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Kinetic studies of polyurethane polymerization with Raman spectroscopy

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Abstract

In this study, the polymerization kinetics of an uncatalyzed polyester based thermoplastic polyurethane formulation was characterized with Raman spectroscopy. Measuring the normalized scattering intensity of a band originating from the TPU diisocyanate, conversion was calculated as a function of time. Kinetic parameters obtained from these experiments correlated well with those obtained from analogous calorimetric experiments and with literature values. It was concluded that Raman spectroscopy is a powerful tool for characterizing the polymerization kinetics of polyurethanes in situ.

Keywords: Raman spectroscopy; Polyurethane; Kinetics

1. Introduction

A large number of characterization methods have been used to monitor the kinetics of polymerization reactions. Kamal [1] and Mussati [2] have given extensive reviews. These methods fall into two groups: indirect methods, which measure a physical property that can be functionally related to the extent of reaction, and direct methods, which measure the concentration of reactant or product species. Rheometry and thermal methods fall into the first group while titration and spectroscopy belong to the second.

Of the indirect thermal methods used to monitor the polymerization kinetics of polyurethanes, differential scanning calorimetry [3,4] (DSC) and adiabatic temperature rise [5–9] (ATR) have the advantage that they are simple. However, given the fact that urethane systems are mixing activated, DSC can only follow slow polyurethane reactions. ATR on the other hand, can follow fast polyurethane reactions. Nonetheless, ATR is still an indirect method and many assumptions have to be made to relate heat evolution to extent of reaction.

Of the direct methods used to monitor the polymerization kinetics of polyurethanes, spectroscopic techniques have the advantage that they can measure extent of reaction directly, are capable of monitoring fast reactions, and can monitor several chemical changes at once. However, the versatility of infrared (IR) spectroscopy is limited due to sample preparation requirements [6]. Even with the use of attenuated total reflectance techniques, IR spectroscopy is still limited in that special sample cells must be constructed [10]. In contrast, Raman spectroscopy has several advantages. These advantages include minimal required sampling volume, the ability to utilize glass and other closed containers for sample cells, and larger frequency ranges for spectral observation on one instrument. However, the first and foremost advantage in Raman spectroscopy is sample preparation. Since the Raman effect is a scattering process, samples of any shape or size can be examined. Moreover, Raman spectroscopy measurements can be conducted remotely using inexpensive, communications grade, fused-silica optical fibers. A theoretical background and mathematical treatment of Raman scattering have been developed by Grasselli [11] and Koenig [12].

These advantageous characteristics make Raman spectroscopy particularly useful for the in situ characterization of polymerization reactions where the removal of samples for off-line characterization is not always possible or practical. Since thermoplastic polyurethanes (TPUs) are produced continuously via reactive extrusion, the value of a versatile on-line characterization technique such as Raman spectroscopy becomes evident. The objective of this study is to characterize the kinetics of TPU polymerization in situ with Raman spectroscopy. More specifically, Raman

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spectroscopy will be used to acquire conversion versus time data from the polymerization of an uncatalyzed polyester based TPU formulation. Kinetics parameters extracted from such data will be compared to those obtained from analogous DSC experiments and literature values.

2. Experimental

2.1. Materials

The soft segment of the TPU used throughout this study was a hydroxyl terminated poly(butylene adipate) (PBA) oligomer supplied by Bayer. This diol had a number average molecular weight of approximately 2000 g/mol. The hard segments of the TPU were derived from 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO). MDI was supplied by Bayer while BDO was supplied by ARCO chemical company.

2.2. Sample preparation

In preparation for TPU synthesis, PBA was melted and dried under a vacuum at 100 °C for a minimum of 4 h while BDO was dried over type 3A molecular sieves at room temperature for at least 2 weeks prior to synthesis. MDI was used as received but was stored under a vacuum at 0 °C until required for synthesis.

The TPU was synthesized with a relatively low hard segment content, corresponding to equimolar quantities of PBA and BDO. Keeping the stoichiometric ratio of hydroxyl to isocyanate functionality at unity, the TPU contained 76.84% PBA, 3.536% BDO, and 19.62% MDI by mass (based on PBA with an equivalent number average molecular weight of 979.1 g/mol). Regardless of the polymerization environment, the ‘one-shot’ process was always the preferred route of TPU synthesis.

In this procedure, dewatered PBA (heated to 100 °C), BDO (at room temperature), and MDI (at room temperature) were gravimetrically metered into a 500 ml polypropylene beaker and vigorously hand mixed for 15 s. Having thoroughly mixed all TPU reactants, samples were removed and prepared for immediate kinetic analysis.

2.3. Raman spectroscopy measurements

A Kaiser Optical Systems Series 5000 Holoprobe Raman spectrometer was used to measure the kinetics of TPU polymerization. Equipped with a thermoelectrically cooled charge coupled device (CCD) detector, the system was capable of collecting spectra over a Raman shift spectral range of approximately 300–3300 cm^{-1}. A 100 mW, 785 nm GaAlAs diode laser was used as the excitation radiation source.

Using a 180° backscattering Raman measurement geometry, TPU reactant mixture samples approximately 1.0 mm in thickness were sandwiched between fused quartz cover slips and placed in a hot stage preheated to a specific isothermal polymerization temperature. Upon aligning the aperture of the hot stage, and thus the sample, with the focused Raman laser beam, a 30-s exposure time was used to generate a spectrum every 30 s. These isothermal experiments were terminated after 60 min. Isothermal polymerization temperatures of 100, 120, 140, and 160 °C were used to evaluate all kinetic parameters.

In preparation for quantitative analysis, all Raman spectra were processed with several chemometric spectral manipulation techniques using Grams/386 software from Galactic Industries Corp. In order to remove Raleigh/fluorescence induced background scattering, a best-fit, fourth order, polynomial baseline was subtracted from all spectra. Because Raman spectroscopy is a single beam method and because the number of scattering sites can never be known in the analysis of solids, all Raman spectra were normalized with respect to an internal standard. To this end, peak intensity of the 1612 cm^{-1} band was used. This band was the result of aromatic ring breathing/stretching vibrational modes present in the phenylene groups of MDI.

Peak height was used as a measure of peak intensity in this study. Although peak areas are most desirable, measurements can only be made in this way when the signal-to-noise (S/N) is very high, and the baseline is well defined. Small errors have a disproportionate effect on the final result using this method because all points in the spectral peak are given equal weight in the calculation. In contrast to peak area measurements, peak height measurements usually give the best results unless there is a significant change in peak shape with concentration. If such measurements are made at a peak’s maximum, the point of optimum S/N is used reducing errors attributed to random noise. However, since this type of measurement is sensitive to high frequency noise, all Raman signals were filtered accordingly.

2.4. Calorimetric measurements

A Thermal Advantage 2920 modulated differential scanning calorimeter operating in the isothermal mode was also used to measure the kinetics of TPU polymerization. In conducting these experiments, TPU reactant mixture samples were carefully weighed to 10 ± 2 mg and sealed in aluminum hermetic pans and lids. Upon placing a sealed sample into the DSC preheated to a specific isothermal temperature, heat flow resulting from the exothermic TPU polymerization reaction was measured as a function of time. After 60 min of isothermal polymerization, samples were immediately quenched to 0 °C at a cooling rate of -100 °C/min and then subjected to a temperature scan from 0 to 200 °C at a heating rate of 20 °C/min. This temperature scan was performed in an effort to quantify any residual heat of reaction not evolved in the previous isothermal scan and to ensure complete TPU polymerization. Isothermal polymerization temperatures of 100, 120, 140, and 160 °C were used to evaluate all kinetic parameters.

3. Results and discussion

3.1. TPU conversion from Raman spectroscopy

Quantitative kinetic analysis of a reacting system with Raman spectroscopy is based on measuring changes in peak intensity of bands belonging to characteristic reactant or product functional groups during the reaction period. Therefore, to elucidate which bands may be suitable for kinetic measurements on the TPU formulation investigated in this study, Fig. 1 shows partial Raman spectra of an uncatalyzed TPU reactant mixture after 1 min, 30 min, and 12 h ($\alpha \cong 1$) of polymerization at 120 °C. Tentative band assignments are made from reference to earlier Raman studies of polyesters [13–16], isocyanates [15,16], and urethanes [15,16] and are listed in Table 1. In principal, Raman scattering intensities of isocyanate (asymmetric stretch at 2275 cm^{-1} and symmetric stretch at 1445 cm^{-1}), hydroxyl, and urethane (N–H stretch, amide I at ca. 1732 cm^{-1}, amide II at ca. 1530 cm^{-1}, and amide III at ca. 1303 cm^{-1}) functional groups can all be used to determine the kinetics of polymerization for this particular TPU formulation. However, bands resulting from hydroxyl and urethane N–H stretching vibrations cannot be used for quantitative kinetic analysis since they are too small or fall outside of the Raman shift spectral range (ca. 300–3300 cm^{-1}) accessible in these experiments. Bands resulting from amide I vibrations in urethane linkages produced during TPU polymerization could be used for quantitative analysis, but these bands overlap those from carbonyl stretching vibrations present in the ester groups of PBA. This coupled with complications arising from H-bonding and low S/N ratios render quantitative measurements on bands from urethane amide I vibrations very difficult. Bands originating from urethane amide II and amide III vibrations are viable candidates for quantitative measurements, but they also suffer from multi-peak overlap and/or low S/N ratios.

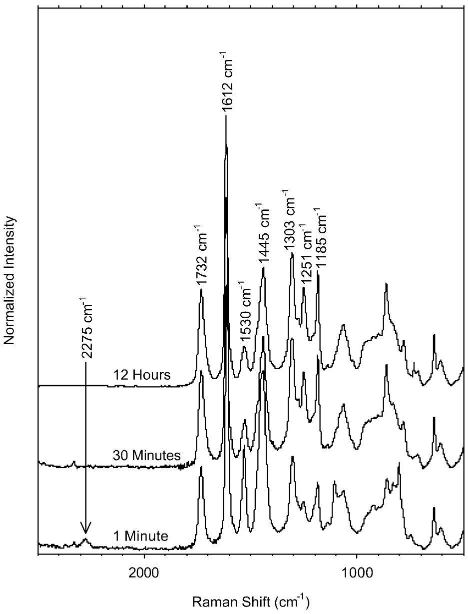

Fig. 1. Partial Raman spectra of the TPU reactant mixture polymerized at 120 °C for 1 min, 30 min, and 12 h.

Table 1
Tentative band assignments in the partial Raman spectra of TPU reactive mixture polymerized at 120 °C

Raman shift (cm^{-1})	Assignment
2275	$\nu_{\text{assym.}}$(N=C=O)
1732	Ester ν(C=O), urethane amide I ν(C=O)
1612	ν(Ar)
1530	ν(Ar), Urethane amide II: ν(C–N) + δ(N–H)
1445	$\nu_{\text{sym.}}$(N=C=O), δ(CH_2)
1303	δ(CH), urethane amide III?
1251	Urethane amide III?
1185	Urethane amide?

Of particular interest in Fig. 1 are the asymmetric and symmetric isocyanate stretching vibrations of MDI. Both of these bands noticeably decrease in intensity with polymerization time. Very strong in IR spectra, band intensity of the asymmetric isocyanate stretching vibration is quite weak in Raman spectra. This fact is clearly shown in Fig. 1 where this band is barely discernable from the baseline at a Raman shift of 2275 cm^{-1}. With such a low S/N, this band could not be used for kinetic analysis. The symmetric isocyanate stretching vibration can be observed as a medium intensity band at approximately 1445 cm^{-1}. Unfortunately, there is considerably overlap of this band with other bands resulting from CH_2 bending vibrations present in all reactants of the TPU formulation. Therefore, this band was not particularly tractable for kinetic analysis either.

As shown in Fig. 1, a band at 1530 cm^{-1} is similar to the isocyanate asymmetric and symmetric stretching vibrations in that its intensity decreases with increasing polymerization time. At room temperature, this band is clearly present in both the Raman and IR spectra of pure MDI as shown in

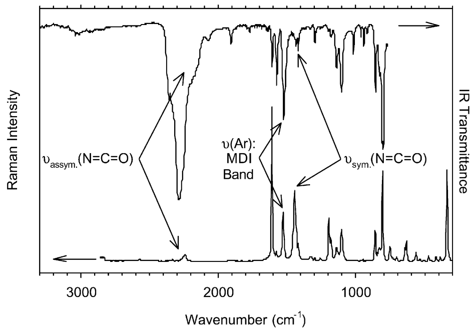

Fig. 2. Raman and IR spectra of pure MDI at room temperature.

Fig. 2. A careful review of the literature suggests that this band arises from *para* (4,4′-isomer) disubstituted phenylene ring vibrations in MDI [17]. Other studies involving band assignment in the Raman and IR spectra of phenyl isocyanate suggest that this band represents one of thirty fundamental C–C stretching vibrational modes present in the phenyl groups of monosubstituted benzenes [18,19]. Of the 30 fundamental frequencies for $C_6H_5{-}X$ type molecules, six vibrations are dependent on the mass of X. It is speculated that an analogous vibration is responsible for the 1530 cm^{-1} band in the phenylene rings of MDI. Regardless, peak intensity of the 1530 cm^{-1} band, hereon out termed the MDI band, was assumed directly proportional to the concentration of MDI, and thus isocyanate groups, not yet polymerized. Therefore, it was used for determining the polymerization kinetics of this TPU formulation.

Assuming peak height of the MDI band is a suitable measure of peak intensity, and thus concentration, the relationship between TPU conversion and MDI band peak height can be expressed as

$$\alpha(t) = \frac{I_0 - I(t)}{I_0} \tag{1}$$

where $\alpha(t)$ is the time-dependent TPU conversion, $I(t)$, the time dependent peak height of the MDI band, and I_0 is the peak height of this band at zero conversion. Because of the former assumption and the fact that all Raman spectra were normalized with respect to a conversion independent vibrational mode in MDI itself, a method of external calibration was not used in this study.

The step growth polymerization of this TPU formulation results in the formation of urethane linkages. These urethane linkages in turn contain C–N stretching and N–H bending vibrations that are Raman active. Unfortunately, these amide II vibrational modes generate scattering at a Raman shift of approximately 1530 cm^{-1}. Shown in Fig. 1 after 12 h of polymerization time at 120 °C ($\alpha \cong 1$), these vibrations generate weak yet significant bands in the Raman spectrum of fully polymerized TPU. As a result, Eq. (1) must be modified to account for a growing amide II band at approximately the same Raman shift as the MDI band.

Assuming peak height of the 1530 cm^{-1} band is a time dependent sum of both MDI and amide II bands and that peak height of the latter band is directly proportionally to conversion, peak height of the MDI band can be written as

$$I(t) = S(t) - A_\infty \alpha(t) \tag{2}$$

where $S(t)$ represents the experimentally measured, time-dependent peak height of the composite 1530 cm^{-1} band and A_∞ is peak height of the amide II band at complete conversion. Substituting Eq. (2) into Eq. (1) results in

$$\alpha(t) = \frac{I_0 - [S(t) - A_\infty \alpha(t)]}{I_0} \tag{3}$$

After realizing that I_0 equals the composite 1530 cm^{-1} band at zero conversion (ca. 0.40), S_0, and A_∞ equals the composite 1530 cm^{-1} band at complete conversion (ca. 0.12), S_∞, Eq. (3) can be rearranged and solved for conversion. This expression

$$\alpha(t) = \frac{S_0 - S(t)}{S_0 - S_\infty} \tag{4}$$

was used to calculate TPU conversion data from Raman spectra acquired over the course of an experiment.

The symbols in Fig. 3 show conversion versus polymerization time profiles calculated from Eq. (4) applied to chemometrically processed Raman spectra of uncatalyzed TPU reactant mixtures polymerized at various temperatures. As expected, higher polymerization temperatures result in higher conversion rates and final conversions after 30 min of polymerization time. The scattering of data points in Fig. 3 is due to noise in Raman spectra and to errors introduced into the calculation method (i.e. baseline subtraction, normalization, peak height measurement), which are usually inevitable in the quantitative analysis of Raman spectra, especially in kinetic studies.

3.2. TPU conversion from calorimetry

After completing a temperature scan on a particular sample, TPU conversion versus time data was extracted from the corresponding isothermal scan through application of the proper energy balance. Assuming a constant enthalpic heat of reaction, no significant interference from side reactions, and heat evolved during polymerization was proportional to the extent of polymerization, conversion as a function of time was calculated from

$$\alpha(t) = \frac{\Delta H_1 + \Delta H(t)}{-(\Delta H_{\mathrm{rxn.}})} \tag{5}$$

where ΔH_1 is the molar enthalpic heat of reaction lost during sample preparation, sample loading, and DSC stabilization, $\Delta H(t)$, the time dependent TPU polymerization exotherm measured in an isothermal scan, and $\Delta H_{\mathrm{rxn.}}$ is the total molar enthalpic heat of reaction for TPU step growth polyaddition which was assumed constant for all isothermal polymeriz-

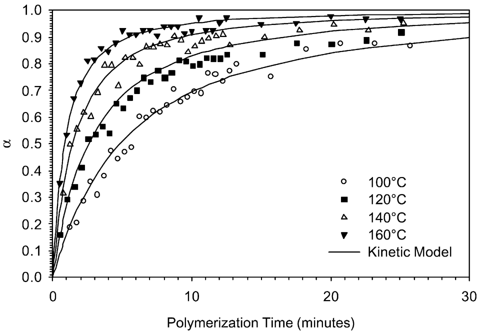

Fig. 3. Experimental and predicted isothermal Raman conversion versus time profiles for the TPU reactant mixture polymerized at different temperatures.

ation temperatures. ΔH_l was calculated from the relation

$$H_l = -(\Delta H_{\mathrm{rxn.}}) - \Delta H_t - \Delta H_r \quad (6)$$

where ΔH_t is the total TPU polymerization exotherm measured in an isothermal scan and ΔH_r is the residual molar enthalpic heat of reaction measured in subsequent temperature scan experiments.

Since TPU step growth polymerization is mixing activated and thus starts with sample preparation, sample loading, and DSC stabilization, DSC was not able to measure exothermic heat flow from the entire course of reaction. Therefore, $\Delta H_{\mathrm{rxn.}}$ was measured from independent ATR experiments. In these experiments, the temperature rise of a highly catalyzed, bulk TPU polymerization was followed under quasi-adiabatic conditions. A combination of short total reaction times, fast rate of temperature rise during the major portion of the reaction, and slow heat loss due to low thermal conductivity of the TPU itself ensured that reaction conditions were close to adiabatic. In relating maximum temperature rise to the molar enthalpic heat of reaction for this TPU formulation, $\Delta H_{\mathrm{rxn.}}$, the following assumptions were made: the TPU reactant mixture was homogeneous, the polymerization was not limited by diffusion, there were no other heat sources other than the polymerization reaction, and density and $\Delta H_{\mathrm{rxn.}}$ were constant. Under these assumptions, the overall energy balance for a single irreversible polymerization reaction, excluding heat loss is

$$C_p \frac{\mathrm{d}T}{\mathrm{d}t} = -(\Delta H_{\mathrm{rxn.}}) \frac{\mathrm{d}\alpha}{\mathrm{d}t} [\mathrm{NCO}]_0 \quad (7)$$

where C_p is the heat capacity per unit mass, T the experimentally measured temperature, α the conversion, and $[\mathrm{NCO}]_0$ is initial isocyanate molality.

If we eliminate time from both sides of Eq. (7) and assume $\alpha \rightarrow 1$, we can integrate the resulting differential equation to solve for $\Delta H_{\mathrm{rxn.}}$ as a function of maximum temperature rise. Hence,

$$-(\Delta H_{\mathrm{rxn.}}) = \frac{1}{[\mathrm{NCO}]_0} \int_{T_0}^{T_f} C_p(T)\mathrm{d}T \quad (8)$$

where T_0 and T_f are initial and final TPU reactant mixture temperatures, respectively. If $C_p(T)$ is assumed to be a linear function of temperature and changes very little with conversion from monomer to polymer as is the case for amorphous polymers [20], simple weight average additivity of TPU reactant heat capacities can be used to calculate $C_p(T)$. Using data obtained from Steinle et al. [7], the $C_p(T)$ relation used for the TPU reactant mixture formulation in this study was

$$C_p(T) = 0.9634 + 0.002776T \quad (9)$$

In Eq. (9), T is in Kelvin to obtain C_p values in kJ/kg K. For the catalyzed TPU formulations investigated here, the average ATR was approximately 67 °C. This leads to an average $\Delta H_{\mathrm{rxn.}}$ of -90 kJ/mol equiv. isocyanate, which is in excellent agreement with the value obtained by other investigators [5–9] studying similar systems.

The symbols in Fig. 4 show conversion versus polymerization time profiles calculated from Eq. (5) applied to isothermal DSC scans of uncatalyzed TPU reactant mixtures polymerized at various temperatures. Overall, conversion versus polymerization time profiles obtained from calorimetry correlated reasonably well with those obtained from Raman spectroscopy obtained at the same isothermal polymerization temperature (Fig. 3).

3.3. Kinetic parameter determination

Elemental kinetic mechanisms describing urethane formation from active hydrogen bearing compounds and isocyanates are not well understood. Due to the complexities of urethane reaction mechanisms, most studies have adopted the following Arrhenius type, phenomenological rate law with success [21].

$$\frac{\mathrm{d}[\mathrm{NCO}]}{\mathrm{d}t} = -k[\mathrm{NCO}]^a[\mathrm{OH}]^b \quad (10)$$

where

$$k = A\,\mathrm{e}^{-E_a/RT} \quad (11)$$

In Eq. (10), k is the rate constant and [NCO] and [OH] are the concentrations of isocyanate and active hydrogen bearing compounds, respectively. Similarly, the exponents a and b represent the order of reaction with respect to isocyanate and active hydrogen bearing compounds, respectively. As shown in Eq. (11), k is most often expressed with Arrhenius type temperature dependence where A is a frequency factor, E_a is activation energy, R is the universal gas constant, and T is temperature in Kelvin. It should be noted that Eq. (10) is not a mechanistic model. It has only one rate constant with a single activation energy to express a multitude of reaction mechanisms and rates of reaction.

If we assume the urethane reaction is run at equal stoichiometry (i.e. $[\mathrm{C}] = [\mathrm{NCO}] = [\mathrm{OH}]$) and express concentration in terms of conversion (i.e.

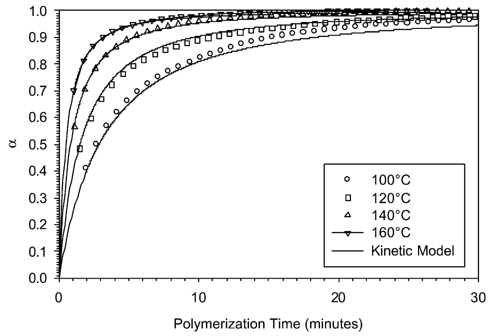

Fig. 4. Experimental and predicted isothermal DSC conversion versus time profiles for the TPU reactant mixture polymerized at different temperatures.

$[C] = [C]_0(1 - \alpha))$, Eq. (10) can be rewritten as

$$\frac{d\alpha}{dt} = k[C]_0^{n-1}(1 - \alpha)^n \tag{12}$$

where $[C]_0$ is equal to initial isocyanate or active hydrogen bearing compound concentration and $n = a + b$ is the overall order of reaction.

In order to calculate kinetic parameters for this TPU formulation polymerized at different temperatures, the data in Figs. 3 and 4 was fitted to the kinetic rate law model described by Eqs. (11) and (12) with least squares linear regression techniques. In determining the kinetic parameters k and n from the spectral data, significant data scatter eliminated the possibility of reliably evaluating $d\alpha/dt$. Therefore, the differential equation described by Eq. (12) was solved via the separation of variables technique and rearranged into the following form

$$-\frac{(1 - \alpha)^{-n+1}}{-n + 1} = -\frac{1}{-n + 1} + k[C]_0^{n-1}t \tag{13}$$

The left-hand side of Eq. (13) was then calculated from the conversion data in Fig. 3 and plotted versus respective polymerization time for different values of n. The value of n resulting in linear curves, which corresponded to the overall order of reaction, was found to be 1.7 for all four polymerization temperatures investigated. The resulting curves calculated with $n = 1.7$, which have slopes equal to $k[C]_0^{n-1}$ and y-intercepts equal to $-1/(-n + 1)$, are shown in Fig. 5. Using least squares linear regression, each curve was fitted with a regression line and a value of k was found for each polymerization temperature.

In determining the kinetic parameters k and n from the calorimetric data, log–log plots of $d\alpha/dt$ versus $(1 - \alpha)$ were constructed from the conversion data in Fig. 4 and are shown in Fig. 6. Using least squares linear regression, the linear portion of each curve was fitted with a regression line and a value of n and k was found for each polymerization temperature. Regardless of polymerization temperature, an overall order of reaction of 1.7 afforded the best fit to all the data.

It should be noted that only the Arrhenius controlled conversion regime (i.e linear portion) of the curves in Figs. 5 and 6 were fitted with a regression line. Past a critical conversion, which increases with temperature, hard segment phase separation from the reactant mixture results in diffusion controlled kinetics and hence a deviation from the kinetic model described by Eqs. (11) and (12). This is especially evident in Fig. 6 at 100 °C. Such an effect could significantly influence the TPU polymerization exotherm and thus introduce errors into the calculation of conversion from Eq. (5).

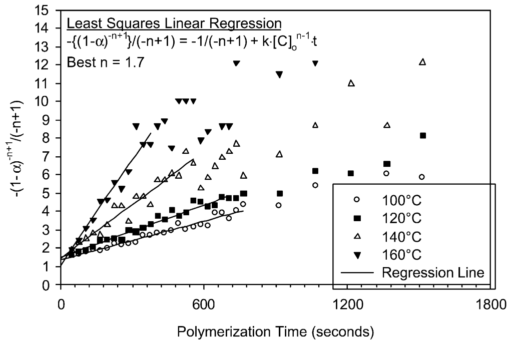

Fig. 5. Plots of Raman $-\{(1 - \alpha)^{-n+1}\}/(-n + 1)$ versus time for the TPU reactant mixture polymerized at different temperatures.

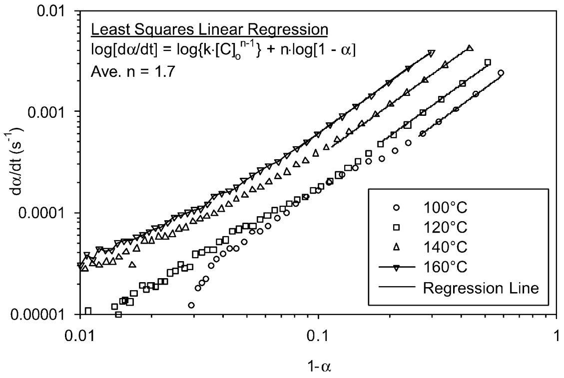

Fig. 6. log–log plots of DSC conversion rate versus conversion remaining for the TPU reactant mixture polymerized at different temperatures.

Next, values of k from the linear regression analyses in Figs. 5 and 6 were used to calculate the Arrhenius kinetic parameters A and E_a from both the spectral and calorimetric data, respectively. Assuming the kinetic rate law model given by Eq. (12) is valid and n remains constant throughout the entire reaction, a semi-ln plot of k versus $1/T$ should yield a straight line with slope equal to $-E_a/R$ and y-intercept equal to $\ln[A]$. Indeed, as shown in Fig. 7, values of k obtained from the two sets of data do form linear curves when plotted versus $1/T$ and almost coincide showing that the two different measurement techniques yielded similar results. The Arrhenius parameters A and E_a were evaluated from the least squares linear regression lines also shown in Fig. 7. Table 2 lists all kinetic parameters calculated for the step growth polymerization of this TPU formulation and Figs. 3 and 4 show the corresponding model predictions.

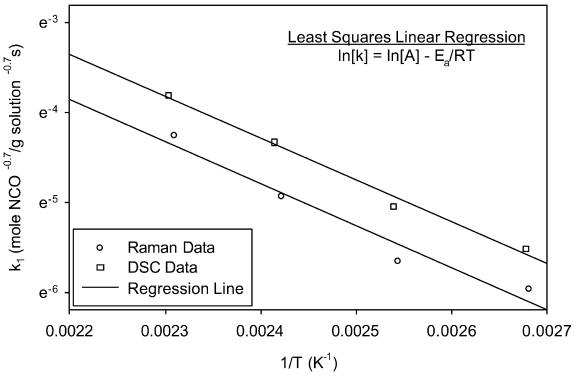

Fig. 7. Evaluation of A and E_a/R from semi-ln plot of Raman and DSC k versus $1/T$ data for TPU reactant mixtures polymerized at different temperatures.

Table 2
Listing of kinetic parameters obtained from TPU investigated in this study $\mathrm{d}[\mathrm{C}]/\mathrm{d}t = -A\,\mathrm{e}^{-E_a/RT}[\mathrm{C}]^n$

Characterization technique	A (mole NCO$^{-0.7}$/kg solution$^{-0.7}$ s)	E_a (J/mol)	n
Raman	$6.02 \times 10^2 \pm 1.62 \cdot 10^2$	$3.87 \times 10^4 \pm 5.73 \times 10^3$	1.7
DSC	$9.92 \times 10^2 \pm 1.18 \times 10^2$	$3.87 \times 10^4 \pm 2.74 \times 10^3$	1.7

Note: [C]=[NCO]=[OH] has units of mole/kg.

In summary, both Raman spectroscopy and DSC yielded similar results when used to measure the kinetics of TPU polymerization. Both measurement techniques yielded 1.7 for the overall order of reaction, n. This is in agreement with almost all urethane reaction kinetic data in the literature, where n varies from 1 to 2 [9,21]. For example, using isothermal and non-isothermal DSC, Hager et al. [3] calculated n to be 2.0 while Hernandez-Sanchez and Vera-Graziano [4] calculated n to be 1.63, respectively. Utilizing the ATR measurement technique, Lipshitz and Macosko [5] calculated n to be 1.5 while Camargo et al. [8] calculated n to be 1.4.

The activation energy, E_a, calculated from both measurement techniques was approximately 3.9×10^4 J/mol, which is general agreement with the literature. For example, Hager et al. [3] calculated E_a to be 4.1×10^4 J/mol with isothermal DSC and Camargo [9] calculated E_a to be approximately be 5.5×10^4 J/mol with ATR. Incidentally, values of E_a closer to that obtained by Camargo [9] are obtained from both measurement techniques if the 100 °C data in Fig. 7 is not included. As previously discussed, it is probable that micro-phase separation results in a significant deviation from Arrhenius controlled reaction kinetics at this temperature. A deviation from the kinetic model described by Eqs. (11) and (12) caused by urethane bond thermal dissociation is also possible. Several publications [22–24] have shown that this process starts at 150–160 °C and becomes significant at 190–200 °C. In this study, it is assumed that such depolymerization is insignificant at all of the temperatures investigated. Given the linearity of the data in Fig. 7 at 120, 140, and 160 °C, this assumption appears reasonable.

The frequency factor, A, obtained from DSC is approximately 50% larger than that obtained from Raman spectroscopy. While both are in general agreement with literature values for uncatayzed TPU systems [3], this disparity probably results from errors introduced into the calculation of conversion (i.e. baseline subtraction and normalization in Raman spectroscopy and the calculation of $\Delta H_{\mathrm{rxn.}}$ in DSC) from both measurement techniques. Another probable source for this difference comes from the fact that Raman spectroscopy is a direct (i.e. measures reactant concentration) technique while DSC is an indirect (i.e. measures heat evolution) technique. Differences in measurement technique sample geometry and preparation could also be significant. Regardless, kinetic parameters obtained from both measurement techniques agreed favorably with classical literature values [3–9] proving that Raman spectroscopy is a useful method for characterizing the kinetics of polyurethane polymerization.

4. Conclusions

Peak intensity of a band in MDI was assumed proportional to isocyanate concentration and thus conversion in the polymerization of this TPU formulation. Given the capability to calculate conversion from Raman spectra acquired over the course of an experiment, conversion versus time data was collected from the isothermal polymerization of this TPU formulation at different temperatures. Such data was modeled with an Arrhenius type, phenomenological rate law with success. Kinetic parameters agreed reasonably well with those obtained from analogous calorimetric measurements and with literature values. Since the Raman effect is a scattering process, sample preparation is relatively simple compared to other spectroscopic techniques. Hence, it can be concluded that Raman spectroscopy is a powerful tool for characterizing the polymerization kinetics of polyurethanes in situ.

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