# In Situ FT-IR-ATR Studies on the Structure Development of Polyurethane-Urea Systems

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**ABSTRACT:** This article reports the application of Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) technique for investigation of *in situ* polymerization of polyurethane-urea elastomers. Formulations comprising of diisocyanates, a polyether diol and a diamine based chain extender have been used in this study. The diisocyanates used were 4,4'-diphenylmethane diisocyanate and toluene diisocyanates. The polyether diol and diamine used were propyleneglycol block-PEO-*b*-PPO and 4-(4-(2-(4-(4-amino-2-(trifluoromethyl) phenoxy) phenyl) propan-2-yl) phenoxy)-3-(trifluoromethyl) benzeneamine, respectively. These reactants were mixed and placed on the ATR cell, and then the infrared spectra were recorded at an interval of 1.75 s while continuously heating. The polyurethane-urea formation was monitored by the decay in the intensity of isocyanate band at 2258 to 2261 cm$^{-1}$.

As the polymerization progressed, new peaks appeared at wavenumbers of 1711 cm$^{-1}$, 1697 cm$^{-1}$, and 1655 cm$^{-1}$. These peaks correspond to the urethane carbonyl, hydrogen bonded urethane, and urea carbonyl groups, respectively. It was found that with the progress of the reaction, the shift in the peaks at 1655 and 1697 cm$^{-1}$ occurs gradually. This shift in peaks is attributed to the hydrogen bonding. The hydrogen bonding and hence the shift in the peak is a cumulative effect of three phenomena namely: (1) degree of polymerization, (2) macro and microphase separation, and (3) temperature effect. A rationale is discussed to deconvolute these three effects. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1012–1018, 2011

**Key words:** polyurethane-urea; structure; phase separation; FTIR-ATR; reactive processing

## INTRODUCTION

The understanding of the relationships between the reactivity of the reactants and the structure development of the product during the reactive processing of certain monomers is of primary importance. This concept applies to many systems and particularly to the polyurethane (PU) compositions used in the reactive injection-molding processes.[1] These polymers are formed through a sequence of parallel step-growth polymerization reactions and it is possible, in principle at least, to predict with sufficient accuracy the detailed composition of the system as it evolves with time. As a result of these reactions a block copolymer containing three main components, a polyol, a diisocyanate, and a chain extender, is formed. The most important diisocyanates for the industrial uses, are 2,4- and 2,6-toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). Mainly polyether and polyester based polyols with

molecular weights ranging from 1000 to 4000 g/mol are used for the synthesis of PU elastomers. The typical chain extenders used are short-chain aliphatic diamines such as ethylenediamine, or diols such as butanediol. These ingredients are used to produce PU of having alternating hard and soft segments in the backbone structure. The hard and soft segments tend to separate into small domains due to their mutual incompatible nature. This separation of the domains is known as the microphase separation.[2] The extent of phase separation depends on the thermodynamic driving forces and the kinetic parameters during the reaction. The morphology and structure developed as a result of the reaction between the active hydrogen bearing group and the isocyanate, usually consists of urethane and urea hard segment rich domains, with sizes ranging from tens to hundreds of angstroms, dispersed in the matrix of the soft segments.[3–5] The soft segments that do not form hydrogen bond can particularly facilitate the microphase separation.[6–9] In addition to the microphase separated domain structures, PUs exhibit extensive hydrogen-bonding. The proton donor is the NH group of the urethane/urea linkage, while the hydrogen-bond acceptor may be either in the

hard segment (the carbonyl of the urethane/urea group) or in the soft segment (e.g., ether oxygen). The extent and nature of hydrogen bonding seems to be one of the most important parameters that may affect the morphology and the final properties of the PUs. Therefore, it has been a subject of number of studies, including those performed by using infrared spectroscopy.[4,10–11] Some criticism exists to the previous work concerning the interpretation of the infrared spectroscopic changes that occur during the urethane formation reaction as a function of polymerization temperature. However, the FT-IR spectroscopy is a very versatile technique that can be applied to study the urethane and urea formation in the PUs and to deduce phase-separated structures in such polymeric systems.[12–14]

In this article we present the results of *in situ* Fourier Transform-Infrared-Attenuated Total Reflectance (FT-IR-ATR) studies of the structure development in the polyurethane-urea (PUU) systems. To follow this, a combination of diisocyanates with polyether diols in the presence of a diamine as chain extender was used. The reaction in the PUU systems was monitored with the FTIR-ATR technique via the absorption intensity of the diisocyanates -NCO group vibrational band at 2258 cm$^{-1}$. Simultaneously, the absorption intensity and variation in the peak position of the urethane and urea groups was also monitored. The obtained results are interpreted and discussed in detail.

## EXPERIMENTAL

### Materials

The chemicals used in this study were obtained from Sigma-Aldrich Chemie GmbH Stienheim, Germany and used without any purification. Two formulations were employed (1): 4,4-diphenylmethane diisocyanate, polyol (propyleneglycol block-PEO-*b*-PPO) and (2) toluene diisocyanate, polyol (propyleneglycol block-PEO-*b*-PPO). PEO and PPO stand for polyethylene oxide and polypropylene oxide, respectively. Both formulations are based upon 100 g of polyol by convention. An isocyanate index of 88 and 105 was used in this work. In both formulations a diamine (4-(4-(2-(4-(4-amino-2-(trifluoromethyl) phenoxy) phenyl) propan-2-yl) phenoxy)-3-(trifluoromethyl) benzeneamine) was used as crosslinking agent.

### FT-IR-ATR spectroscopy

FT-IR measurements were carried out on a Varian FTS 7000 FT-IR spectrometer (Darmstadt, Germany) equipped with a Golden Gate diamond single attenuated total reflectance (ATR) cell heatable up to 200°C. The ATR cell installed in the spectrometer was from LOT Oriel (Darmstadt, Germany).

All the chemicals were mixed together for 10 s and immediately a small portion of the reaction mixture was placed on the ATR cell, and spectra were recorded with 1.75 s intervals. The temperature of the ATR cell was raised from room temperature to 150°C with heating rate of 10 K°/min. The reaction was continued for 25 min, during which over 800 spectra were recorded. The each data point reported in the Results and Discussion section is a mean of 32 values of the original spectra. The change in the intensity of the isocyanate band at 2258 cm$^{-1}$ was used to monitor the *in situ* curing kinetics and structure development during reactive processing of the PUUs. For an overview, a detailed reaction Scheme 1 is also depicted as under.

## RESULTS AND DISCUSSION

It is important to mention that the PUU polymerization is a fast exothermic reaction that initiates as soon as the monomers come into contact with each other. Therefore, in the present work a new approach has been developed for studying such polymerization reactions. Figure 1 shows the two FT-IR-ATR spectra at the starting time and after 25 min, of the formulation 2 given in the Experimental section above. The peaks at wavenumbers 2258 cm$^{-1}$, 1711 cm$^{-1}$, 1697 cm$^{-1}$, and 1655 cm$^{-1}$ correspond to the -NCO, urethane, and urea groups, respectively. The decay in the intensity at a wavenumber 2258 cm$^{-1}$ of the -NCO group is used to monitor the progress of the reaction.

The three-dimensional FTIR-ATR spectra of the formulation 2, covering the wavenumber range from 2100 to 2400 cm$^{-1}$ for 25 min is shown in Figure 2(a). The -NCO peak area data at a wavenumber of 2258 cm$^{-1}$ for MDI and TDI reported in Figure 2(b), is derived from the Figure 2(a). The intensities reported in the Figure 2(b) are normalized by dividing all the prevailing intensities with the initial intensity. The net result is that the initial intensity (at time = 0) becomes 1 and the subsequent intensities are less than 1. The decrease in its value suggests that the reactants (-NCO group) concentration is decreasing and is being converted to the product. The decay in the intensity of the -NCO group with the time and temperature represents the progress of reaction. It is evident from the Figure 2 that the conversion of the -NCO group in both types of isocyanate follows the similar trend. In the early stage of the reaction it follows almost a linear trend. This behavior can be approximated by linear function having a negative slop. After about 12 to 13 min the temperature reaches 150°C. The temperature is then maintained constant till the end of the
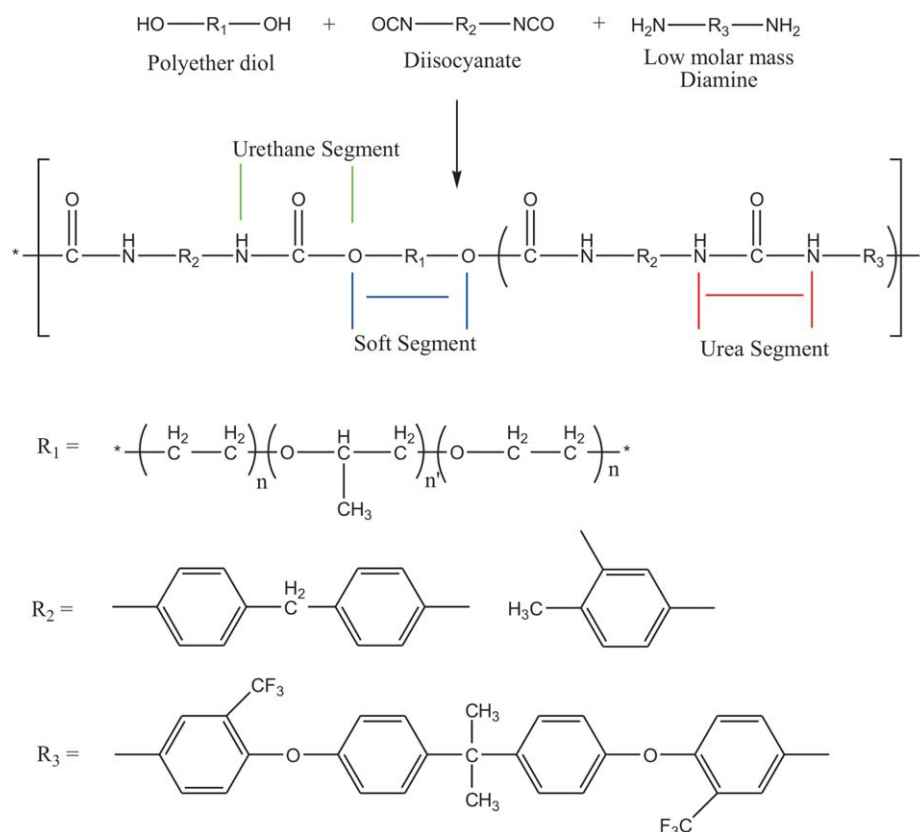
**Scheme 1** Reaction chemistry taking place during polyurethane-urea formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization reaction. During this time, the conversion rate of the -NCO group decelerates. This is obvious since the slope of the curve decreases. This behavior can be explained as follows; initially less number of monomers are polymerized and the viscosity of the reaction mixture is rather low and therefore the reactants can flow and mix easily and that leads to the rate of reaction rather fast i.e., slope is higher. With the passage of time as the polymerization progresses the reaction mixture become more viscous. It is common practice that the extent of reaction is reported as conversion.[15] Therefore, the data given in the Figure 2 was converted to conversion by using eq. (1).

$$\alpha = 1 - \frac{C_t}{C_0} = 1 - \frac{A_t}{A_0} \qquad (1)$$

where "$\alpha$" is the conversion, $C_t$, is the -NCO group concentration at time, $t$, and $C_0$, is the concentration at the start of the reaction. The concentration is proportional to the (normalized) intensity, $A$, reported in Figure 2; $A_0 = 1$ at the start of the reaction and $A_t$ is the intensity at any given time, $t$. The computed values of the conversion, $\alpha$, for the two systems are plotted in Figure 3, which shows that the conversion of the -NCO group follows a similar trend in gen-eral, for both the systems (MDI and TDI based formulations). The molar masses of the two isocyanates are different, and the PUU formed from these
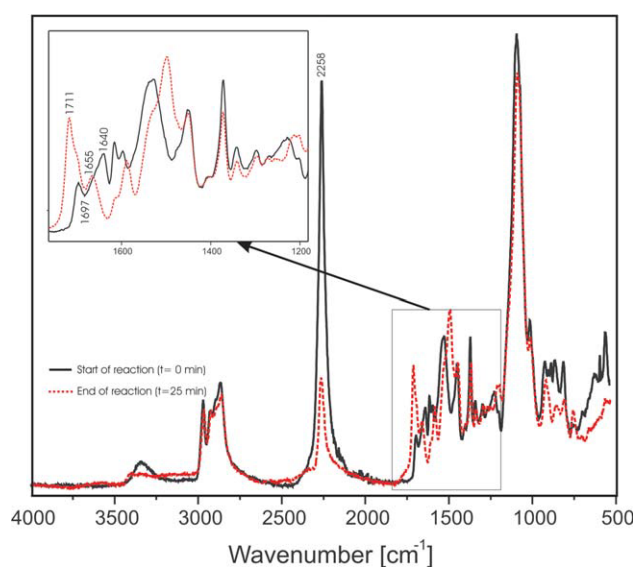


**Figure 1** FT-IR-ATR spectra of the PUU system at the start of the reaction ($t = 0$ min, 20°C) and at the end of the reaction ($t = 25$ min, 150°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
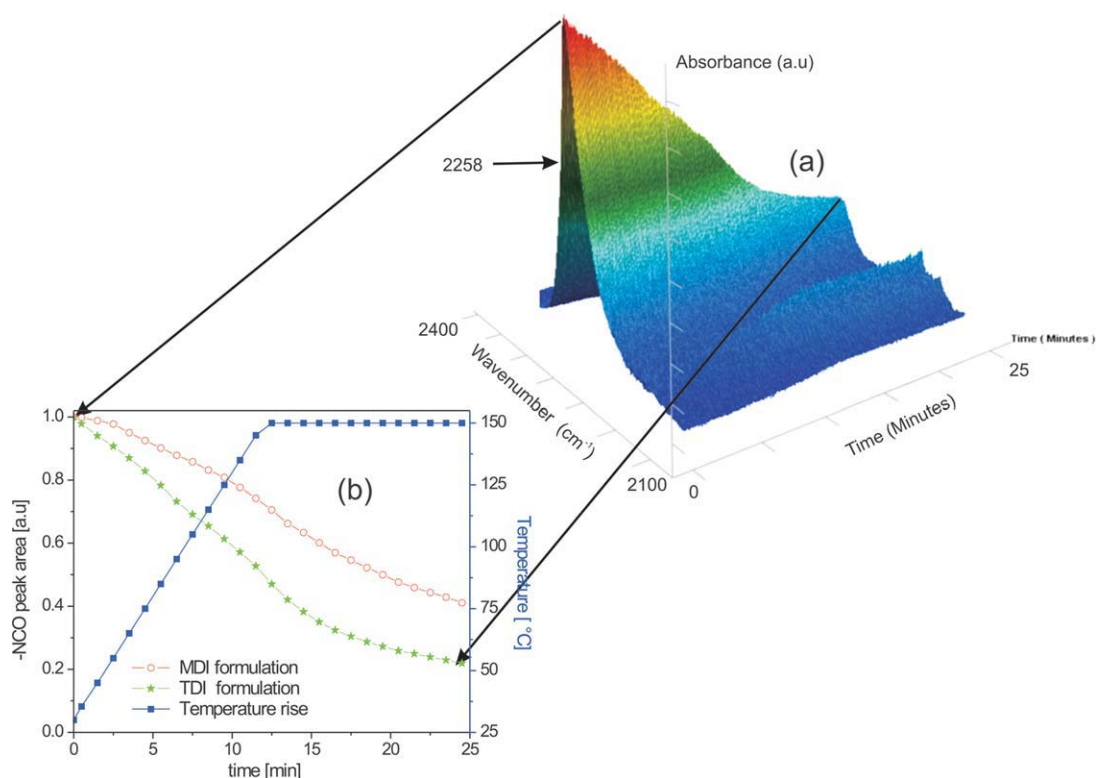
**Figure 2** (a) Three-dimensional plot showing the decay in the concentration of the -NCO group at a wave number 2258 cm$^{-1}$; (b) the corresponding data plot of the -NCO group in the MDI and TDI based PUU formulations as a function of time and temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isocyanates will have different molar masses. The molar masses affect the rate of reaction which also could affect the conversion. Therefore, TDI has higher conversion compared with the MDI system.

After 12 to 13 min the slope of the two curves decreases, this indicates that the reaction proceeding changes. This change happens because the reaction becomes from a chemical controlled regime to diffusion controlled one. It is caused by various mechanisms when a monomer of functionality 2 or greater is used. With the passage of time as the reaction progresses, the number (concentration) of the reactive species/groups reduces and as a result the rate of conversion ($d\alpha/dt$) i.e., slope of the curves (Fig. 3) should decrease. At the same time there is no more change (rise) in the temperature [see Fig. 2(b)]. The other phenomenon occurs due to the thermodynamic immiscibility of the PUU segments which results in their phase separation, therefore, hindering the accessibility of the reactive groups. The combined affect is the change in slope of the conversion versus time curve at about 12 to 13 min.[16]

At relatively low temperatures, the hard segments form crystalline domains, while the soft segments form the amorphous phase.[17] A schematic representation of these two phases is shown in Scheme 2. At a temperature below the melting temperature of the crystalline domains, the hard segments are quite

rigid and the individual polymerization in it remains fixed at their relative position. The hard domains are held together through strong intermolecular forces, such as the hydrogen bonding. When the temperature rises, the hard segments separate apart from
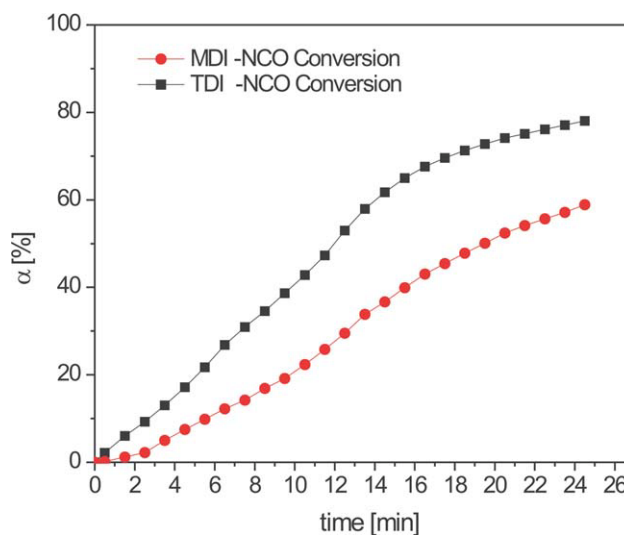


**Figure 3** Plot of the conversion ($\alpha$) as a function of time for the two PUU formulations for *in situ* bulk polymerization starting at room temperature to 150°C reaction conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
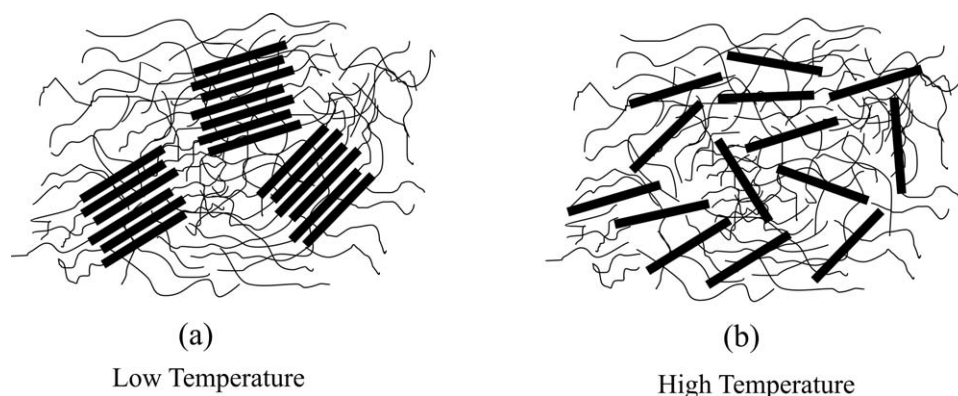
**Scheme 2** Schematic representation of the hard segment domains in the PUU system.

each other and are distributed in the polymer matrix. This behavior is shown in Scheme 2(b). For up to 12 to 13 min these two opposing factors cancel out each other and the net result is nearly a linear relationship for the two systems up to 12 to 13 min. Keeping this in view, the progress of the reaction and thereby formation of the hard segments domain (urethane and urea) was followed in FT-IR-ATR spectra. The data obtained are shown in Figure 4(a,b) for the two isocyanate systems. It can be seen from the Figure 4 that the formation of the urethane hard segments follows the similar trend for the two systems. The formation of the hard segment domains is accompanied by a shift in peak as well. The shift in peak behavior is observed due to the fact that with the temperature changes the intermolecular forces e.g., hydrogen bonding etc. are changing as described in Scheme 2.

The temperature rise affects the reaction progress in a number of ways. The increase in the temperature increases the rate of reaction, $r$, initially, as represented by eq. (2).[18]

$$r = f(T).g(\alpha).h(P,T) \tag{2}$$

where, $f(T)$ is a function of the temperature, $T$, and generally written as given in eq. (3).

$$f(T) = k(T) = A.e^{-E/RT} \tag{3}$$

This is well-known Arrhenius equation.[19] In this equation $k(T)$ is the rate constant, $E$ is the activation energy, and $R$ is the universal gas constant.

$g(\alpha)$ is the function of the conversion, $\alpha$, and for a first-order reaction it can be written as:

$$g(\alpha) = C_0(1 - \alpha) \tag{4}$$

where $C_0$ is the initial concentration of the reactant.

$h(P,T)$ is the diffusion factor and is a complex function of the degree of polymerization which

depends on conversion, $\alpha$; and is also a function of temperature, $T$. If the temperature is constant and the viscosity of the reacting mixture does not change, $h(P,T)$ will become 1.

Referring back to Figure 4(a,b), initially the value of $f(T)$ increase, $g(\alpha)$ decreases and $h(P,T)$ possibly
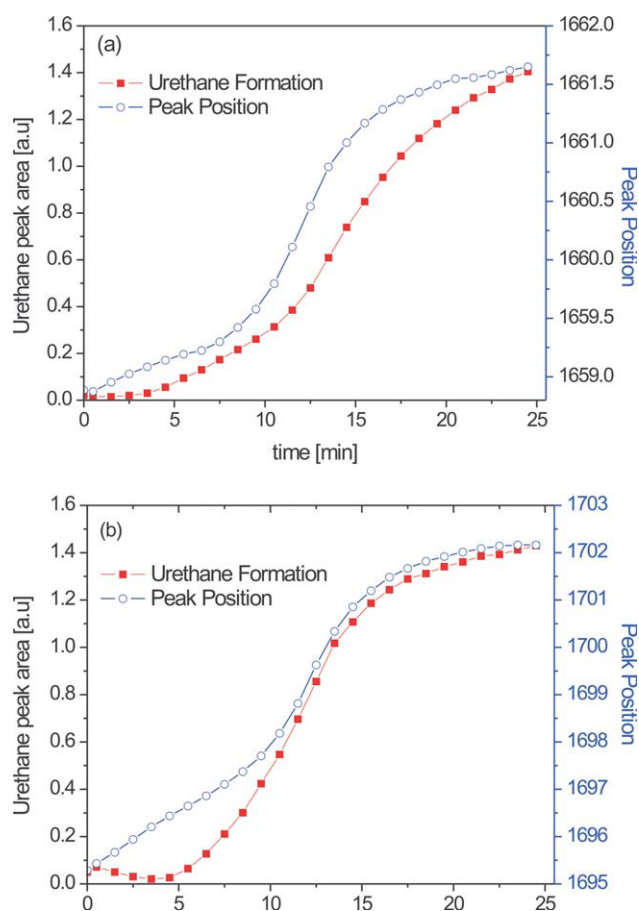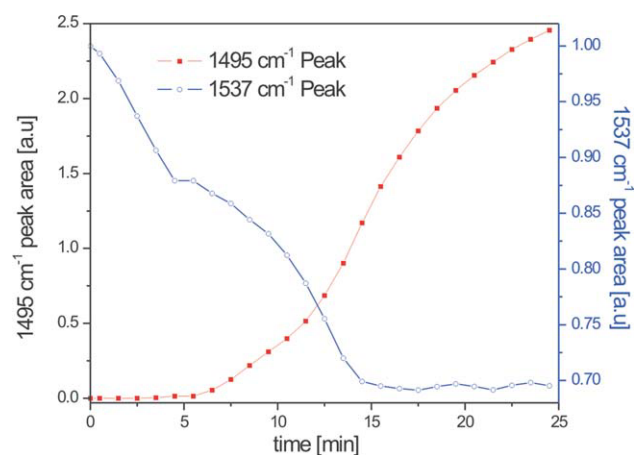


**Figure 4** Plot of the urethane formation and the peak shift in the MDI (a) and TDI (b) based formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
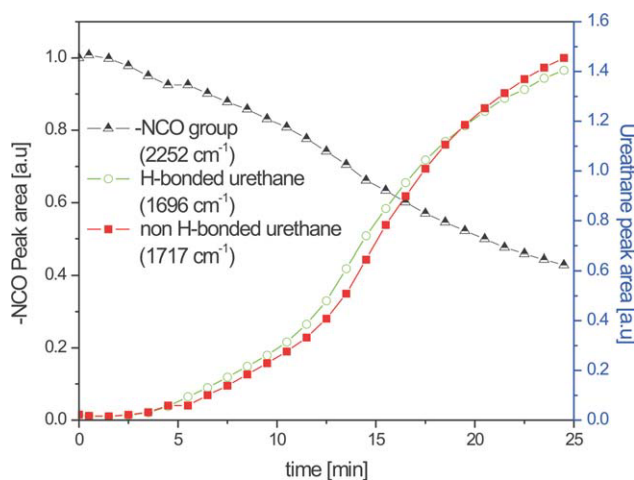
**Figure 5** Plot of the peak areas of the -NCO, hydrogen bonded and nonbonded urethane groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases; the net effect is steady increase in both the urethane formation and the peak shift.

In the middle of the curve, where the temperature is comparatively higher (e.g., 7–15 min), $f(T) = A.e^{-E/RT}$ dominates and contributes more to the formation of the urethane, and, therefore, the change in peak shift is higher. This dominance is due to the fact that it is an exponential function, and even a small rise in the temperature changes the value of $f(T)$ to a great extent. Towards the end of the curve, the temperature becomes constant, [see Fig. 2(b)] but at the same time the conversion has increased making the value of $g(\alpha)$ small, since $g(\alpha)$ is the decreasing function with respect to the increase in the conversion, $\alpha$. The value of $h(P,T)$ will also decrease as the temperature is constant in this region (after 12
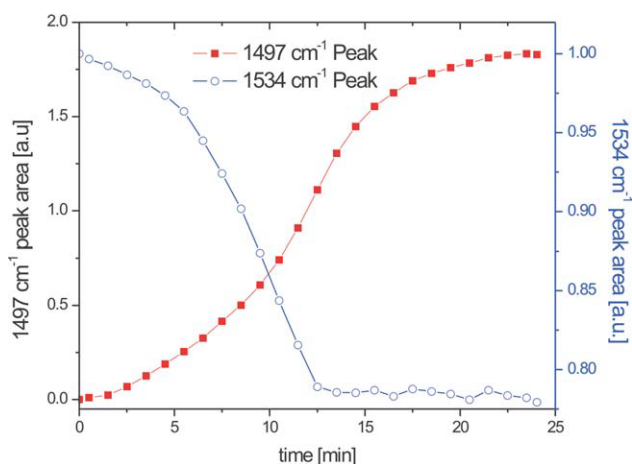
min), and, the degree of polymerization is higher. The net affect in this region is that the rate of reaction is slow and will eventually reduce to zero at infinite time. The peak shift follows the same trend as the urethane formation. The above argument in support of the urethane formation also applies to the peak shift.

Figure 5 shows the peak area plot of the -NCO functional group and the hydrogen bonded and non-hydrogen bonded urethane groups. The formation of the urethane increases, while the -NCO group concentration decreases. However, the trends of the conversion and formation of these two groups with the time, is similar. At the start of the reaction, it appears that there are few urethane groups present in the reaction mixture. The initial difference in the hydrogen bonded and non hydrogen bonded, is possibly due to the shifting of the reaction mixture to the ATR cell. After 2 min of the reaction time, the urethane formation follows a similar trend to that the conversion of -NCO functional group. In the early stage of the reaction the nonhydrogen bonded urethane formation has a very low concentration. The curve follows the same trend to that of trend followed by the hydrogen bonded urethane peak.

The data shown in Figure 6 reveals a decrease in the intensity of 1495 cm$^{-1}$ (amide II) for TDI system. After 15 min it turns to a minimum value. This is the result of the microphase separation with the proceeding of the reaction. However, at the same time an increase in the intensity of the soluble urea group peak at 1537 cm$^{-1}$ is observed. It follows the same trend as the trend followed by the formation of the hydrogen bonded urethane and the nonbonded urethane group. The behavior of the MDI system for these two groups is comparable as shown in Figure 7.



**Figure 6** Time dependent change in the peak area of 1495 and 1537 cm$^{-1}$ corresponding to the amide bonds in the TDI formulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7** Time dependent change in the peak area of 1497 and 1534 cm$^{-1}$ corresponding to the amide bonds in the MDI formulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## CONCLUSIONS

The results presented in this article highlight the utility of FT-IR-ATR spectroscopy for an *in situ* monitoring of the polymerization of the PUU systems. The results indicate that the conversion of the -NCO functional group follow a similar trend in the two types of isocyanates. The formation of the urethane and urea segments is accompanied by a peak shift. The urethane formation and the shift in peak position of the same group in the two systems show the similar behavior. The shift in peaks is attributed to the hydrogen bonding and is a cumulative effect of the three phenomena namely: (1) degree of polymerization, (2) macro and microphase separation, and (3) temperature effect.

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