Hydrogen Bonding in Polyurethanes: Preliminary Results of Simultaneous DSC-FTIR Experiments

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**Title:** Hydrogen Bonding in Polyurethanes: Preliminary Results of Simultaneous DSC-FTIR Experiments

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**Abstract:**
The hydrogen bonding behavior of segmented polyurethane elastomers and model hard segment compounds has been examined by performing simultaneous Differential Scanning Calorimeter (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) measurements. In model hard segments of 4,4'-diphenylmethane diisocyanate (MDI) extended with [2,2,3,3-d4] butanediol (BDO), and 2,4-toluenediisocyanate also chain extended with BDO, the spectra show a linear decrease in the apparent degree of hydrogen bonding over most of the temperature range. In the case of...
-MDI-BDO, there is thus no clear correlation between DSC multiple endotherms and the degree of hydrogen bonding. Examination of an elastomer containing 70% bwt. of MDI/BDO hard segment and polyether soft segment however reveals a transition in the degree of hydrogen bonding coincident with an endotherm whose origin has been previously ascribed to the onset of a microphase mixing transition. This result clearly demonstrates that thermally induced morphological changes can affect markedly the hydrogen bonding behavior of polyurethanes. The study also illustrates that chemical changes occur during a typical DSC thermogram. In particular, reversal of the polyurethane reaction equilibrium is evidenced by emergence of an isocyanate absorption band at high temperatures for all materials.
HYDROGEN BONDING IN POLYURETHANES: PRELIMINARY RESULTS
OF SIMULTANEOUS DSC-FTIR EXPERIMENTS

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Investigations concerning the development of structure-property relations for polyurethane elastomers have frequently focused on elucidating the influence of hydrogen bonding on material properties. The N-H group of the urethane linkage serves as the proton donor, while possible proton acceptors include the carbonyl or adjacent oxygen of the urethane, the ether oxygen of a polyether soft segment, or the ester carbonyl of a polyester soft segment. The nature of hydrogen bonding in polyurethanes has been studied extensively using infrared spectroscopy.\textsuperscript{1-10} The infrared vibrational spectra of hydrogen-bonded groups show absorbance bands composed of two contributions attributed to either "bonded" or "free" groups. Bands corresponding to hydrogen-bonded groups exhibit characteristic changes in frequency, breadth, and adsorption coefficient that may be related to the intergroup distance and strength of the donor-acceptor complex.\textsuperscript{11-14} There have consequently been many attempts to attribute changes in spectral features to changes in the microdomain morphology. The intensity ratios of bonded to non-bonded absorbance bands, for example, have been related to the degree of microphase separation\textsuperscript{4,10,15} under the assumption that donor groups dissolved within the soft segment do not form hydrogen bonds. The degree of hydrogen bonding defined in this fashion has been found to be insensitive to strain\textsuperscript{7} but dependent on temperature.\textsuperscript{4-6,8,9}

The temperature dependence of infrared spectra, particularly in the N-H stretching region, forms the basis of a number of methods for estimation of the thermodynamic parameters of hydrogen-bond equilibria.\textsuperscript{5,8} A recent communication\textsuperscript{12} discussed the validity of these procedures, and demonstrated that van't Hoff plots are inappropriate for evaluating the enthalpy and
entropy changes for hydrogen bond dissociation. This conclusion was reached based upon the observation that absorption coefficients are strongly dependent on the band frequency and therefore on the temperature. For bulk polyurethanes however there is an additional objection to the application of these procedures, that being their inherent non-equilibrium nature. We have shown recently for example that the morphology, crystallinity, and thermal properties of polyurethanes are subject to strong thermal history effects.\textsuperscript{16,17} The so-called equilibrium temperature dependence of hydrogen bond dissociation therefore cannot be distinguished from thermally-induced morphological changes.

In the present communication, we demonstrate the effects of morphological transitions by performing Fourier Transform Infrared (FTIR) spectroscopic analysis of hydrogen bond dissociation concurrently with the collection of a Differential Scanning Calorimeter (DSC) thermogram. In addition to providing the capability for correlating thermal and morphological transitions, the infrared spectra also reveal any chemical changes that may occur.

**Experimental**

The segmented polyurethane block copolymer (PU-70) studied was obtained from Union Carbide.\textsuperscript{18} Sample purification and molding procedures have been described previously.\textsuperscript{16,17} This material contains 70\% by weight of hard segments comprised of 4,4'-diphenylmethane diisocyanate (MDI) and butane diol. The soft segments are composed of 2000 molecular weight polyoxypropylene end-capped with 30\% by weight oxyethylene. Two hard-segment model compounds were prepared by standard synthesis procedures,\textsuperscript{19} based upon 2,4-toluene diiso-
cyanate (TDI) and MDI (Kodak) with tetradeutero butane diol (Merck & Co.),
HO-CH₂-CD₂-CD₂-CH₂-OH, (d₄-BD). All specimens were thermally conditioned by
holding at 240°C for 1 minute, rapidly cooling to 150°C, annealing at that
temperature for 30 minutes, followed by rapid cooling to room temperature.
The thermal conditioning was carried out in a Mettler FP80/82 Thermal
Microscopy Hot Stage. Specimens were subsequently mounted in a Mettler
FP80/82 cell for the simultaneous DSC-FTIR measurements. The DSC was mounted
in an IBM 98 FTIR such that the IR beam passed through the hole in the
microscope stage. It was not possible to obtain a direct DSC thermogram from
the infrared specimen due to the requirement of a thin film for the FTIR
transmission experiment. To circumvent this problem, two specimens were used
for each DSC-FTIR measurement. The first specimen consisted of a thin polymer
film (~ 1-2 mg) coated onto a 6 mm by 1 mm KBR disk (Harrick) by slow solvent
evaporation from solutions in either tetrahydrofuran or dimethyl formamide.
This specimen was mounted over the sample position of the DSC cell, through
which the IR beam passed. The second specimen was a bulk specimen (~ 20 mg)
encased in a standard aluminum DSC crucible and placed in the reference posi-
tion of the DSC cell. Both specimens were preconditioned simultaneously, and
in principal experienced identical thermal cycles throughout the experiment.
The DSC signal is thus furnished by the reference specimen while the FTIR
spectra are recorded simultaneously from the sample specimen. The DSC-FTIR
experiment was carried out at a scan rate of 10°C per minute in vacuum.
Temperature calibration was accomplished with indium and phenacetin standards.
The DSC thermograms were recorded with a Bascom-Turner Model 4120 digital
recorder and were not corrected for baseline effects. The spectral resolution
was 4 cm$^{-1}$ and each spectra was averaged 20 times, corresponding to a temperature span of ca. 5°C per spectrum.

Results and Discussion

TDI/d$_4$-BD

The 2,4-TDI-(d$_4$-BD) copolymer is completely amorphous. The hydrogen bonding behavior should consequently be independent of any morphological effects. Previous DSC thermograms for these copolymers exhibit only a single glass transition at 73°C.$^{20}$ The DSC thermogram for TDI/d$_4$-BD (Figure 1) is similarly quite featureless except for the onset of a broad endotherm near 100°C. This apparent transition cannot be associated with either a melting point (the material is non-crystalline) or glass transition temperature. One explanation for this behavior, although speculative at this time, is the release of adsorbed water from the material. It is well known that non-crystalline polyurethanes absorb significant amounts of water. During a DSC scan under vacuum conditions, as in the present study, it is possible that rapid water desorption might occur at elevated temperatures thereby imparting some endothermic character to the thermogram, as visible in Figure 1. A second alternative explanation would be sample flow leading to a different effective thermal contact area on the DSC sensor. Flow effects are accentuated for the present experimental geometry by the fact that the sample is pressed sideways against the sensor rather than being held on top of the sensor as in the conventional DSC experiment.

The spectra collected simultaneously with the thermogram do not show any evidence that would indicate the occurrence of a transition at ca. 100°C. The
integrated absorbances of the NH, C=O, C-H, and C-D bands show only gradual changes throughout this temperature range. The obvious decrease in magnitude of the N-H absorbance can be attributed to dissociation of hydrogen bonds as the temperature increases. Previous workers have demonstrated that the absorptivity of the free N-H group is much lower than that of the hydrogen bonded group. The total integrated absorbance therefore decreases as the fraction of free N-H groups increase. This interpretation is supported by the spectral data presented in Figure 2 for the temperature dependence of the N-H absorbance bands. As can be seen from the figure, increasing temperature causes a continuous shift in the spectra from the bonded N-H peak at 3310 cm\(^{-1}\) to the free N-H peak at 3450 cm\(^{-1}\), and an overall decrease in absorbance. The diminution of integrated N-H absorbance (Fig. 1) is approximately linear with temperature up to ca. 180°C. A similar but less pronounced trend is evident for the integrated carbonyl absorbance. The carbonyl spectra (not shown) also display a gradual shift from the bonded C=O peak at 1708 cm\(^{-1}\) to the free C=O peak at 1735 cm\(^{-1}\) as temperature is raised within this range.

Above 180°C, the DSC thermogram shows a transition to slight exothermic behavior which is reflected as a change in slope of the integrated absorbances. Closer examination of the spectral data reveals that the DSC response can be attributed to two related phenomena. The first is reversibility of the urethane reaction, which is indicated by rapid falloff in the N-H and C=O integrated absorbances and emergence of the isocyanate band (NC=O) at 2270 cm\(^{-1}\). The second is the possible loss of material as evidenced by the slight decrease in the integrated C-H absorbance above 180°C. Material loss could occur if urethane reversal led to the formation of free butanediol which is volatile at 180°C under vacuum conditions.
The spectra in Figure 3 demonstrate clearly the reversibility of the urethane reaction. Below 180°C, two bands are visible at 2215 cm⁻¹ and 2130 cm⁻¹. These may be attributed to the C-D₂ stretching vibrations of the d₄-butanediol residue. Above 180°C, the NC=O bond appears at 2270 cm⁻¹. In addition, there is an apparent tradeoff in intensities between the C-D bands at 2215 cm⁻¹ and 2130 cm⁻¹.

Reversibility of the urethane reaction has also been observed in recent studies of monodisperse model hard segments. Above temperatures of ca. 180°C, the materials were found to randomize to form polydisperse compounds. The postulated mechanism for this process is a rearrangement reaction referred to as transurethanification.

MDI/d₄-BD

The MDI/d₄-BD copolymer is known to crystallize into a number of polymorphic structures. DSC studies have generally documented multiple endotherms that have been attributed to melting of individual polymorphs or transformation between polymorphs by a melt-recrystallization process. The DSC thermogram (Figure 4) for MDI/d₄-BD shows both crystallization and multiple endothermic behavior. The first feature visible at ca. 105°C is not reproducible, and may be attributed to sample flow at the glass transition temperature (110°C). All other features of the thermogram are qualitatively reproducible. A crystallization exotherm at ca. 155°C is followed by endotherms at ca. 180°C, 195°C, and 215°C.

It is surprising to note that, within experimental error, the integrated absorbance data for MDI/d₄-BD (Fig. 4) are insensitive to any of the apparent morphological changes suggested by the DSC thermogram. The decrease in N-H
absorbance is linear in temperature up to ca. 215°C, similar to the behavior of the non-crystalline TDI/d₄-BD hard segment. The N-H spectra (Fig. 5) show only a gradual shift from the hydrogen bonded to free species up to 220°C.

Above ca. 215°C, the DSC thermogram shows exothermic character. The accompanying decrease in C-H, N-H, and C=O absorbance coupled with the appearance and growth of the N-C=O band, are again indicative of reversal of the urethane reaction and the associated loss of volatile material. This "degradation" temperature is approximately 35°C higher than that for TDI/d₄-BD, and is coincident with onset of the highest temperature endotherm. Clearly, crystallization appears to stabilize the urethane bond. The question arises however as to why the non-crystalline fraction of material does not begin to degrade at 180°C. The urethane linkage may be intrinsically more stable in MDI/d₄-BD as compared to TDI/d₄-BD; or alternatively, the "non-crystalline" fraction in MDI/d₄-BD may be low. Additional experiments carried out as a function of annealing conditions may provide further insight into this important question.

PU-70

The hydrogen bonding behavior of PU-70 is potentially more complex than that of either MDI/d₄-BD or TDI/d₄-BD. In addition to possible polymorphic crystal structures in the MDI/BD hard segment component, there may be consequences due to incompleteness of the microphase separation between soft and hard segments. Indeed, these latter effects may also be temperature dependent. The DSC thermogram of PU-70 (Figure 6) however is actually less complex than that of MDI/d₄-BD, consistent with previous investigations of this material.¹⁶,¹⁷
A hard segment glass transition is not detectable, however the onsets of two endotherms are found at 175°C and ca. 195°C. Simultaneous DSC/X-ray experiments suggested that the 175°C endotherm was associated with the onset of intersegmental mixing, while the 195°C endotherm could be ascribed to the melting of microcrystalline hard segments. The DSC-FTIR results fully support this interpretation.

The onset of intersegmental mixing determined from the DSC/X-ray results is denoted by the vertical arrows in Figure 6. The arrows are coincident with a weak DSC endotherm, and a change in slope of the integrated N-H absorbance plot. The more rapid decline in N-H absorbance above 175°C is consistent with additional hydrogen bond disruption due to intersegmental mixing. Reversal of the urethane reaction, evidenced by the appearance of the N C=O absorbance band and slight decreases in the C=O and C-H absorbances, occurs during the 215°C endotherm. Comparison with the MDI/d4-BD behavior suggests that this endotherm is associated with hard segment melting.

Inspection of the spectra for PU-70 provides additional support for these assignments. The N-H spectra (Figure 7) show a very gradual shift from bonded to free species up to a temperature of ca. 170°C after which there is a rapid shift to free N-H. This trend is more clearly apparent from the C=O spectra in Figure 8. The bonded C=O band (1705 cm⁻¹) intensity diminishes only slightly up to ca. 165°C after which the band intensity falls off markedly. The spectra confirm that hydrogen bond dissociation occurs rapidly above ca. 170°C consistent with the onset of intersegmental mixing at that temperature.

These results clearly demonstrate the tremendous potential that simultaneous FTIR/DSC measurements offer for furthering the understanding of the
complex thermal behavior in multiphase polymer systems. The technique is not only sensitive to morphological changes, but in addition furnishes the simultaneous capability for monitoring any chemical changes that may occur. In the particular case of the polyurethanes, the technique can easily distinguish morphological transitions related to microphase separation, but appears to be insensitive to crystallization and/or melting transitions within the hard microdomain. It should be emphasized however that the experimental conditions were not optimized, and that the spectral data were not fully analyzed. A vast improvement in the signal-to-noise ratio, for example, could be attained through the use of a microsampling device such as a beam condenser. More precise spectral data in turn will enable the application of sophisticated analyses such as peak deconvolution in order to determine quantitative spectral features such as frequency shifts, half-widths, and peak absorbances. This new information will undoubtably contribute immensely to our knowledge and understanding of the complex thermal behavior of segmented polyurethane block copolymers.

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References


22. C. W. Macosko, private communication.


Figure Captions

Fig. 1. Simultaneous FTIR-DSC results for TDI/d$_4$-BD.

Fig. 2. Temperature dependence of the N-H spectral region of TDI/d$_4$-BD recorded during the DSC scan.

Fig. 3. Temperature dependence of the C-D$_2$ and NC=O absorbance bands during the DSC scan for TDI/d$_4$-BD.

Fig. 4. Simultaneous FTIR-DSC results for MDI/d$_4$-BD.

Fig. 5. Temperature dependence of the N-H spectral region of MDI/d$_4$-BD recorded during the DSC scan.

Fig. 6. Simultaneous FTIR-DSC results for PU-70. The vertical arrows denote the onset of intersegmental mixing detected in previous X-ray scattering measurements.$^{17}$

Fig. 7. Temperature dependence of the N-H spectral region of PU-70 recorded during the DSC scan.

Fig. 8. Temperature dependence of the C=O absorbance band during the DSC scan for PU-70.
Fig. 1
Fig. 3
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