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# Far-Infrared Study of Hydrogen Bonding in a Semicrystalline Polyurethane

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ABSTRACT: We have used far-infrared spectroscopy to probe the hydrogen bond vibrational mode of a semicrystalline polyurethane. We assign this vibration to a broad band appearing at 101 $cm^{-1}$ in amorphous samples and 107 $cm^{-1}$ in highly ordered samples. Using a rigid-body approximation, we calculate force constants associated with the hydrogen bond stretching to be 0.52 and 0.58 mdyn/Å for the two forms, respectively. In oriented samples, the band shows the appropriate perpendicular dichroism. The band shows sensitivity to both molecular order and temperature. We also assign a band located at 320 $cm^{-1}$ to a O–C–NH–C bending mode coupled to the methylene chain bending. This band also shows sensitivity to chain conformation and packing as well as having high parallel dichroism in oriented samples.

## Introduction

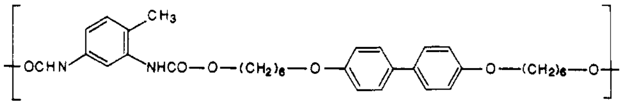
Hydrogen bonding is usually considered the strongest secondary force in the solid state of polymers. The specificity and magnitude of this type of interaction may strongly influence both chain conformation and packing. Because of the importance of hydrogen bonding, its character and its effect on molecular structure and properties have been the topic of numerous studies.[1,2] The hydrogen bond is an essential component of the structure of natural proteins and synthetic polyamides as well as small-molecule association phenomena, intramolecular ring closure, and catalysis.

Due to the incompatibility between the hard and soft segments, polyurethane copolymers undergo microphase separation resulting in hard-segment-rich domains, a soft-segment-rich matrix, and an interphase between them.[3] It is generally accepted that the strength and the elastic behavior of polyurethanes are directly related to the stability of the hydrogen-bonded hard-segment-rich domains, acting as junction points in the network. Extensive research on interurethane hydrogen bonds, based on mid-IR absorption, has been carried out.[4-18] In these studies, the hydrogen bonding characteristics have mainly been interpreted from the observed frequency shifts, either of the NH group or of the C=O group. However, the vibrations between the NH and C=O group which are located in the far-infrared region have attracted comparatively little attention. Direct analysis of the low-frequency vibrations of the hydrogen bonds in synthetic polymers is rare. The most extensive studies have been given to a series of polyamides.[19] To date, we know of no such equivalent studies in polyurethanes.

In this study we present far-infrared spectra of a semicrystalline polyurethane. Among the rich features observed, our results indicate that the band around 105 $cm^{-1}$ can be assigned to a hydrogen bond stretching vibration between the NH and the C=O groups. Its spectroscopic characteristics are sensitive both to the perfection of molecular packing and to temperature changes. In oriented samples it exhibits strong perpendicular dichroism, consistent with its assignment. The band observed at 320 $cm^{-1}$ is assigned to the O–CO–NH–C bending mode coupled with methylene chain bending. It also shows a strong spectroscopic dependence on sample packing and shows high parallel dichroism in oriented samples.

## Experimental Section

The chemical repeat unit of the polyurethane is as follows:



The synthesis and physical characterization of this polymer has been reported elsewhere.[20] The 2,4-toluenediisocyanate (24TDI) used in preparing the polymer was distilled from purified 24TDI (Fluka) to preclude artifacts due to the presence of 2,6-toluenediisocyanate commonly found in commercial 24TDI. The sample polymer used in this study had an intrinsic viscosity of 0.6 and a $M_n$ of 100K, with a polydispersity of 1.6 relative to polystyrene standards as determined by gel permeation chromatography with dimethylacetamide as the eluting solvent. The samples used in our spectroscopic experiments were prepared by pressing the polyurethane at 170 °C between polytetrafluorethylene sheets. Films prepared at such temperatures were approximately 300 μm in thickness. The infrared data were obtained with a Bruker Model IFS 113v Fourier transform infrared spectrometer. Spectral resolution was maintained at 4 $cm^{-1}$. A deuterated triglycine sulfate (DTGS) detector with a polyethylene

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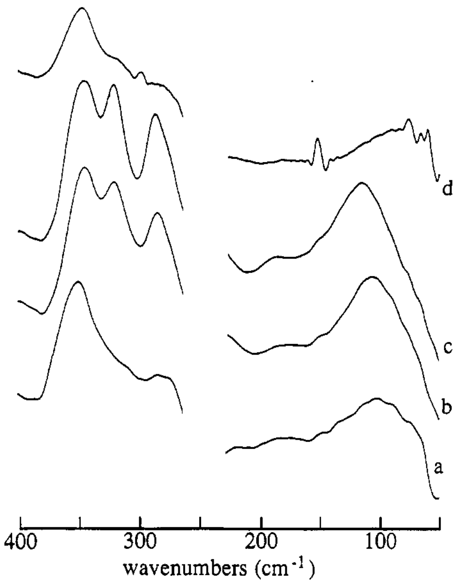

**Figure 1.** Far-infrared spectra of polyurethane: (a) amorphous sample (melted, then quenched in ice-water); (b) highly ordered sample measured at room temperature (annealed at 150 °C for 5 h); (c) sample from (b) measured at approximately −75 °C. (d) sample measured at approximately 180 °C. The sharp features at 300, 160, and 75 $\mathrm{cm}^{-1}$ are artifacts.

window and a helicoil source was used. A 12-$\mu$m poly(ethylene terephthalate) (Mylar) film beam splitter was used which allowed for a usable region of the spectrum between 50 to 400 $\mathrm{cm}^{-1}$. With this beam splitter, very low energy was measured for the 270–230-$\mathrm{cm}^{-1}$ range, making data in this narrow region too noisy to be of utility. Small peaks observed in some of the spectra at 160 $\mathrm{cm}^{-1}$ are artifacts. Each spectrum was the average of 1024 scans. Spectra were all acquired in vacuum, and spectra at elevated temperatures were obtained by holding sample films between brass foil spacers in a heating cell. Examination of the mid-infrared spectrum of the polymer at temperatures up to 170 °C did not show evidence of free isocyanate, in contrast to the spectra of polymers based on 4,4′-methylenebis(phenyl isocyanate) (MDI).[21] This may be due to the heating experiments in this study being performed in vacuum as well as the difference in relative reactivity of TDI and MDI. Low-temperature spectra were obtained by placing samples in between brass foil spacers at the end of a cold finger cooled with liquid nitrogen. Band resolution was accomplished by fitting Gaussian peaks with adjustable bandwidth, peak height, and peak positions to the experimental data using standard nonlinear least-squares methods.

We were quite interested in obtaining infrared spectra of samples with different thermal histories. Various samples of different thermal history were prepared by quenching the polymer from the melt then annealing at different temperatures. A spectrum of the melt was difficult to obtain since suitable windows which transmit far-infrared radiation usually cannot be used at 180 °C. With great care, it was possible to obtain the disordered spectrum for polyurethane samples just prior to melting. We only use these data to illustrate the changing hydrogen bonding characteristics. The far-infrared spectra of samples with significantly different thermal histories are shown in Figure 1.

## Results and Discussion

Most of our attention was given to the broad strong band at approximately 105 $\mathrm{cm}^{-1}$ observed for polyurethane. Previous spectroscopic studies of the far-infrared region indicated that the stretching modes of the hydrogen bond were located in the 250–50-$\mathrm{cm}^{-1}$ region,[1] with the majority occurring in the 180–100-$\mathrm{cm}^{-1}$ region.[22] Theoretical normal vibrational analysis of crystalline polyglycine I also indicated that stretching modes of the hydrogen bonds were located in the 150–100-$\mathrm{cm}^{-1}$ region.[23] Frank et al.[19] has obtained the far-infrared spectra of a homologous series of polyamides (nylon 2, 4, 6, 8, 10, and 12) and found that a common property of all spectra was a band between 100 and 110 $\mathrm{cm}^{-1}$. The only exception was in polyglycine, in which a band at 116 $\mathrm{cm}^{-1}$ appears. In all of these systems this band was observed to be independent of chain conformation. From the rigid-body approximation, the frequency of the hydrogen bond stretching mode can be calculated by using

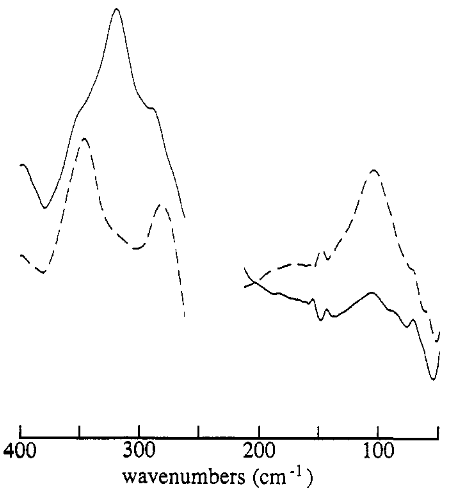

**Figure 2.** Polarized far-infrared spectra of polyurethane at 300% elongation. The solid curve is for an electric vector oriented parallel to the stretch direction. The dashed curve is for electric field vector oriented perpendicular to the stretch direction.

$$\nu_{\mathrm{O\cdots H}} = 130.3(f_2/2M)^{1/2}\quad \mathrm{cm}^{-1}$$

with $M = m_c + m_O + m_N + m_H = 43$ AMU.[19] By use of a coupled oscillator model, from the bonded and nonbonded N–H stretching frequencies reported, the force constant of the hydrogen bond, $f_2$, was calculated to be 0.56 mdyn/Å. The frequency of $\nu_{\mathrm{O\cdots H}}$ was calculated to be 105 $\mathrm{cm}^{-1}$. Figure 2 shows the polarized far-infrared spectrum of a sample of amorphous polyurethane strained to 300% elongation (stretched at 85 °C at a strain rate of 600%/min). As expected for a hydrogen bond vibration, the band at 105 $\mathrm{cm}^{-1}$ was observed to be perpendicularly polarized.

Figure 1a shows the room temperature spectrum of an amorphous sample prepared by quenching a film from the melt directly into ice-water. The room temperature spectrum of a highly ordered sample, obtained by annealing this amorphous sample at 150 °C for 2 h, is shown in Figure 1b. The band observed at 101 $\mathrm{cm}^{-1}$ in the amorphous state shifts to 107 $\mathrm{cm}^{-1}$ for the highly ordered sample. This is consistent with the notion that this band is sensitive to the packing structure of the polymer. If we accept the assignment that this band is associated directly with a hydrogen bond, the force constants calculated by using the rigid-body approximation will be 0.52 and 0.58 mdyn/Å for amorphous and highly ordered states, respectively.

Figure 3 shows the far infrared spectra of polyurethane samples with various degrees of order. First an amorphous sample was fixed in a sample holder and its spectrum measured. Then the sample still fixed in the holder was placed into an oven and annealed at 90, 110, 130, and 150 °C for 2 h at each temperature and the spectrum was then measured at room temperature. It is important to emphasize that the spectra have not been arbitrarily scale expanded, so these spectra can be compared with each other directly.

A number of studies have established that the carbonyl stretching vibration in the 1700-$\mathrm{cm}^{-1}$ region of polyurethanes is extremely sensitive to the degree of chain packing.[16,18] In most observations, this carbonyl band is

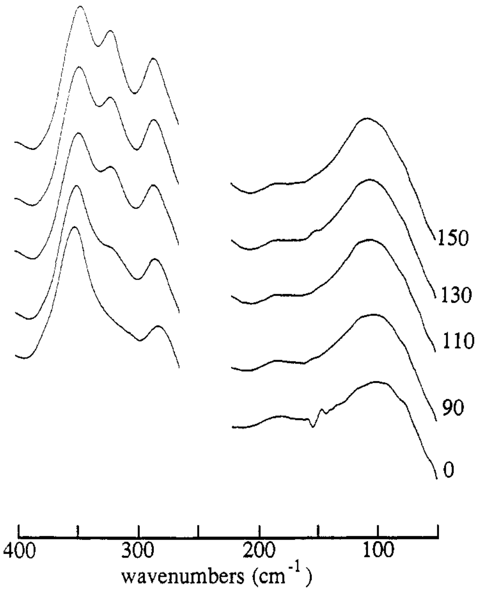

**Figure 3.** Far-infrared spectra of differently ordered polyurethane samples measured at room temperature (annealed at the indicated temperature (°C) for 2 h).

a composite of several components with contributions from ordered and disordered hydrogen-bonded carbonyl groups and "free" (non-hydrogen-bonded) carbonyl groups. In other studies of this polymer,[24,25] it has been shown that as the sample is annealed at increasing temperatures, the hydrogen-bonded carbonyl bands show significant narrowing and increase in intensity, indicative of a decrease in the variety of hydrogen-bonded environments.

Similar information should exist for the absorption at 101 cm$^{-1}$. Because of the weaker hydrogen bonds in the disordered state, we would expect that starting with purely amorphous polyurethane, the low-frequency band should shift to higher frequency with a decreasing bandwidth as the degree of order in the sample increases. If the polymer consists of both amorphous and ordered phases, this band should consist of two bands assigned to ordered and disordered hydrogen-bonded bands. As the degree of order of the sample increases, the contribution of the ordered hydrogen bond vibration band should increase. If the ordered and dissorderd bands were resolved, the higher frequency ordered band should increase at the expense of the low-frequency disordered band. If the bands were not completely resolved, the band center should shift to higher frequency. The latter situation is what is found in the spectrum of this polymer.

In order to assess the changes in the distribution of hydrogen bonding environments, band resolution of the hydrogen bonding vibration band was attempted. It is anticipated that the hydrogen bonding in the amorphous regions would not have a specific geometry and therefore would not have a single strong absorbance peak. Since the hydrogen bonding vibration band represents the sum of many broad bands due to hydrogen bonds of differing environments, and no distinct band for the ordered vibration is observed, resolution to a set of specific bands is not readily accomplished. Therefore, the data in this region have been fitted with a single Gaussian band. The resultant peak width, intensity, and position are more a description of the distribution of the hydrogen bonding environments than a measure of the position of a particular band. The data in Table I shows that the integral absorbance of the band due to the hydrogen bond vibrations increases and the band maximum shifts to higher frequency with increasing annealing temperature. This increase in absorbance and frequency of the hydrogen bond vibration band is indicative of an increase in the order of the sample.

**Table I**
**Band Parameters for the Hydrogen Bond Vibration of Polyurethane as a Function of Annealing Temperature**[a]

| | as quenched | 90 °C | 110 °C | 130 °C | 150 °C |
|---|---|---|---|---|---|
| position[b] | 101.2 | 103.1 | 104.0 | 105.2 | 107.0 |
| width[b] | 52.5 | 50.5 | 49.0 | 46.8 | 44.0 |
| area[c] | 9.8 | 11.5 | 12.5 | 13.6 | 14.0 |

[a] Samples were annealed at indicated temperature for 2 h; spectra were measured at room temperature. [b] Reciprocal centimeters. [c] Arbitrary units.

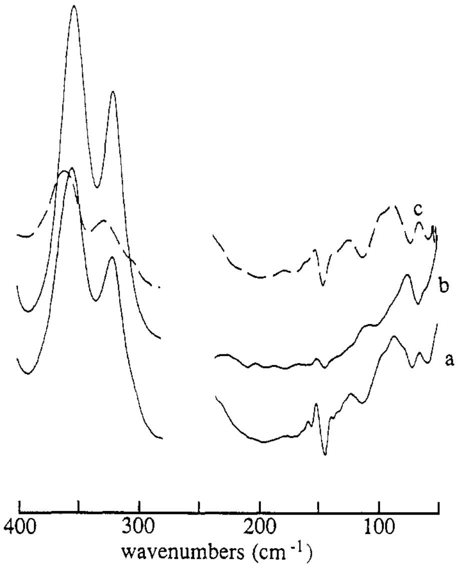

**Figure 4.** Far-infrared spectra of a polyurethane solution: (a) 30% polyurethane (w/v) in DMF; (b) pure DMF; (c) subtraction of (spectrum b) − (spectrum a) (dashed curve).

The low-frequency vibration band is also sensitive to temperature changes. At low temperatures, the magnitude and specificity of intermolecular interactions increase, causing a concomitant increase in the force constant for the hydrogen bonding vibration. This should be observed as an increase in the frequency of this vibration. As expected, the band shifted upward to 115 cm$^{-1}$ (measured at −75 °C, Figure 1c). As Figure 1d indicates, when the sample melts this band does not disappear but shifts to a lower frequency (88 cm$^{-1}$). It is important to consider the perturbing effects of temperature at these low frequencies. The broad width of this band is directly related to the existence of a distribution of different hydrogen bonds in the solid state, each with a slight different frequency. In the absence of changes in the force constant of the vibration, lowering the temperature should increase the population of the species with intensity of the bands of lower frequency, shifting the band center to lower frequency. If this latter effect were to be dominant, we would expect a shift to lower frequency relative to a room temperature spectrum. The opposite effect is in fact observed. Therefore, we conclude that the temperature dependence observed indicates the 101-cm$^{-1}$ band is sensitive to intermolecular packing.

If the band at 101 cm$^{-1}$ is due to hydrogen bonding, disrupting the hydrogen bond structure should reduce its intensity. Figure 4 shows the far-infrared spectrum of a 30% solution of the polyurethane in dimethylformamide (DMF), a strong hydrogen bond accepting solvent. In solution, the hydrogen bond vibration band shifts to lower frequency and appears to be a sum of two bands (98 and

**Table II**
**Band Parameters of the Conformationally Sensitive Vibrational Mode as a Function of Annealing Temperature**[a]

| | as quenched | 90 °C | 110 °C | 130 °C | 150 °C |
|---|---|---|---|---|---|
| band A | | | | | |
| position | 350.7 | 349.5 | 347.7 | 346.7 | 346.7 |
| width | 32.6 | 30.5 | 30.0 | 29.5 | 29.5 |
| area | 17.4 | 16.4 | 16.1 | 15.8 | 15.8 |
| band B | | | | | |
| position | 314.8 | 318.0 | 318.0 | 318.5 | 318.5 |
| width | 40.0 | 33.5 | 27.7 | 25.0 | 23.5 |
| area | 7.7 | 7.8 | 8.0 | 8.2 | 8.8 |
| band C | | | | | |
| position | 277.3 | 281.3 | 282.5 | 282.5 | 282.5 |
| width | 31.6 | 31.2 | 30.0 | 30.0 | 29.5 |
| area | 8.2 | 8.7 | 9.1 | 9.9 | 10.8 |

[a] Samples were annealed at indicated temperature for 2 h; spectra were measured at room temperature. Peak position and width are in reciprocal centimeters; integrated peak areas are in arbitrary units.

87 cm$^{-1}$). Deconvolution suggests that the origin of the 98-cm$^{-1}$ band perhaps is above 100 cm$^{-1}$. The 98-cm$^{-1}$ band is probably due to the hydrogen bond vibration between polyurethane molecule chains and the 87-cm$^{-1}$ band is the hydrogen bond vibration between the NH group of polyurethane and the C=O group of DMF. One would anticipate that the difference in hydrogen bond strength between DMF and the urethane versus that of a hydrogen bond between two urethane moieties could account for the frequency shift observed. Additionally, in Frank's model it is assumed that the amide group motion is nearly free in a direction perpendicular to the chain backbone.[19] In fact, this translational motion would be expected to be influenced by an additional bending force arising from the chain backbone. But for small molecules such as DMF, the motion is nearly free, causing the hydrogen bond band shifts to a lower frequency.

As shown in Figure 1, there are also other intense bands, located at 346, 320, and 284 cm$^{-1}$. The behavior of the 320-cm$^{-1}$ band is most interesting. The polarized infrared measurement (Figure 2) indicates that this band has high parallel dichroism. Figure 3 shows that the width of this band is very sensitive to the structure change of the polyurethane sample. In the spectrum of a highly ordered sample, the 320-cm$^{-1}$ band is very narrow. Its bandwidth is directly related to the degree of packing perfection. As the degree of order of the sample decreases, the bandwidth increases. In amorphous samples, this band is extremely broad and almost disappears.

The curve-fitting results in the 400–260-cm$^{-1}$ region of different polyurethane samples annealed at a variety of temperatures are summarized in Table II. Representative curve-fitted data (annealed at 90 and 150 °C for 2 h) are shown in Figure 5. Our results show that the width of the 320-cm$^{-1}$ band increases substantially as the degree of order of the samples decreases, but the integral absorbance decreases only slightly. This observation suggests that the 320-cm$^{-1}$ band is sensitive to the conformational structure of molecular chains rather than to the nature of the hydrogen bond.

An assignment of the low-frequency spectra of nylon 6 has been carried out by several authors.[19,26-29] From normal vibrational analysis of nylon 6 and poly($\epsilon$-caprolactone), Tadokoro et al.[27] assigned the high parallel dichroism band at 295 cm$^{-1}$ in the spectrum of nylon 6 to a C–CO–NH–C bending mode coupled with methylene chain bending and the high parallel dichroism band at 315 cm$^{-1}$ in poly($\epsilon$-caprolactone) to a O–CO–CH$_2$–C bending mode coupled with methylene chain bending. From normal vibrational analysis of methyl $N$-methylcarbamate CH$_3$NHCOOCH$_3$ (MMC), Randhawa et al.[30] assigned the 350-cm$^{-1}$ band in MMC spectrum to the bending mode involving C′NC, CO, NCO, and COC′. Due to fact that the 320-cm$^{-1}$ band in the polyurethane has high parallel dichroism and appears to demonstrate particular sensitivity to the conformation change of molecule chains, we can assign this band to a O–CO–NH–C bending mode coupled with methylene chain bending. In the highly ordered regions of this polyurethane, the CH$_2$ chains would be anticipated to be in the nearly all-trans conformations. But in the amorphous regions the conformations of CH$_2$ chains should be more disordered, causing this band to broaden.

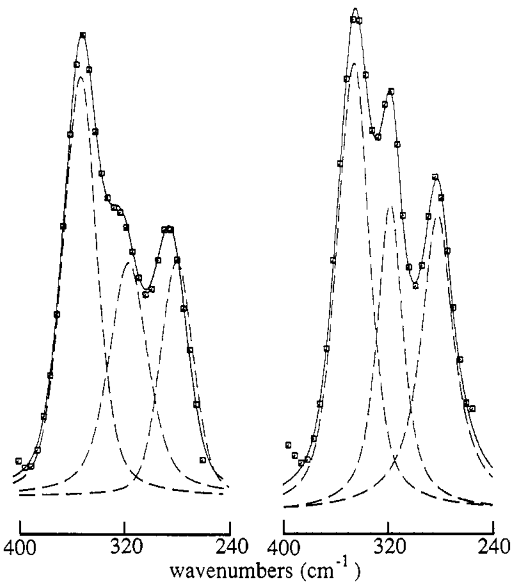

**Figure 5.** Curve-fitting results in the 400–240-cm$^{-1}$ region of polyurethane spectra. The left spectrum is for a sample annealed at 90 °C for 2 h. The right spectrum is for a sample annealed at 150 °C for 2 h. The solid curve represents best-fit data. The squares are original data plotted every 10th point. The dashed curves are for fitted Gaussian peaks.

The two bands near 350 and 280 cm$^{-1}$ have perpendicular dichroism (Figure 2). As shown in Figure 5 and Table II, the 350-cm$^{-1}$ band is less sensitive to structural change of the sample. In analogy to previous studies of the assignment of nylon 6 bands,[28,29] this band can be assigned to a torsional motion of the rigid amide group with the N–C bond as an axis of rotation. In comparison with the 350-cm$^{-1}$ band, the 280-cm$^{-1}$ band is more sensitive to the conformation change of molecule chains based on changes in the relative intensity of the two bands as a function of annealing conditions. Considering the assignment of nylon 6 and poly($\epsilon$-caprolactone) spectra,[28] this band is possibly the torsional motion of CH$_2$ chains which connect with the OCONH urethane group.

In addition to changes in the hydrogen bond vibration band, the conformationally sensitive band shows an interesting sensitivity to temperature. In highly ordered samples (Figure 6), the 320-cm$^{-1}$ band becomes broader during the heating procedure due to disordering of the polymer at the higher temperature. The far-infrared spectrum of amorphous polyurethane, recorded as a function of increasing temperature, is shown in Figure 7. The behavior of the 320-cm$^{-1}$ band proved quite interesting. During the heating procedure the band narrows and becomes a dominant feature in the spectrum. After the sample began to melt (at 180 °C), the band became broad again and the peak nearly disappeared. This indicates that the quenched sample was disordered. During

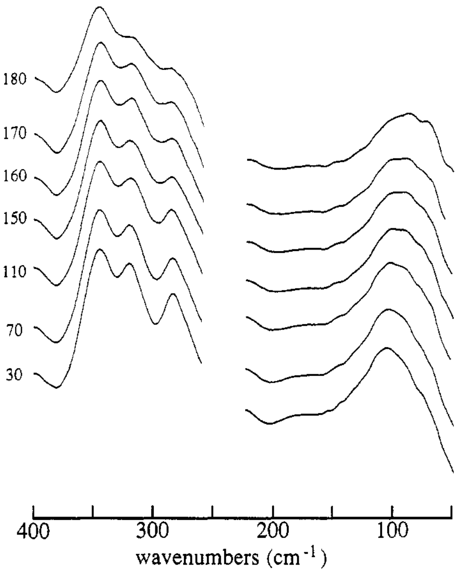

**Figure 6.** Far-infrared spectra of a highly ordered sample of polyurethane recorded as a function of increasing temperature from 30 to 180 °C.

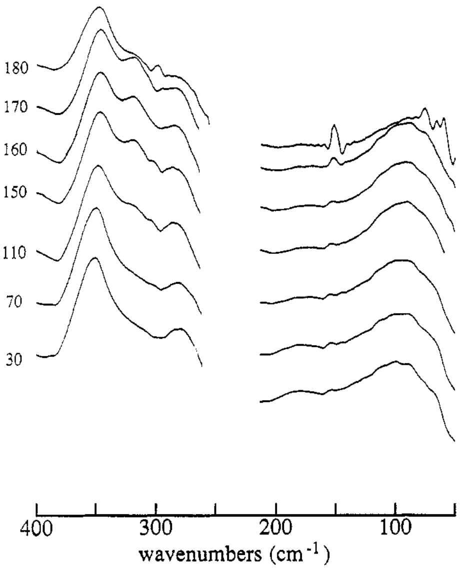

**Figure 7.** Far-infrared spectra of an amorphous sample of polyurethane recorded as a function of increasing temperature from 30 to 180 °C.

the heating process, enough molecular mobility is gained so that the sample can form ordered structures.

## Conclusions

In the far-infrared spectrum of this polyurethane, the band around 105 cm$^{-1}$ is assigned to the hydrogen bond vibration between NH and C=O groups. Polarized measurements indicated that the band has perpendicular dichroism. When the sample melts, this band did not disappear but shifted to lower frequency. This fact indicated that the band does not belong to lattice vibration modes but is sensitive to intermolecular forces. In the far-infrared spectrum of DMF solution of the polymer, the band shifted to lower frequency.

The hydrogen bond band is sensitive to the packing structure of polyurethane samples. The band is located at 101 cm$^{-1}$ for amorphous samples and at 107 cm$^{-1}$ for highly ordered samples. This band should consist of two bands assigned to ordered and disordered hydrogen bonded bands corresponding to ordered and amorphous structures, respectively.

The hydrogen bond band is also sensitive to temperature changes. At low temperature, the intermolecular forces increase, so the band shifts to higher frequency. When the sample melts, the intermolecular forces become weaker and the band shifts down to 88 cm$^{-1}$.

The band at 320 cm$^{-1}$ is assigned to a O-CO-NH-C bending mode coupled with methylene chain bending. In oriented samples, the band exhibits high parallel dichroism consistent with this assignment. The bandwidth is very sensitive to the conformation of molecular chains and temperature change. In the spectrum of highly ordered samples this band is very sharp. As the degree of order of the sample decreases, the 320-cm$^{-1}$ band becomes broader and almost disappears.

The two bands at 350 and 280 cm$^{-1}$ have perpendicular dichroism. The 350-cm$^{-1}$ band is less sensitive to the structure change of the polyurethane and is assigned to a torsional motion of the rigid amide group with the N-C bond as an axis of rotation. Compared with the 350-cm$^{-1}$ band, the 280-cm$^{-1}$ band is more sensitive to the conformation change of the molecular chains. This band is most probably due to the torsional motion of the methylene chains which connect with OCONH group.

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**Registry No.** (24TDI)(4,4'-HO$(CH_2)_6OC_6H_4C_6H_4O(CH_2)_6$OH) (copolymer), 117252-65-0; (24TDI)(4,4'-HO$(CH_2)_6OC_6H_4C_6H_4O$-$(CH_2)_6$OH) (SRU), 117308-04-0.

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# Preparation of Polycyclooctyne by Ring-Opening Polymerization Employing $d^0$ Tungsten and Molybdenum Alkylidyne Complexes

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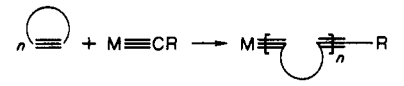
ABSTRACT: Polycyclooctyne ("polyoctynamer") can be prepared by adding cyclooctyne (up to 500 equiv) to $W_2(O\text{-}t\text{-}Bu)_6$ in toluene (preferably) or dichloromethane. Polyoctynamer has a $T_m$ = 62 (±4) °C, a $T_g$ = −65 (±8) °C, and a decomposition temperature of 390 °C. Samples could be hydrogenated to give polyethylene, which had a polydispersity between 4 and 7. Mass spectra of cyclooctyne oligomers (5 equiv), prepared by quenching living oligomers with benzoic acid and methanol, were consistent with the presence of macrocycles rather than linear molecules. Analogous oligomers and polymers can be prepared by using $Mo(CR)(O\text{-}t\text{-}Bu)_3$ species as catalysts and quenching with phenylacetylene. Oligomers prepared by quenching after short reaction times consist of linear species, $(HC)[C(CH_2)_6C]_n(CPr)$, as well as macrocyclic species, but if the reaction is quenched after 15 min of reaction time, only macrocycles are observed in a distribution predicted by the Jacobson–Stockmayer relationship. These results suggest that secondary metathesis of triple bonds in the polymer is a significant complication in the molybdenum system as well as the tungsten system, although it is much slower in the molybdenum system. Other results corroborate these findings, among them the fact that $Mo(CR)(O\text{-}t\text{-}Bu)_3$ complexes *will* react with internal acetylenes (several equivalents in minutes) if R is not *tert*-butyl. Attempts to prepare polyoctynamer by adding cyclooctyne to $W(CR)(DIPP)_3$ (DIPP = 2,6-diisopropylphenoxide) yielded only relatively stable tungstacyclobutadiene complexes. Metathesis of 2,8-dodecadiyne by a $W(CR)(O\text{-}t\text{-}Bu)_3$ complex also yields polyoctynamer (plus 2-butyne), whose $T_m$ is virtually identical with that prepared from cyclooctyne. Complexes of the type $(t\text{-}BuO)_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-}Bu)_3$ were prepared for $x$ = 0, 2, 4, 5, and 6.

## Introduction

Ring-opening polymerization of cyclic olefins by classical olefin metathesis catalysts is well-known.[1] In the past few years, well-characterized catalysts have been discovered that allow living polymers of certain cyclic olefins to be prepared.[2] Since acetylene metathesis catalysts of the type $M(CR')(OR)_3$ are known,[3] and since their activity can be controlled through choice of M (Mo or W) and OR (O-*t*-Bu, $OCMe_2(CF_3)$, O-2,6-$C_6H_3$-*i*-$Pr_2$, etc.), it should be possible to ring-open polymerize a cyclic acetylene under the right circumstances (eq 1) to give a living polymer, i.e., one in which the terminal M≡C bond does not react readily with a triple bond in the chain (either intramolecularly, to give cyclic oligomers, or intermolecularly). Cyclooctyne is an interesting possibility for a reaction of this type since it has a significant amount of ring strain[4] and therefore should be more reactive than the triple bonds in the polymer. In this paper we evaluate the ring-opening metathesis polymerization of cyclooctyne using $d^0$ alkylidyne complexes as catalysts. A preliminary communication on this subject has appeared.[5]



(1)

## Results and Discussion

**Ring-Opening Metathesis of Cyclooctyne by $W_2(O\text{-}t\text{-}Bu)_6$.** $W_2(O\text{-}t\text{-}Bu)_6$ is an interesting potential ring-opening catalyst for cyclooctyne for several reasons. First, $W_2(O\text{-}t\text{-}Bu)_6$ is known to react readily with disubstituted acetylenes to give alkylidyne complexes of the type $W(CR)(O\text{-}t\text{-}Bu)_3$.[6] Therefore, the first product of the reaction between cyclooctyne and $W_2(O\text{-}t\text{-}Bu)_6$ should be $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$. Subsequent reaction of $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$ with cyclooctyne at each W≡C bond should give a polymer of the type $(t\text{-}BuO)_3W[C(CH_2)_6C]_nW(O\text{-}t\text{-}Bu)_3$. This approach eliminates the need of preparing $W(CR)(O\text{-}t\text{-}Bu)_3$ compounds separately. A second reason is that $W_2(O\text{-}t\text{-}Bu)_6$ can be prepared in relatively large quantities from readily available starting materials. Finally, Freudenberger[7] has shown that treatment of $W(CR)(O\text{-}t\text{-}Bu)_3$ complexes with 2 equiv of carboxylic acids initially protonates the alkylidyne carbon atom to give an alkylidene ligand, which then rearranges to an olefin that can be displaced by $PMe_3$ or upon treatment with methanol. Therefore, the polymer should be removed cleanly from the metal center:

$$(t\text{-}BuO)_3W[C(CH_2)_6C]_nW(O\text{-}t\text{-}Bu)_3 \xrightarrow[\text{methanol}]{2RCO_2H} [H_2C{=}CH(CH_2)_5C]_2[C(CH_2)_6C]_{n-2} \quad (2)$$

Addition of $n$ equiv ($n$ = 10–500) of cyclooctyne to a toluene solution of $W_2(O\text{-}t\text{-}Bu)_6$ at 25 °C gives a gelatinous polymer in a few minutes. The reaction was quenched by adding benzoic acid followed by methanol. Polymerization in pentane gives a polymer with similar properties but with a more fibrous structure. Polymers prepared in either manner, where $n \gg 50$, are insoluble in toluene (80 °C, 4 days), methylene chloride (40 °C, 1 day), 1,2,4-trichlorobenzene (140 °C, 2 days), *o*-dichlorobenzene (140 °C, 2 days), and tetrahydrofuran (25 °C, 2 weeks). "Polyoctynamer" swells and expands when exposed to aromatic solvents and methylene chloride. Exposure of swelled samples to nonpolar and especially oxygenated solvents (ethers, alcohols) removes the aromatic solvent

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