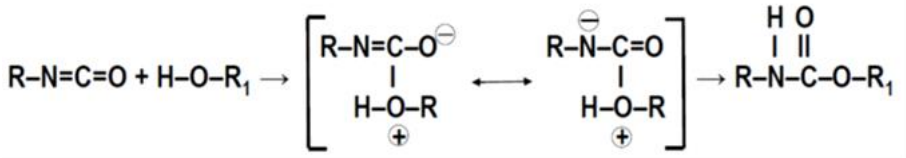


Figure 2. Isocyanate-alcohol reaction leading to the formation of the urethane linkage in bulk

In the presence of a solvent reaction mechanism and kinetics change depending on the polarity, hydrogen bonding capacity and solvation power of the solvent. According to a mechanism shown in Figure 3 for a model study between phenyl isocyanate and butanol [10], alcohol and isocyanate form a hydrogen bonded complex in bulk (Figure 3a). In the presence of a solvent

isocyanate-alcohol complex is solvated by the interaction of alcohol with the solvent (S) molecule. If the interaction is between alcoholic hydrogen and the solvent (e. g. through hydrogen bonding), as in the case of dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) or dimethylsulfoxide (DMSO), a solvated ion-pair is produced (Figure 3b), where the oxygen atom on alcohol becomes more nucleophilic and attacks to the electrophilic carbon more readily, resulting in an increase in reaction rate, which indicates catalytic activity of the solvent (6, 10). If the interaction is between the oxygen of the alcohol and the solvent (Figure 3c) then oxygen becomes less nucleophilic, leading to a reduction in reaction rate. If the solvent does not interact with the alcohol through hydrogen bonding, such as in cyclohexane or toluene, reaction rate is not influenced.

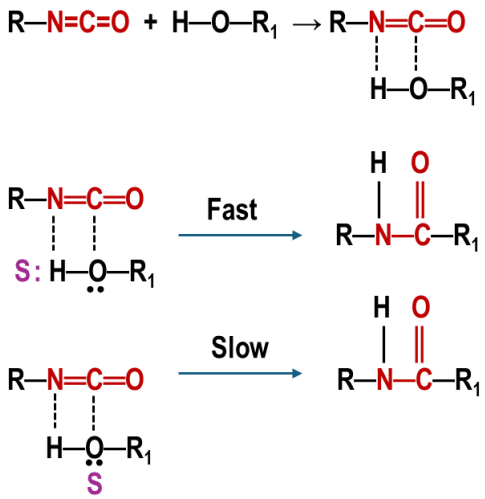


Figure 3. Proposed mechanisms for the interaction of solvent molecules with alcohol, strongly affecting the reaction rate, during the formation of urethane linkages in solution [10].

In addition to the formation of urethane linkages, during polymerization reactions, as shown in Figure 4, N─H group on the urethane can also react with the diisocyanate to form an allophanate group [11-13] and furthermore, allophanate N─H can further react with the diisocyanate to from biuret groups [11-15]. Extent of allophanate and biuret side reactions depend on the type of the diisocyanate (aromatic or aliphatic), reaction temperature and the catalyst (type and amount) used [3, 6, 10-17]. Allophanate and biuret formation reactions consume excess diisocyanate and upset the reaction stoichiometry. It is also important to note that while the urethane reaction leads to the formation of linear polymers, allophanate and biuret reactions lead to the formation of branched and crosslinked polymers, respectively.

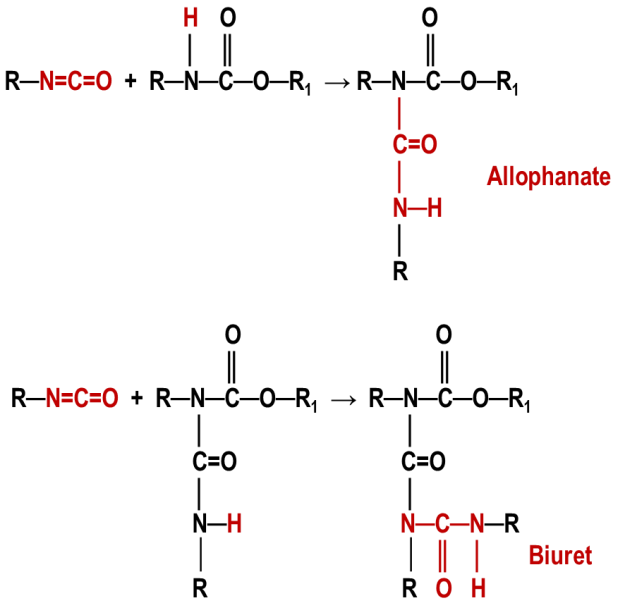


Figure 4. Side reactions of urethane groups with isocyanates producing allophanate and biuret groups.

Side reactions consume excess amount of diisocyanate and upset the reaction stoichiometry. This leads to the formation of poorly defined TPU structures. Unfortunately, during the TPU synthesis this point is usually overlooked, most probably since most of the fundamental studies on polyurethane formation reactions and kinetics were performed between 1960s and 1980s [3, 6, 16, 17]. To compensate the side reactions usually about 5% excess of diisocyanate is added to the initial reaction mixture. However, depending on the reaction conditions, as shown in this study, much more diisocyanate may be needed. To have a good control over the chain extension reaction, isocyanate content of the prepolymer must be determined by dibutylamine back titration method [18] and the stoichiometric amount of the chain extender must be calculated accordingly. Otherwise poorly defined TPU structures will be produced, which is unfortunately the case in many published studies. Several excellent review articles providing a broad overview of the kinetic analysis of polyurethane formation reactions are available, where effect of the diisocyanate structure, reaction temperature, reaction time and catalysts on urethane formation and on the extent of possible side reactions are discussed [2, 3, 6].

One of the critical factors that has a strong influence on the backbone structure and especially on the macromolecular architecture or topology of a TPU is the synthetic procedure followed, and the reaction conditions employed. There are two main methods for the preparation of TPUs.

First method is a one-step or "one-shot" procedure, where all ingredients (polyol, diisocyanate, diol chain extender and catalyst) are all mixed and reacted in a constant temperature oven at desired temperature. Second method is a two-step procedure, called "prepolymer method", where in the first step the polyol is reacted with excess diisocyanate to prepare an isocyanate terminated prepolymer, which in the second step is chain extended with stoichiometric amount of a diol or diamine to produce a high molecular weight TPU. Prepolymer method, which can be carried out in solution or in bulk in a twin-screw extruder, provides better control on the formation of hard segments compared to the one-shot method, which leads to a more random structure.

Reaction of a diisocyanate and a diol follows second order kinetics as shown in Eq. 1, where *k* is the rate constant [10, 17, 19, 20].

$$\frac{-\mathrm{d}[\mathrm{R_1NCO}]}{\mathrm{d}t} = k.[\mathrm{R_1\,NCO}][\mathrm{R_2OH}] \qquad (1)$$

However, when allophanate formation reactions take place, a deviation from second order to third order reaction kinetics is observed as shown in Eq. 2 [6, 16, 17].

$$\frac{-\mathrm{d}[\mathrm{R_1NCO}]}{\mathrm{dt}} = k.[\mathrm{R_1NCO}][\mathrm{R_2OH}][\mathrm{R_1NHCOOR_2}] \qquad (2)$$

Allophanate formation reactions are especially favored at high conversions and temperatures above 60 °C for aromatic diisocyanates or for aliphatic diisocyanates in the presence of catalysts [2, 16, 17]. Influence of biuret formation on reaction kinetics is usually neglected since extent of these reactions is limited. When equimolar concentrations [C] of diisocyanate and the diol is used, Eq. 1 becomes:

$$\frac{-\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k.[\mathrm{C}]^2 \qquad (3)$$

After integration the rate equation can be written as shown in Eq. 4:

$$\frac{1}{[\mathrm{C}]_t} - \frac{1}{[\mathrm{C}]_o} = kt \qquad (4)$$

Where $[C]_o$ is the initial concentration of isocyanate and $[C]_t$ is the concentration at time *t*. According to Eq. 4, if no side reactions take place in MDI-Polyol reactions, one would obtain a straight line when $(1/[C]_t - 1[C]_o)$ is plotted against time (*t*). Slope of this line will give the rate constant (*k*). Side reactions, which consume excess isocyanate leads to deviation from second order kinetics and instead of a straight line, a curve is obtained in $(1/[C]_t - 1[C]_o)$ versus (*t*) plots.

Furthermore, as already mentioned, allophanate and biuret formation reactions will affect the polymer topology or macromolecular architecture by leading to the formation of branched and even covalently crosslinked materials. This in turn will strongly influence the nature of the hydrogen bonding, microphase separation, TPU morphology, and TPU properties [2].

Main aim of this study was the investigation of the effect of dimethylformamide (DMF) as solvent or cosolvent, on the reaction kinetics between 4,4'-diphenylmethane diisocyanate (MDI) and poly(tetramethylene oxide)glycol (PTMO) with M_n=1000 g/mol. Effect of initial reaction stoichiometry [NCO]/[OH] (1/1 or 2/1), and temperature on reaction kinetics were investigated. Dimethylacetamide (DMAC), toluene and tetrahydrofuran (THF) were also used as reaction solvent for comparison, as well as bulk reactions as the control. Influence of the structure of the polyether glycol oligomers were also investigated.

2. Experimental

2.1. Materials

4,4'-Diphenylmethanediisocyanate (MDI) with purity better than 99.5%, as determined by dibutylamine back titration method [18] was kindly provided by Covestro, Germany. Primary hydroxyl terminated poly(propylene oxide)glycol (M_n = 1020 g/mol) (Acclaim PPG), poly(tetramethylene oxide)glycol (M_n = 985 g/mol) (PTMO) and poly(ethylene oxide)glycol (M_n = 1050 g/mol) (PEO) oligomers were supplied by Covestro, Du Pont and BP respectively. All oligomers were dried in vacuum oven at 60 °C for 24 hours before use. Reagent grade dimethylformamide (DMF), dimethylacetamide (DMAC), toluene, tetrahydrofuran (THF) and triethylamine (TEA) were obtained from Aldrich. All solvents were dried over molecular sieves before use and their water contents were determined to be lower than 300 ppm by Karl-Fisher titration using Mettler Toledo Titrator Compact V10S.

2.2. Polymerization reactions and characterization methods

Reactions were carried out in 100 mL, 3-neck round bottom Pyrex flasks equipped with an overhead stirrer, nitrogen inlet and a thermometer. Calculated amounts of MDI, polyol (PTMO, PEO or PPG) and solvent were weighed into the reaction flask and reactions were carried out under continuous stirring (150 rpm) at desired temperature. In solution reactions solids content of the reaction mixtures were kept constant at 25.0±0.5% by weight. Samples were taken at regular intervals from the reaction mixture, thin films were cast onto KBr pellets and flash-dried with a heat gun. Reactions were followed by monitoring the change in the strong

isocyanate absorption peak centered at 2270 cm^{-1} using a ThermoScientific Nicolet 6700 FTIR spectrometer, with a resolution of 4 cm^{-1}. For kinetic analysis all FTIR spectra were normalized with respect to an internal standard. For this purpose intensity of the aliphatic C-H stretching peak in polyols at 2850 cm^{-1} was used, since concentration of polyols remained constant throughout the reactions. FTIR spectra obtained for stoichiometric MDI-PTMO reactions in DMF at 23.0±0.5 °C, at the beginning, at an intermediate state and at the completion of the reactions are reproduced in Figure 5.

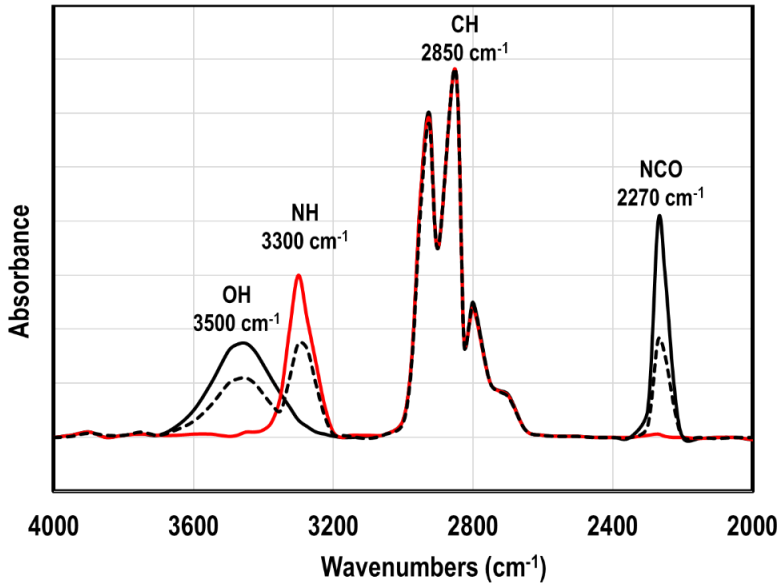


Figure 5. Infrared spectra of stoichiometric MDI-PTMO reaction in DMF at 23.0±0.5 °C at various stages. t=0 (—), t=60 min (---), t=180 min (—).

3. Results and Discussion

Segmented thermoplastic polyurethanes (TPU) are one of the most popular material systems investigated for the last 60 years, due to their composition and morphology dependent properties ranging from strong plastics to soft elastomers. Synthesis of TPUs seems fairly simple, where diisocyanates, polyols and diol chain extenders are reacted by using the so called "one-shot" or "prepolymer" methods. MDI is the most widely utilized diisocyanate for TPU production. Electron withdrawing ability of the phenylene rings increases the electropositivity of the carbon on the isocyanate (─N=C=O) group. Therefore, aromatic diisocyanates are much more reactive towards alcohols when compared with their aliphatic homologs [2]. When the TPU synthesis is carried out in solution, chemical structure and polarity of the solvent used play critical roles in determining the solubility and molecular weight of the product formed. Furthermore, the solvent used may also affect the reaction rate and the extent of side reactions,

which in turn influence the macromolecular architecture (topology), microphase morphology and properties of the polyurethanes formed.

In this study our main goal was the investigation of the influence of the reaction solvent, especially the DMF on the reaction between MDI and PTMO (M_n=1000 g/mol), Reactions were conducted at two different initial stoichiometric ratios of [MDI]/[PTMO]=1.0 and [MDI]/[PTMO]=2.0 (to mimic the "one shot" and "prepolymer" methods) and at two different reaction temperatures of 23.0±0.5 (room temperature) and 50.0±0.5 °C. MDI-PTMO reactions were first conducted in bulk as control reactions. To understand the effect of solvent reactions were also carried out in DMF, DMAC, toluene, THF and toluene/DMF mixtures with different compositions. Stoichiometric reactions can be considered as model one-shot reactions [19, 21]. However, TPU synthesis is usually carried out with excess MDI following the prepolymer method, to enable controlled chain extension, which is the reason why reactions with [MDI]/[PTMO]=2.0 were also investigated [2-9].

3.1. Comparison of the kinetics of stoichiometric [MDI]/[PTMO]=1.0 reactions in bulk and in DMF solution

Plots of the isocyanate consumption as a function of time for [MDI]/[PTMO]=1.0 reactions carried out at 23.0±0.5 °C and 50.0±0.5 °C in bulk and in DMF solution (25 wt% solids) are reproduced in Figure 6.

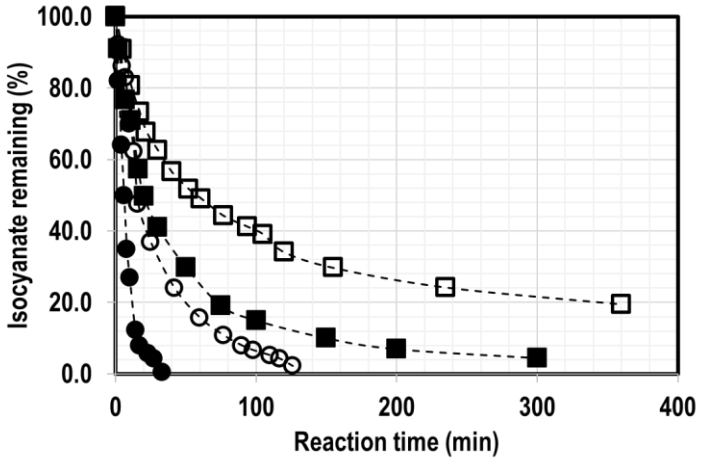


Figure 6. Isocyanate consumption as a function of time for stoichiometric MDI-PTMO1k reactions in bulk and in DMF solution. (□) Bulk at 23.0±0.5 °C, (■) Bulk at 50.0±0.5 °C, (o) DMF at 23.0±0.5 °C, and (●) DMF at 50.0±0.5 °C.

Isocyanate conversion versus time curves provided in Figure 6, clearly show that isocyanate consumption rates in DMF solution is much faster when compared with bulk reactions. For example, while reaction in DMF at 23.0±0.5 °C is completed in about 120 minutes, bulk reaction still has about 25% isocyanate left even after 250 minutes of reaction. As the reaction temperature increases to 50.0±0.5 °C, the reaction in DMF reaches completion in about 30 minutes, whereas bulk reaction needs over 200 minutes for completion.

As discussed earlier, isocyanate alcohol reaction is second order. In equimolar mixture of [MDI]/[PTMO]=1.0 in bulk, concentration of the isocyanate group [C_o] is 1.65 M, compared with 25% by weight DMF solution, where [C_o] is 0.39 M. Therefore, according to Eq. 1, in terms of initial concentrations, one would expect much faster reactions in bulk when compared with solution. However, as shown in Figure 6, just the opposite is observed, where bulk reactions proceed much slower when compared with reactions in 25% DMF solution, at both temperatures. Interestingly, even the reactions at 23.0±0.5 °C in DMF solution are much faster than the bulk reactions at 50.0±0.5 °C. These results clearly show significant catalytic activity of DMF on urethane formation reactions between MDI and PTMO.

As given in Eq. 4., for a second order reaction a plot of ($1/C_t - 1/C_o$) versus time (t) should give a straight line, passing from origin, where the slope is the rate constant (k). Such plots for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C and at 50.0±0.5 °C in bulk and in 25 wt% solids DMF solutions are provided in Figures 7A and in expanded scales in Figure 7B. As can be seen in these figures, in DMF solution there is a dramatic deviation from the second order kinetics very early in the reaction indicated by the parabolic curves, whereas in bulk second order kinetics is followed throughout the reaction, as shown by the straight lines, at both temperatures. Deviation from the second order kinetics means extensive side reactions between MDI and the N-H group on the urethane linkages formed, leading to excess isocyanate consumption and allophanate formation as shown in Figure 4, which results in branching of the polymer backbone. This strongly affects the nature and extent of hydrogen bonding, microphase morphology and thermal and mechanical properties of the TPU.

To quantitatively determine the reaction time when the deviation starts, x- and y-scales are expanded in Figure 7B. Tangent lines show the deviation from the second order kinetics to start after only a few minutes of reaction in DMF solution at 50 °C and after about 15 minutes of reaction at 23 °C. In terms of percent isocyanate consumption, the deviations start at about 50%

at both temperatures. From the initial tangents (for DMF reactions) and lines shown in Figure 7B rate constants for these reactions are calculated and provided in Table 1. Comparison of the rate constants given in Table 1 for reactions at 23 °C and 50 °C indicates the reactions in DMF to be about 15 faster than the bulk at both temperatures. These results very clearly show the significant catalytic activity of DMF in MDI-PTMO reactions.

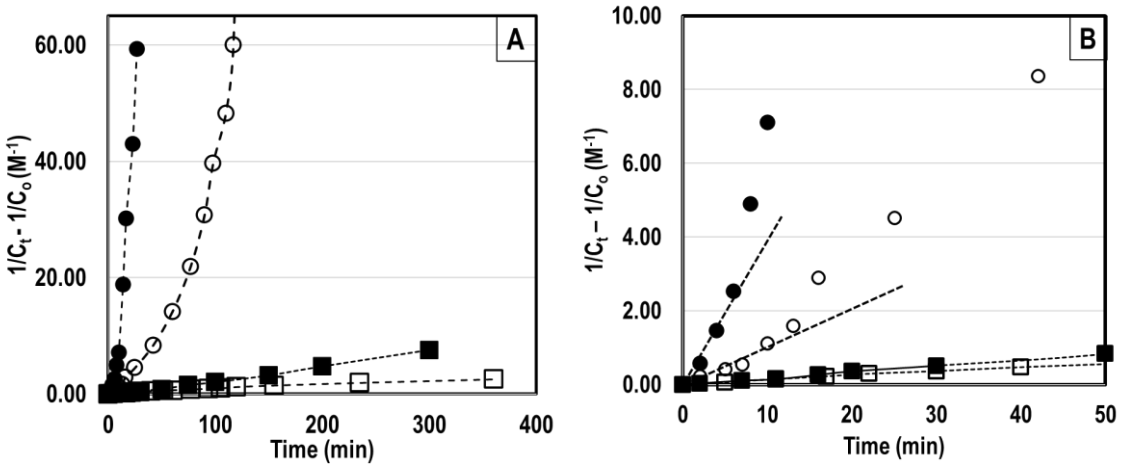


Figure 7. Second order kinetic plots for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C and 50.0±0.5 °C in bulk and in 25 wt% solids DMF solution. (□) Bulk at 23 °C, (■) bulk at 50 °C, (o) DMF at 23 °C, and (●) DMF at 50 °C.

Table 1

Second order rate constants for [MDI]/[PTMO] =1.0 reactions in bulk and in DMF solutions at 23.0±0.5 °C and 50.0±0.5 °C

Reaction medium	Temperature (°C)	Rate constant ($M^{-1}.min^{-1}$)
Bulk	23.0±0.5	$8.70x10^{-3}$
DMF	23.0±0.5	$1.35x10^{-1}$
Bulk	50.0±0.5	$2.15x10^{-2}$
DMF	50.0±0.5	$3.60x10^{-1}$

3.2. Effect of the type and nature of the solvent on the kinetics of stoichiometric reactions [MDI]/[PTMO]=1.0

Like DMF, DMAC is also a very widely used polar aprotic solvent in TPU synthesis [2-4, 19]. These disubstituted amides have very similar structures and polarities. Dielectric constants of DMF and DMAC are 36.7 and 37.8 and their solubility parameter values are 24.8 $MPa^{1/2}$ and 22.1 $MPa^{1/2}$ respectively [21, 22]. Although the main goal of this study was to investigate the

catalytic effect of DMF as the reaction solvent on MDI-PTMO reactions, we also wanted to compare it with DMAC and two other less polar aprotic solvents, tetrahydrofuran (THF), and toluene to better understand the influence of the structure, polarity, and nature of the reaction solvent on the kinetics of MDI-PTMO reactions. Toluene and THF which are also utilized in polyurethane synthesis have much smaller dielectric constants of 2.38 and 7.58 and solubility parameter values of 18.2 $MPa^{1/2}$ and 19.4 $MPa^{1/2}$ respectively [21, 22]. They are much less polar when compared to DMF and DMAC.

Isocyanate consumption-time curves for [MDI]/[PTMO] =1.0 reactions at 23.0±0.5 °C in bulk, and in DMF, DMAC, toluene and THF solutions (all solutions at 25% by weight solids concentration) are comparatively provided in Figure 8. Data provided in Figure 8 indicates very similar reactivities (or isocyanate consumption rates) in stoichiometric MDI-PTMO reactions in DMF and DMAC solutions at 23 °C, which is expected. Isocyanate consumption rates for reactions carried out in less polar solvents, toluene and THF are much slower when compared with DMF and DMAC. Interestingly, although the reactions in bulk are much slower than those in DMF and DMAC, they are faster than reactions in toluene and THF solutions. These results also clearly demonstrate significant catalytic activity of amide type solvents, DMF and DMAC on isocyanate-hydroxyl reactions between equimolar amounts of MDI and PTMO at room temperature compared to less polar THF and toluene.

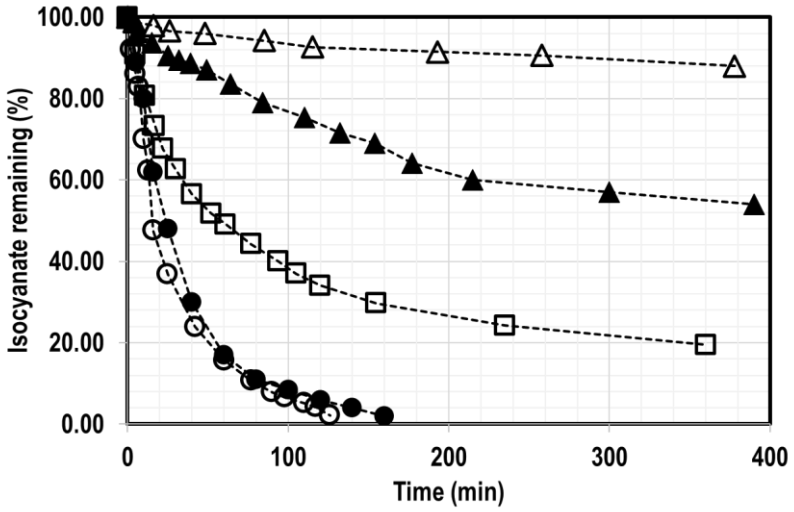


Figure 8. Isocyanate consumption as a function of time for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C in bulk and in different solvents. (□) Bulk, (o) DMF, (●) DMAC, (▲) Toluene, and (Δ) THF.

($1/C_t - 1/C_o$) versus time plots for MDI-PTMO reactions in bulk, and in DMF, DMAC, toluene and THF solutions are provided in Figures 9. As already discussed, Figure 9A shows significant deviation from second order kinetics for reactions in DMF and DMAC very early in the reaction, while reactions in bulk, toluene and THF follow second-order kinetics. Slope of the initial tangent drawn for DMAC reaction in Figure 9A gives a second order rate constant of $1.25x10^{-1}$ $M^{-1}.min^{-1}$, which is very close to that of the reaction in DMF, $1.35x10^{-1}$ $M^{-1}.min^{-1}$. Deviation from the second order kinetics starts around 20 minutes for the reaction in DMAC solution, which corresponds to about 50% isocyanate consumption, also like DMF. Figure 9B gives second order plots with expanded ($1/C_t - 1/C_o$) axis for reactions in bulk, toluene and THF, clearly indicating no deviation from second order kinetics for all reactions. Second order rate constants determined from Figure 9A and 9B for DMF, DMAC, bulk, THF and toluene reactions are reported in Table 2.

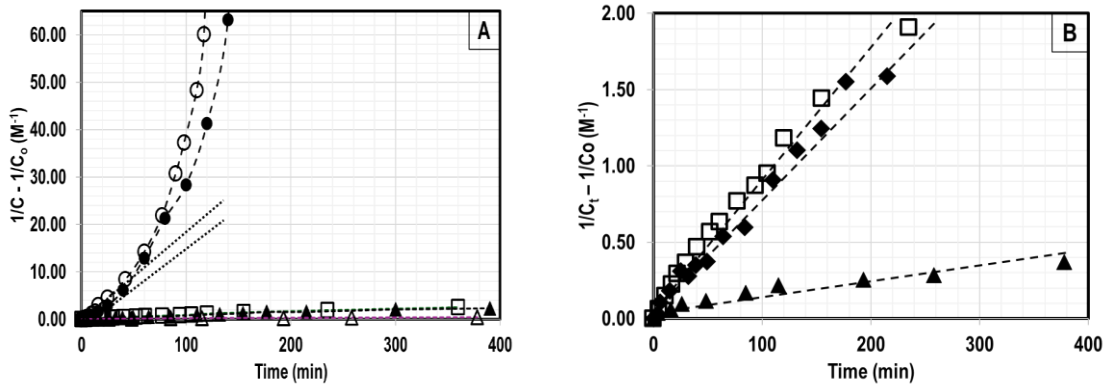


Figure 9. Second order kinetic plots for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C in (□) Bulk, (o) DMF, (●) DMAC, (▲) Toluene, and (Δ) THF.

Table 2

Second order rate constants for [MDI]/[PTMO]=1.0 reactions in bulk and in various solvents at 23.0±0.5 °C

Reaction medium	Rate constant ($M^{-1}.min^{-1}$)
Bulk	$8.70x10^{-3}$
DMF	$1.35x10^{-1}$
DMAC	$1.25x10^{-1}$
Toluene	$7.40x10^{-3}$
THF	$1.20x10^{-3}$

Dramatic difference between the rate constants of [MDI]/[PTMO]=1.0 reactions in bulk and in various solvents at 23.0±0.5 °C can comparatively be observed in the bar chart provided in Figure 10. Significant catalytic activities of DMF and DMAC on the kinetics of the reaction between MDI and PTMO at room temperature is easily seen compared with bulk reactions and reactions in toluene and THF.

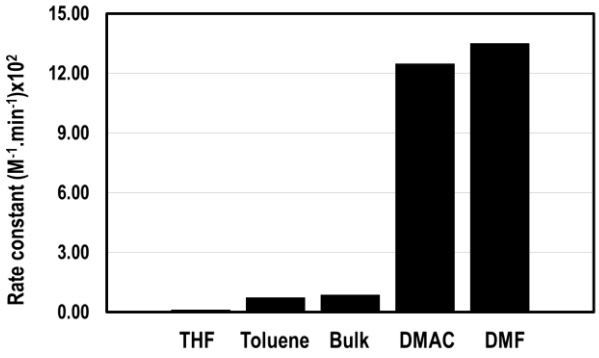


Figure 10. Comparison of the second-order rate constants for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C in bulk and in various solvents. Solids contents of all solutions is 25% by weight.

3.3. Effect of DMF concentration in toluene on the kinetics of [MDI]/[PTMO]=1.0 reactions at 50.0±0.5 °C

As discussed above, MDI-PTMO reaction in toluene at 23 °C is slow, but follows second order kinetics, indicating no side reactions. On the other hand, as we have shown, DMF acts as an efficient catalyst for MDI-PTMO reactions. Based on these observations we wanted to investigate the influence of DMF concentration on the kinetics of MDI-PTMO reactions in toluene. Toluene/DMF mixtures with volumetric ratios of 75/25, 90/10 and 99/1 were investigated as the reaction medium for [MDI]/[PTMO]=1.0 reactions, at a concentration of 25% by weight solids. Isocyanate consumption curves as a function of time for these reactions at 50.0±0.5 °C, Toluene/DMF (75/25), Toluene/DMF (90/10), and Toluene/DMF (99/1) are provided in Figure 11, together with those in bulk, and DMF for comparison.

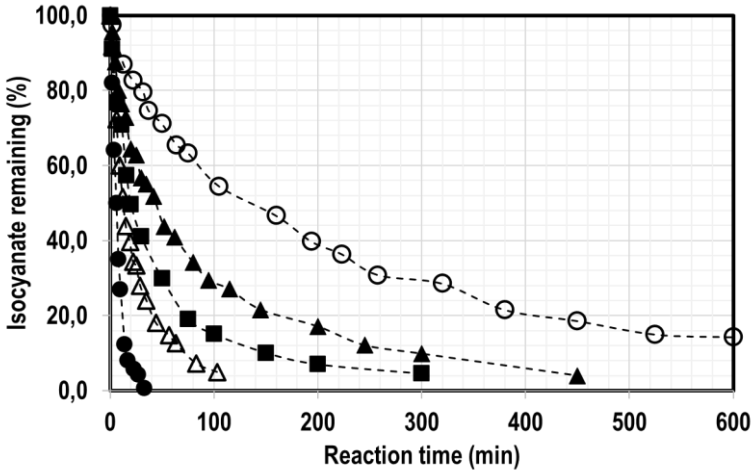


Figure 11. Isocyanate consumption as a function of time in [MDI]/[PTMO]=1.0 reaction at 50.0±0.5 °C. (●) DMF, (■) Bulk, (Δ) Toluene/DMF (75/25), (▲) Toluene/DMF (90/10), and (o) Toluene/DMF (99/1). Solids content of all solutions is 25% by weight.

As shown in Figure 11, in DMF and in bulk [MDI]/[PTMO]=1.0 reactions are completed in about 30 minutes and 6 hours respectively. In toluene/DMF (75/25) the reaction is much faster than in bulk and is completed in about 2 hours. In toluene/DMF (90/10) completion of the reaction takes about 7 hours, whereas in toluene/DMF (99/1) it takes well over 10 hours. Data provided in Figure 11 clearly shows the significant catalytic activity of DMF when added into an inert solvent toluene, where isocyanate consumption becomes considerably faster as the amount of DMF in the mixture increases. Second order kinetic plots for [MDI]/[PTMO]=1.0 reactions carried out at 50.0±0.5 °C in bulk, DMF and toluene/DMF mixtures are provided in Figures 12A and 12B.

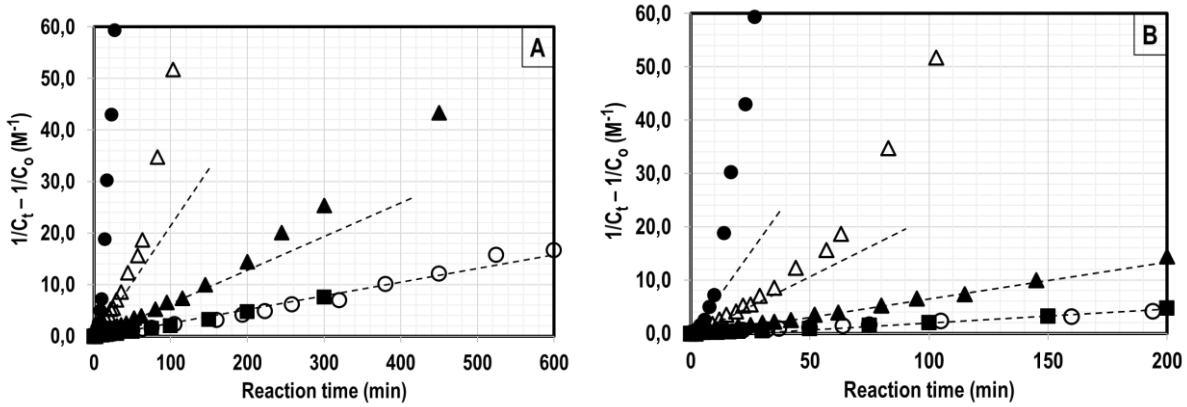


Figure 12. Second order kinetic plots for [MDI]/[PTMO]=1.0 reactions at 50.0±0.5 °C. (●) DMF, (■) Bulk, (Δ) Toluene/DMF (75/25), (▲) Toluene/DMF (90/10), and (o) Toluene/DMF (99/1). Solids content of all solutions is 25% by weight.

As shown in Figure12A, reactions in bulk and toluene/DMF (99/1) follow second order kinetics. Reactions in toluene/DMF (75/25) and (90/10) show deviation from second order kinetics at high conversions, indicating side reactions. It is interesting to note that the rate constant of the reaction in toluene/DMF (99/1) mixture, containing only 1% of DMF is the same as that of bulk. Rate constants calculated from the slopes of the lines are tabulated in Table 3 and provided as a bar chart in Figure 13. These results again clearly demonstrate significant catalytic effect of DMF on [MDI]/[PTMO]=1.0 reactions in toluene, which is a fairly inert solvent.

Table 3

Rate constants for [MDI]/[PTMO] =1.0 reactions in bulk, in DMF and in Toluene/DMF mixtures with different compositions 50.0±0.5 °C

Reaction medium	Rate constant ($M^{-1}.min^{-1}$)
Bulk	$2.15x10^{-2}$
DMF	$3.60x10^{-1}$
Toluene/DMF (75/25)	$2.20x10^{-1}$
Toluene/DMF (90/10)	$6.70x10^{-2}$
Toluene/DMF (99/1)	$2.15x10^{-2}$

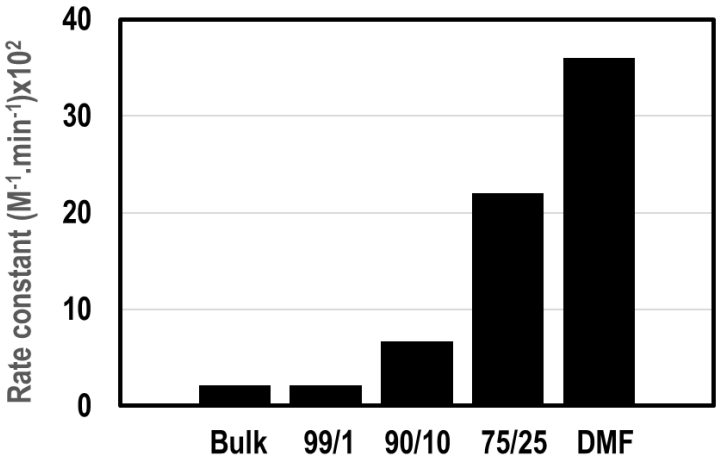


Figure 13. Comparison of the second-order rate constants for [MDI]/[PTMO]=1.0 reactions at 23.0±0.5 °C in bulk, DMF and toluene/DMF mixtures showing the significant catalytic effect of DMF in toluene solutions. Solids content 25% by weight for all solutions.

3.4. Reactions with [MDI]/[PTMO]=2.0 stoichiometric ratio

During the synthesis of segmented TPUs by two-step "prepolymer method", in the first step excess diisocyanate is used to prepare an isocyanate terminated prepolymer, which is then chain extended using stoichiometric amounts of a chain extender to form the urethane (or urea) hard segments and increase the molecular weight of the TPU. Depending on the type (glycol or diamine), chemical structure and amount of the chain extender used, microphase morphology, and thermal and mechanical properties of the TPUs produced are strongly influenced [2-5, 7, 19].

When excess MDI is used compared to the polyol in TPU synthesis, an important problem is much higher consumption of isocyanate groups due to the side reactions with the N-H of the urethane groups formed, which strongly affects TPU properties. To compensate this, in TPU synthesis generally 5 mole percent excess of diisocyanate is used [2-5, 7, 19]. However, based on the results of this study, if carried out in DMF or DMAC or even in bulk under certain reaction conditions, 5 mole percent excess may not be enough to compensate the excess diisocyanate consumption due to side reactions. As already discussed in the previous sections, even in the stoichiometric [MDI]/[PTMO]=1.0 reactions in DMF, significant amount of side reactions was observed early in the reaction based on the deviation from second order reaction kinetics. In this part of the study, [MDI]/[PTMO]=2.0 reactions in bulk, DMF and other solvent combinations were investigated to understand the influence of stoichiometry, reaction temperature and medium on the extent of excess isocyanate consumption due to side reactions.

3.4.1. Effect of reaction medium on [MDI]/[PTMO]=2.0 reactions at 23.0±0.5 °C

Isocyanate consumption-time curves for [MDI]/[PTMO]=2.0 reactions at 23.0±0.5 °C in bulk, DMF, toluene and THF are reproduced in Figure 14. As expected, reactions in DMF are much faster than those in bulk, toluene and THF. Since two-fold excess of MDI is used compared to PTMO, if there were no side reactions, one would expect these curves to level off around 50% isocyanate consumption, as indicated by the dotted line in Figure 14. Interestingly, excess isocyanate consumption due to side reactions is observed in both bulk and DMF even at 23 °C. More surprisingly, excess isocyanate consumption starts after about 30 minutes of reaction in DMF solution at 23 °C and complete consumption (100% excess) is observed after about 3 hours of reaction. In bulk reaction, which is slower, excess isocyanate consumption starts after

60 minutes and seems to level off around 35-40% isocyanate remaining, indicating around 15% excess isocyanate consumption. Excess isocyanate consumption is not observed in toluene and THF up to about 10 hours of reaction.

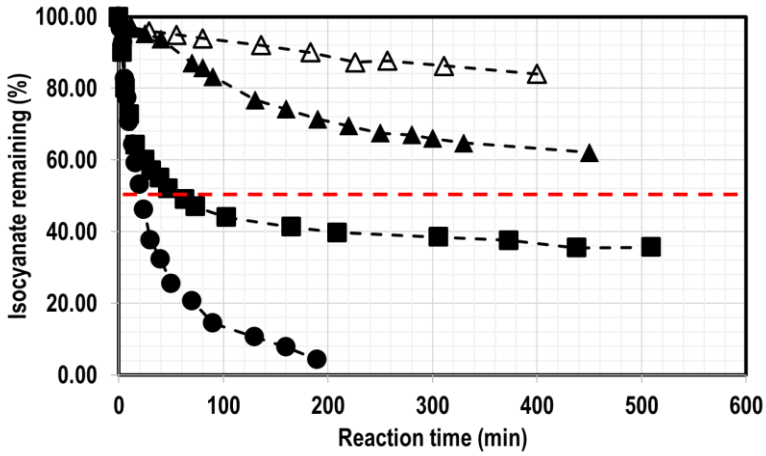


Figure 14. Isocyanate consumption as a function of time in [MDI]/[PTMO]=2.0 reactions at 23.0±0.5 °C in, (●) DMF, (■) Bulk, (▲) Toluene, and (Δ) THF.

These results clearly demonstrate that although the reactions are slower, to prevent the side reactions, and to produce linear TPUs, toluene and THF are better solvents for prepolymer synthesis than DMF in MDI+PTMO systems at room temperature. More importantly, during TPU synthesis with MDI, to determine the stoichiometric amount of chain extender needed isocyanate titration must be performed [18].

3.4.2. Effect of DMF concentration in toluene on [MDI]/[PTMO]=2.0 reactions at 50.0±0.5 °C

Considering the prepolymer formation reactions, we also investigated the catalytic effect of DMF as a solvent or cosolvent for [MDI]/[PTMO] =2.0 reactions at 50.0±0.5 °C. Isocyanate consumption curves as a function of reaction time are reproduced in Figure 15. In pure DMF almost all isocyanate is consumed due to extensive side reactions in about 90 minutes, even though the initial reaction stoichiometry was [MDI]/[PTMO] =2.0. As expected, DMF has a strong catalytic activity, where isocyanate consumption rate increases with an increase in DMF content of the solvent mixture. Reactions in toluene/DMF (75/25) mixture also show significant amount of excess isocyanate consumption after about 50 minutes. Reactions in THF/DMF (90/10) is slower but still show slight excess of isocyanate consumption after 150 minutes of reaction. Interestingly, in the reactions carried out in toluene/DMF (90/10) solution isocyanate

consumption levels off at 50%, which is the theoretical limit. This indicates no significant side reactions in this solvent system. As a result, toluene/DMF (90/10) can be considered as the best solvent for prepolymer formation reactions among all systems investigated in this study.

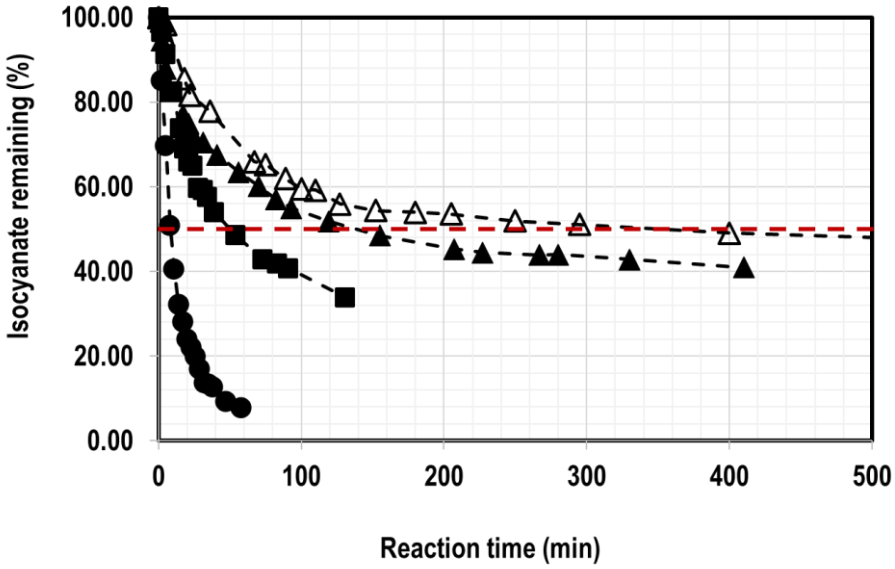


Figure 15. Isocyanate consumption as a function of time in [MDI]/[PTMO]=2.0 reactions at 50.0±0.5 °C. (●) DMF, (■) Toluene/DMF (75/25), and (Δ) Toluene/DMF (90/10). and (▲) THF/DMF (90/10).

3.4.3. Influence of the polyether glycol structure on [MDI]/[PTMO]=2.0 reactions at 23.0±0.5 °C

Although poly(tetramethylene oxide) glycol (PTMO) is the most preferred polyether soft segment in TPU synthesis, poly(ethylene oxide) glycol (PEO) and poly(propylene oxide) glycol (PPG) are also widely utilized. Influence of the polyether structure on reaction with MDI was investigated using PEO1k and PPG1k in DMF solution at 23.0±0.5 °C and compared with that of PTMO1k. For these reactions [MDI]/[Polyether]=2.0 was used, to mimic the prepolymer reactions. As shown in Figure 16, although two-fold stoichiometric excess of MDI was used and the reactions were carried out at room temperature, in about 3 hours almost all isocyanate was consumed due to side reactions for all polyethers, which are normally expected to reach a plateau around 50% isocyanate content as shown by the dotted line in Figure 16. These results show that the structure of the polyether had no effect on the

isocyanate consumption rate, which may be expected, since all oligomers had primary hydroxyl groups.

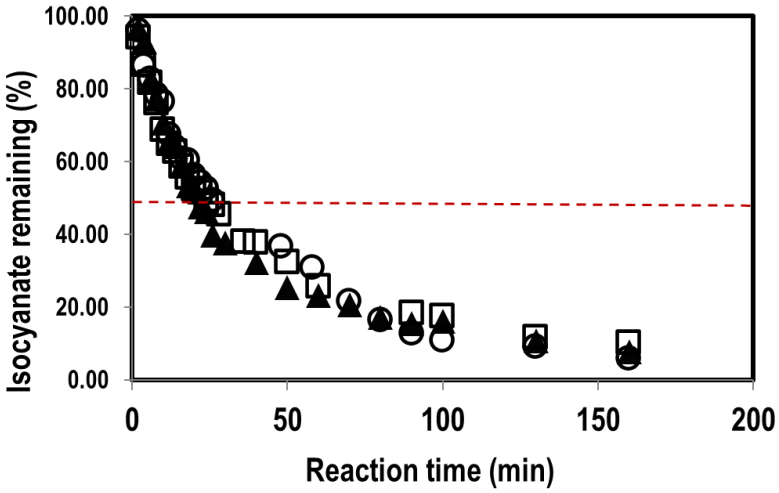


Figure 16. Isocyanate consumption as a function of time in [MDI]/[Polyether]=2.0 reaction mixture in DMF at 23.0±0.5 °C for (o) PTMO1k, (□) PPG1k and (▲) PEO1k. All solutions 25% by weight.

Conclusions

Segmented thermoplastic polyurethanes (TPU) based on MDI are one of the most widely investigated polymeric systems, because of their composition dependent morphologies and broad range of properties from rigid plastics to extremely soft elastomers, which find numerous applications in various fields. Polarity difference between the soft and strongly hydrogen bonded hard segments lead to microphase separated morphologies and mechanically strong TPUs even if they are poorly synthesized and/or have low molecular weights. This is mainly due to the presence of strong hydrogen bonding in TPUs to supersede the critical entanglement molecular weight in determining the properties. Conventionally, especially in academic research laboratories, MDI based TPUs are prepared by prepolymer method, in solution and at moderately high temperatures of 60-100 °C, sometimes even in the presence of a catalyst. In most cases, about 5 mole percent excess of MDI is used to compensate the excess MDI consumption due to side reactions. However, as demonstrated by the results of this study excess MDI consumption is far more than 5 mole percent if the reaction is carried out in DMF or even in bulk at fairly low temperatures of 23.0±0.5 and 50±0.5 °C. Results of this study clearly show that it is very critical to monitor the isocyanate consumption during prepolymer formation reactions of MDI with polyethers, especially if DMF or DMAC is used as the solvent. Before the chain extension step, to find out the exact stoichiometric amount of the chain extender to be

used, it is necessary to determine the isocyanate content of the prepolymer by dibutyl amine back titration method. Conventionally employed 5 to 10% excess MDI use to compensate the side reactions is usually not sufficient, especially if the reactions are conducted at moderate temperatures (50 - 100 °C). We demonstrated that during prepolymer formation in [MDI]/[PTMO]=2.0 system at 50 °C, side reactions can be minimized or eliminated by using THF/DMF (90/10) or toluene/DMF (90/10) solvent mixtures.

References

1. C. S. Schollenberger, H. Scott, and G. H. Moore, *Polyurethane VC, a virtually crosslinked elastomer, Rubber World*, vol. 137, pp. 549–555, 1958
2. I. Yilgor, E. Yilgor and G.L. Wilkes, *Critical parameters in designing segmented polyurethanes and their effect on morphology and properties: A comprehensive review.* **58**: p. A1-A36.
3. P. Krol, *Synthesis methods, chemical structures, and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers.* Progress in Materials Science, 2007. **52**(6): p. 915-1015.
4. C. Hepburn, *Polyurethane elastomers*. Second edition ed. 1992, London, UK: Elsevier Science Publishers.
5. J. Datta and P. Kasprzyk, *Thermoplastic polyurethanes derived from petrochemical or renewable resources: A comprehensive review*. Polym Eng Sci, vol. 58, no. S1, pp. E14–E35, May 2018.
6. E. Delebecq, J. P. Pascault, B. Boutevin and F. Ganachaud, *On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane.* Chemical Reviews, 2013. **113**(1): p. 80-118.
7. C. Prisacariu, *Polyurethane Elastomers*. Vienna: Springer Vienna, 2011. doi: 10.1007/978-3-7091-0514-6.
8. S. L. Cooper and A. V. Tobolsky, *Properties of Linear Elastomeric Polyurethanes*, J Appl Polym Sci, vol. 10, pp. 1837–184, 1966.
9. J. H. Saunders, and K.C. Frisch, *Polyurethanes: Chemistry and Technology*. 1962, New York: Interscience Publishers.
10. M. C. Chang and S. A. Chen, *Kinetics and mechanisms of urethane reactions: Phenyl isocyanate-alcohol systems*, J. Polym. Sci., Part A, Polym. Chem., 25, 2543-2559 (1987)
11. K. Dusek, M. Spirkova, and I. Havlicek, *Network formation of polyurethanes due to the side reactions*. Macromolecules, 1990. 23(6): p. 1774-1781.
12. K. Dusek, M. Spirkova, and M. Ilavsky, *Network formation in polyurethanes due to allophanate and biuret formation - Gel fraction and equilibrium modulus*. Makromol. Chem.-Macromolecular Symposia, 1991. 45: p. 87-95.
13. M. Spirkova and K. Dusek, *Extent of side reactions and gelation of polyether polyurethanes*. Polym. Bull., 1989. 22(2): p. 191-198.
14. M. Spirkova, M. Kubin and K. Dusek, *Side reactions in the formation of polyurethanes. Model reactions between phenyl isocyanate and 1-butanol*. J. Macromol. Sci., Chemistry, 1987. A24(10): p. 1151-1166.

15. M. Spirkova, M. Kubin and K. Dusek, *Side reactions in the formation of polyurethanes. Stability of reaction products of phenyl isocyanate.* J. Macromol. Sci., Chemistry, 1990. A27(4): p. 509-522.
16. M. Sato, *The rate of reaction of isocyanates with alcohols. II.* J. Org. Chem., **27**(3): p. 819-825 (1962).
17. I. Yilgor and J.E. McGrath, *Effect of catalysts on the reaction between a cycloaliphatic diisocyanate (HMDI) and n-butanol.* J. Appl. Polym. Scie, **30**(4), 1733-1739 (9185).
18. D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes*, High Polymer Series, XVI, Part 111, Wiley, New York, 1969.
19. N. M. K. Lambla, K. A. Woodhouse and S. L. Cooper, *Polyurethanes in biomedical applications*. Boca Raton, FL, USA: CRC Press; 1998.
20. I. Yilgör, E. H. Orhan and B. M. Baysal, *Kinetics of the reaction of a glycol with a diisocyanate*, Macromol. Chem. 179, 109-112 (1978).
21. D. W. V. Krevelen, Properties of polymers, Amsterdam, Netherlands, Elsevier Science Publishers, 1990, Ch. 7
22. *Hansen solubility parameters*, https://www.accudynetest.com/solubility_table.html

Highlights:

MDI reacts very fast with primary hydroxyl groups even at room temperature.

DMF is a very effective catalyst for MDI-polyol reactions.

DMF also catalyzes allophanate side reactions leading to branched TPUs.

Side reactions during prepolymer formation can be minimized if THF/DMF (90/10) or toluene/DMF (90/10) mixtures are used as solvent.

Abstract

Thermoplastic polyurethanes (TPU) are one of the most widely investigated polymeric systems due to their interesting structure-morphology-property behavior. They also find broad range of applications in various fields. Global TPU market is projected to grow about 7.3% annually from $2.30 billion in 2021 to $3.80 billion in 2028. 4,4'-Diphenylmethane diisocyanate (MDI) is the most widely used diisocyanate for the preparation of TPUs both in academia and industry. When TPU synthesis is carried out in solution, a polar aprotic solvent is necessary to obtain high molecular weight polymers. Most preferred solvents for TPU synthesis are high boiling, polar, aprotic solvents, such as dimethylacetamide (DMAC), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP). When MDI is used as the diisocyanate, depending on the solvent used and reaction temperature, extensive side reactions may be observed, which consume excess diisocyanate and affect reaction stoichiometry. Side reactions strongly influence TPU structure, topology, microphase morphology, and properties. In this study influence of the solvent, initial [NCO]/[OH] stoichiometry and reaction temperature on the rate of isocyanate consumption and kinetics of the reactions between MDI and poly(tetramethylene oxide)glycol (PTMO) were investigated. Strong catalytic effect of DMF even at reactions conducted at room temperature were observed, resulting in significant excess MDI consumption due extensive side reactions. During prepolymer formation in [MDI]/[PTMO]=2.0 system at 50 °C, side reactions were minimized or eliminated by using THF/DMF or toluene/DMF (90/10) solvent mixtures.

Decleration of interests

No financial or non-financial assistance was provided by a third party for the reported work.

No patent application was made for the work reported.