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Development of Crystallinity in a Semiflexible Thermotropic Polyurethane. 2. Structure and Dynamics

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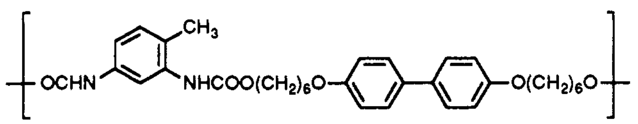
ABSTRACT: The microstructure and dynamics of a monotropic liquid-crystalline polyurethane containing a biphenyl mesogen are examined using infrared, ^{13}C NMR, and dynamic mechanical spectroscopic techniques. The development of crystallinity is found to increase the conformational regularity of the polymer and, in particular, lead to development of two unique conformations of TDI urethane linkages in hydrogen bonding. Secondary relaxation processes involving reorientational motion of the inner hexamethylene spacer carbons, possibly a three-bond conformational jump motion, and the biphenyl mesogen are also identified and readily correlated with mechanically active relaxation processes of this material. The dynamic disorder associated with the crystalline phase of this mesogenic polyurethane indicates that it may best be characterized as a conformationally disordered crystal.

Introduction

Many studies which detail long-range order in the crystalline state of liquid-crystalline main-chain polymers currently exist.[2-10] For semiflexible systems possessing both rigid mesogenic groups and flexible aliphatic spacers in the polymer backbone, considerable evidence, obtained by X-ray diffraction of a number of diverse systems,[9-10] supports the occurrence of three-dimensional order.[7-10] Even polymers which contain asymmetric mesogens exhibit crystalline order despite inefficient chain packing.[8-10] Many of these systems, however, also display evidence of considerable disorder in the aliphatic spacers,[10] especially in instances where spacers of mixed length are used. As these microstructural features are ultimately reflected in the physical properties of these polymers, it is of great interest to understand how these systems form the crystalline phase and the degree to which molecular mobility remains.

In the previous paper,[11] phase behavior of the polymer poly[4,4′-bis(6-hydroxylhexoxy)biphenyl/2,4-toluenediyl diisocyanate] (24TDI/BHHBP)



was examined with emphasis on development of the crystalline phase. This polymer was shown to be monotropic and involved in complex crystallization processes, with formation of spherulitic and threaded crystalline morphologies from the isotropic and liquid-crystalline phases, respectively.[11] To continue characterization of the solid-state behavior of this interesting polymer, studies were undertaken to examine polymer mobility in the solid state and further understand the nature of packing in the crystalline phase.

The present paper reports results of infrared, ^{13}C NMR spectroscopy, and dynamic mechanical investigations of 24TDI/BHHBP. Perturbing features characteristic of the crystalline state for the various infrared absorption bands, previously reported,[12] are examined using these experimental methods in concert. Possible conformations for the urethane linkage in the crystalline state, the alkyl spacers, and the mesogenic biphenyl moiety are also investigated. Subglass transition molecular relaxation processes which appear to occur in both crystalline and noncrystalline phases of the sample are also identified by NMR and correlated with mechanically active relaxation processes.

Experimental Section

The synthesis of BHHBP, 24TDI/BHHBP, and the polymer derived from the reaction of 1,6-hexanediol (HD) and 2,4-toluenediyl diisocyanate (24TDI/HD) has been described elsewhere.[13] In this study the 24TDI/BHHBP samples had an intrinsic viscosity of 0.6 dL/g corresponding to the high molecular weight material described in ref 13. Model methyl carbamate esters were obtained by refluxing distilled 2,4-toluenediyl diisocyanate or 2,6-toluenediyl diisocyanate (Fluka) with methanol, cooling the reaction mixture, and removing the residual methanol to yield 24TDI/MeOH$_2$ or 26TDI/MeOH$_2$, respectively. The former compound melted at 172 °C; the latter sublimed at roughly the same temperature.

All infrared spectra were obtained using a Bruker IFS 113V Fourier transform infrared spectrometer equipped with a liquid-nitrogen-cooled MCT detector, globar source, and KBr beam splitter. Spectra were collected at 2-cm^{-1} resolution in vacuo in order to minimize spectroscopic interferences from moisture and oxidative degradation at higher temperatures. Polymer spectra were obtained from free films or films sandwiched between KBr windows. Films were cast onto disposable aluminum pans from hexafluoroisopropanol (HFIP; Aldrich) solutions (1% w/v), and the solvent was allowed to evaporate slowly. Films thus formed were free of voids and defects. To remove residual HFIP, these films were then held in vacuum overnight at 90 °C. Complete solvent removal was confirmed by the absence of HFIP bands in the infrared spectra of the samples.

High-temperature infrared spectra were obtained by placing films between KBr windows in a temperature-controlled cell with temperature monitored via thermocouples placed adjacent to the sample windows. Spectra of model compounds were obtained from KBr pellets (1% w/w). High-temperature spectra of the model compounds were obtained using the heating cell described above and clamping KBr pellets between recessed brass holders.

Solid-state ^{13}C NMR spectra were recorded on a Bruker AF200 NMR spectrometer equipped with IBM Instruments solids accessories under conditions of cross polarization, dipolar decoupling, and magic angle sample spinning (CP/DD/MASS).[14] All ^{13}C NMR shifts are referenced to TMS and spectra displayed with 20-Hz line broadening to reduce the apparent noise level. The spectrometer was operated at a carbon frequency of 50.323 MHz with decoupler and transmitter field strengths matched at 55.6 kHz to satisfy the Hartmann–Hahn cross-polarization

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requirement.[15] Samples of roughly 300 mg in weight, in the form of a fine powder, were packed into 7-mm-diameter sapphire rotors fitted with Kel-F or ceramic end caps and spun at 3.5–4.5 kHz in a Doty Scientific Co. solids CP/MASS probe. Sample temperature was controlled to ±2 °C using a Bruker BST 500 temperature controller. For subambient temperatures, dry nitrogen was used for sample spinning, while above room temperature, a compressed air supply was employed.

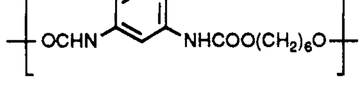
In addition to the standard cross-polarization (CP) pulse sequence (2-ms cross-polarization time), short contact time (SC)[16] and dipolar dephasing (DD)[17] pulse sequences were employed. The SC sequence differs from the CP sequence only in the use of a much shorter cross-polarization time (20 μs) so as to preferentially select those carbons with strong ^{13}C–^{1}H couplings which polarize most rapidly. The DD sequence differs from the CP sequence only by insertion of a short (50-μs) delay between the end of the cross-polarization stage and onset of high-power proton decoupling and data acquisition. In the DD sequence, carbons with strong ^{13}C-^{1}H coupling dephase the most rapidly during the period the decoupler is gated so that the pulse sequence discriminates in favor of carbons with the weakest ^{13}C–^{1}H couplings.

Dynamic mechanical measurements were performed on a Polymer Laboratories DMTA system interfaced to a HP 200 microcomputer. This DMTA was operated in the single-cantilever mode with an 8-mm free length utilizing a polyurethane sample compression molded in vacuum in the form of a beam with a rectangular cross section of 1.22 mm × 9.8 mm.

Results

The most striking feature noted in our initial study of infrared spectra of 24TDI/BHHBP polyurethane was the presence of three clearly discernable bands in the carbonyl stretching region.[12] Two bands are typically observed in the carbonyl stretching region for segmented polyurethanes, one associated with hydrogen-bonded carbonyls and a higher frequency component associated with nonbonded or "free" carbonyls.[18,19] The unusual features first observed for 24TDI/BHHBP were attributed to two types of hydrogen bonds in the liquid-crystalline and/or crystalline phases. In such studies, the degree of order achieved was rather low, as determined by X-ray diffraction. With the recent observation of highly ordered samples,[11,20] prepared by a two-step, high-temperature annealing process, reexamination of the infrared data is warranted.

Our previous study focused on vibrations, carbonyl and NH stretching, generally noted to be most perturbed by hydrogen bond formation.[12] In order to more effectively analyze changes induced by temperature and annealing conditions on the spectrum of 24TDI/BHHBP, a more complete band assignment was required. For this purpose, simple model systems have also been examined. The spectrum of 24TDI/HD



is shown in Figure 1. This polymer, which has been shown to be amorphous,[21] is very similar in chemical composition to 24TDI/BHHBP, lacking only the presence of the biphenyl group and phenyl–ether linkages. Major differences in the carbon–carbon and carbon–oxygen stretching regions (Figure 2), assignable to biphenyl unit and ether linkages, are easily identified. Comparison of the spectra of 24TDI/MeOH$_2$ (Figure 3), 24TDI/HD, and 24TDI/BHHBP permits identification of bands associated with methylene spacers and the urethane groups.

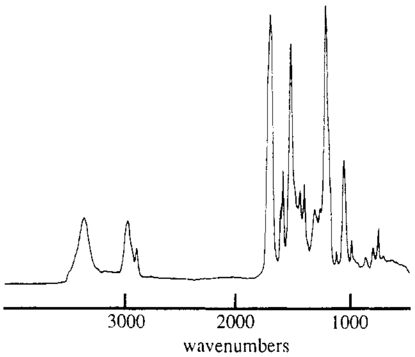


Figure 1. Room-temperature infrared spectrum of 24TDI/HD.

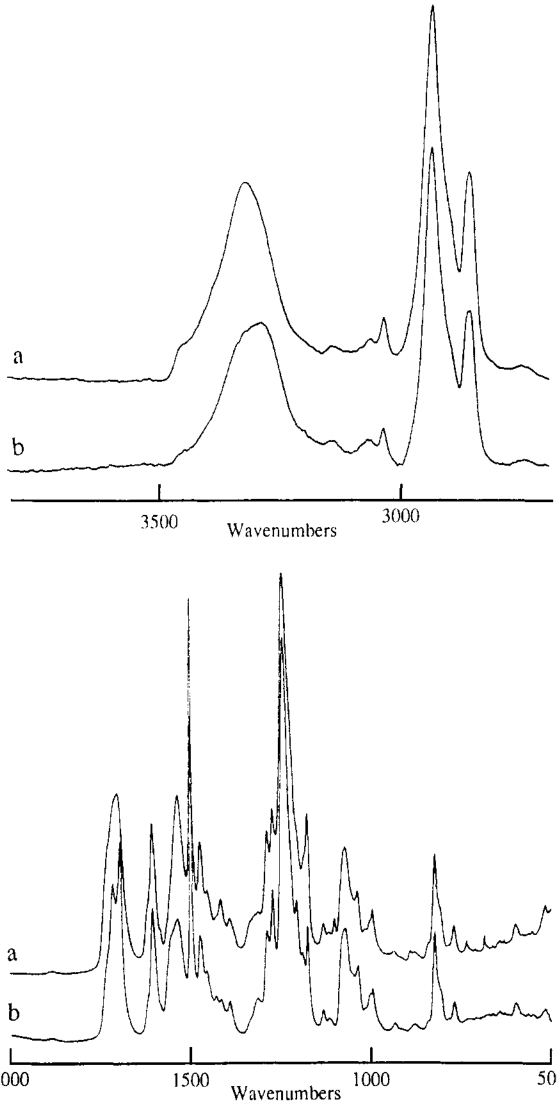


Figure 2. Room-temperature infrared spectrum of 24TDI/BHHBP (a) with no annealing and (b) annealed at 155 °C for 24 h.

Carbonyl bands of 24TDI/BHHBP, after sample annealing for 10 h under vacuum at 90, 120, 150, and 170 °C, are shown in Figure 4. Consistent with a previous study,[22] annealing of 24TDI/BHHBP is found to enhance splitting of the carbonyl region into three distinct bands. The highest frequency component, at 1735 cm^{-1}, was assigned to carbonyls not involved in hydrogen bonding. The other two components, located at 1716 and 1699 cm^{-1}, were initially ascribed to carbonyls involved in hydrogen bonds of differing geometries with the lower frequency band assigned to "ordered" hydrogen bonds and the higher frequency band assigned to "disordered" hydrogen bonds

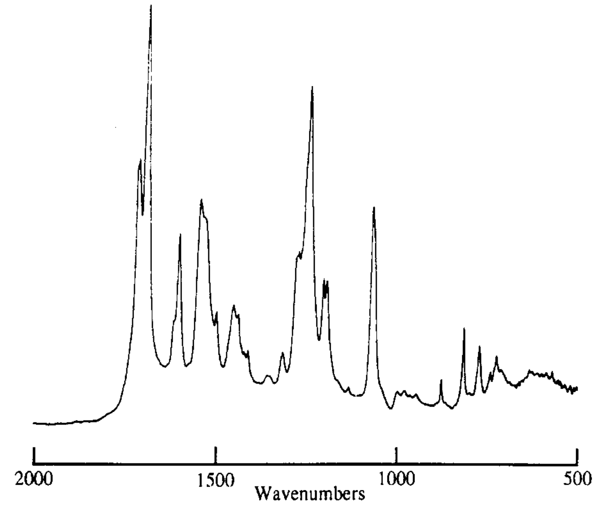


Figure 3. Room-temperature infrared spectrum of 24TDI/MeOH$_2$.

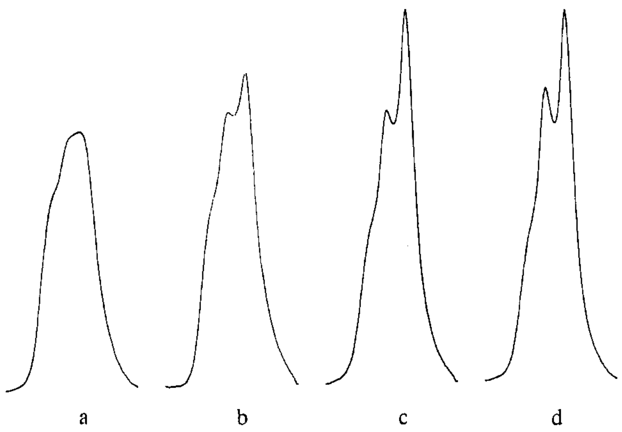


Figure 4. Carbonyl region of 24TDI/BHHBP (1750–1650 cm^{-1}) as a function of annealing temperature: (a) 90, (b) 110, (c) 150, and (d) 170 °C.

in a different environment. In data presented in Figure 4, a progressive decrease in the bandwidth and increase in the intensity of both hydrogen-bonded components is observed. By associating frequency change with hydrogen bond strength, the measured spectroscopic changes suggest a reduction in the distribution of hydrogen-bonding environments occupied by carbonyl carbons.

Sample orderliness is generally increased by annealing. For our model compounds, it is reasonable to associate bands which increase in intensity with crystalline regions. To identify bands associated with the development of the crystalline phase, infrared spectra were recorded at equal time intervals at a fixed annealing temperature. Upon sample heating to the isotropic state at temperatures >170 °C, the infrared spectrum, shown in Figure 5a, exhibits a strong absorbance at 1735 cm^{-1} and a broad shoulder at a lower frequency. Upon sample quenching to 155 °C, three bands develop in the carbonyl stretching region, as shown in Figure 5b. After 15 min, the sample was heated to 165 °C and further annealed. Spectra were collected at regular time intervals up to 2 h. Initially, the spectrum was identical to that observed for the isotropic phase. With increased annealing time, the spectrum developed the distinct bands observed at 155 °C (Figure 6).

The observation of both low-frequency carbonyl components increasing in intensity as a function of the annealing time indicates that both are associated with the development of crystallinity, possibly due to the formation of two different crystalline regions with different geometric requirements for hydrogen-bonded carbonyls. Alternatively, these two carbonyl bands could result from hydrogen-bonded urethane linkages on the same TDI group but with differing conformations within the same crystalline phase. If the first hypothesis is true, then, if the two crystalline morphologies have different rates of crystallization, these peaks should increase in intensity at different rates. If the latter scenario holds, both bands would be expected to exhibit a similar rate behavior as the crystallization process proceeds.

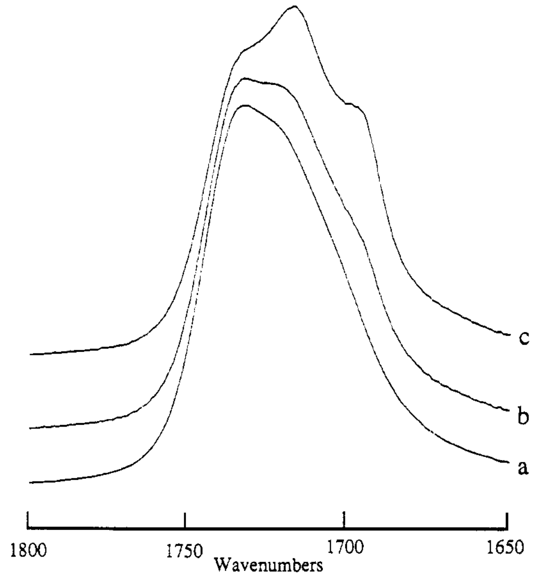


Figure 5. Infrared spectrum of the carbonyl region of 24TDI/BHHBP (a) at 170 °C, (b) after rapid cooling to 155 °C, and (c) at room temperature after annealing at 165 °C for 120 min.

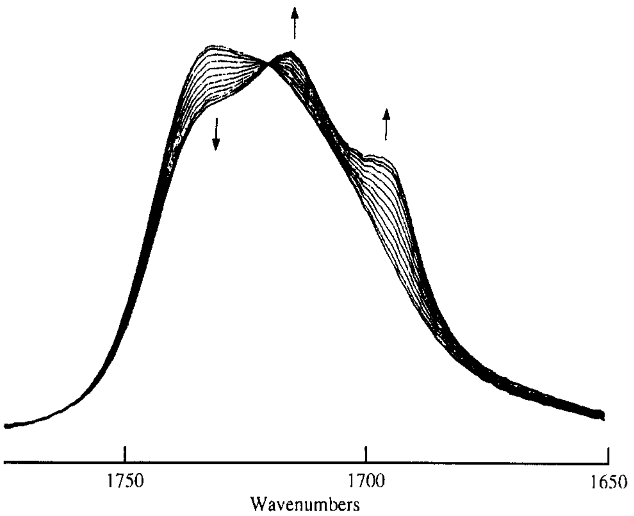


Figure 6. Infrared spectrum of the carbonyl region of 24TDI/BHHBP at 165 °C taken at 4-min intervals after heating from 155 °C.

Previous spectroscopic studies employed an Avrami type analysis based on the relative intensity of hydrogen-bonded and free carbonyl bands to measure the rate of phase separation in segmented polyurethane systems.[19] In order to perform such an analysis for the crystallization process, ideally the value for the peak absorbance at infinite time corresponding to 100% crystallinity, and at time zero, corresponding to a completely amorphous sample, should be available. These values could not be obtained for this 24TDI/BHHBP. Samples without a small degree of crystallinity at $t = 0$ were difficult to obtain and a completely crystalline system was never achieved, as demonstrated by the presence of free carbonyl (1735 cm^{-1}),

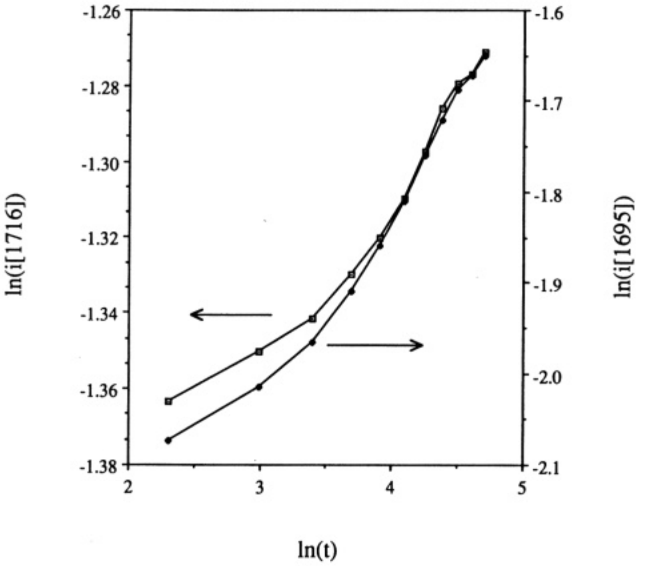


Figure 7. Plot of the natural log of the annealing time at 165 °C versus the base-line-corrected peak intensity (see text).

even after annealing for long times at 165 °C and cooling to room temperature. Utilizing data obtained for the isothermal crystallization described above, the intensity of both hydrogen-bonded carbonyl bands is plotted as a function of the annealing time, as shown in Figure 7. The intensity values represent the maximum value of the bands rather than the value at a fixed frequency. The frequency values for the band maxima do not shift more than 1 cm^{-1} over the total data set. The absorbances are measured relative to a base line drawn between 1800 and 1650 cm^{-1}. The virtually identical rates obtained suggest that both hydrogen-bonded carbonyls are likely to belong to the same phase, contrary to our previous assignment.[12]

Following the annealing experiment, the sample was cooled to ambient temperature. During this time, the intensity of the free carbonyl region decreased while the two bonded carbonyl bands displayed a further increase in intensity along with a reduction in bandwidth (Figure 5c). Previous optical microscopy and DSC studies demonstrated that this polymer undergoes slow crystallization at elevated temperatures to produce spherulitic textures.[11] Cooling the polymer often results in a mixed morphology containing both spherulites and a threaded texture. The development of the two hydrogen-bonded carbonyl bands during isothermal annealing need be associated with material in the spherulitic phase. Subsequent formation of the threaded texture upon cooling leads to a further increase in the intensity of the hydrogen-bonded carbonyl bands as well as a simultaneous decrease in the intensity of the free carbonyl band. These latter changes must reflect structures developed in the threaded phase. The fact that these macroscopically different domains have identical spectroscopic features provides support for similar segmental microstructures, at least for the carbonyl-containing moieties.

Reconsidering the origin of the two hydrogen-bonded carbonyl bands, if, as seems likely, the interpretation of two different hydrogen-bonded geometries within the same phase is accepted, the nature of these geometries needs to be understood. It is thus necessary to examine possible explanations for band origin. A similar splitting of the carbonyl region has been observed in 24TDI/$MeOH_2$.[22] In that study, a difference in the torsion angle to two urethane linkages relative to the plane of the phenyl ring was postulated to be due to the presence of the asymmetrically placed methyl in 24TDI. More specifically, it was proposed that the urethane group ortho to methyl could not achieve coplanarity with the phenyl ring because of steric interactions. The urethane linkage para to methyl could adopt either a nearly planar or nearly perpendicular orientation. It was further stated that differences of the two conformations could be enhanced in the crystalline phase. Such conformational differences have been suggested in the single-crystal X-ray structure of the diethyl ester of 24TDI.[23]

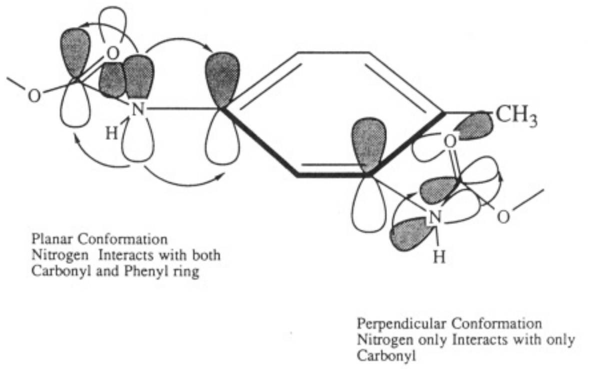
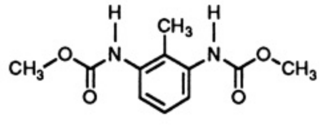


Figure 8. Schematic of resonance interactions in planar and perpendicular geometries of urethane linkages relative to the phenyl ring of the TDI unit.

As shown in Figure 8, if the urethane linkage is perpendicular to the plane of the phenyl ring, resonance interaction of the phenyl ring with amide-type nitrogen is precluded and the nitrogen is free to participate in resonance interaction exclusively with the carbonyl group. In the coplanar conformation, the phenyl ring may engage in resonance interaction with nitrogen, thereby reducing the nitrogen's availability to interact with the carbonyl group. The greater the degree of nitrogen interaction with the carbonyl, the greater should be the observed shift of the carbonyl to lower frequency. In simple ketones, for example,[24] carbonyl stretching is observed at 1720 cm^{-1} while, in simple amides, it is found at 1650 cm^{-1}. Using this hypothesis, the carbonyl band observed at 1699 cm^{-1} in 24TDI/BHHBP would correspond to a nearly perpendicular conformation of the urethane group in the crystalline phase and the band at 1716 cm^{-1} would be assigned to the nearly coplanar conformer. Since the urethane group para to methyl can adopt either coplanar or perpendicular conformers, it must be inferred that crystalline packing of the polymer favors this group to be in the nearly coplanar orientation in order to account for the two observed frequencies.

Further support for differing urethane conformations in the 24TDI-based polymer comes from examining the spectra of 26TDI/$MeOH_2$.



In this compound, there is only one type of urethane linkage, one that is ortho to a methyl group. Using the argument stated above, both urethane groups would be expected to exhibit nearly nonplanar conformations with respect to the ring and, as such, exhibit the lower carbonyl frequency seen in 24TDI/$MeOH_2$. Figure 9 compares spectra of the two model compounds in the crystalline state. As anticipated, the single strong carbonyl stretch in the 2,6 compound corresponds to the lower frequency band in the 2,4 compound. In addition to the effects of

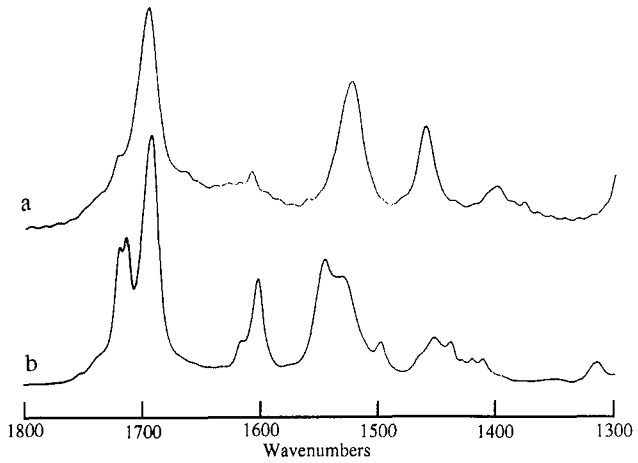


Figure 9. Room-temperature infrared spectra of (a) 26TDI/$MeOH_2$ and (b) 24TDI/$MeOH_2$.

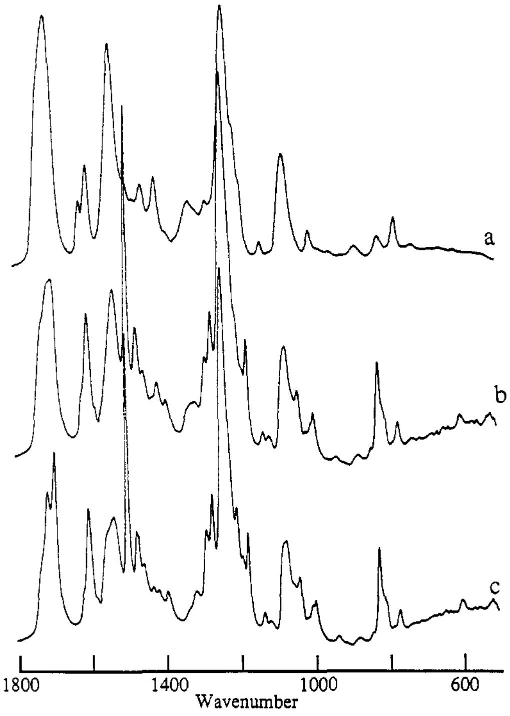


Figure 10. Room-temperature infrared spectra of (a) 24TDI/HD, (b) 24TDI/BHHBP quenched from melt, and (c) 24TDI/BHHBP annealed at 155 °C for 24 h.

the conformation, the nature of hydrogen bonding will affect the exact position of the carbonyl bands.[18,19,25]

The absence of a similar splitting of the carbonyl region in 24TDI-based amorphous polymers has been attributed to the absence of a strong driving force for well-defined conformations of the two urethane linkages.[22] This explanation is consistent with a relatively broad hydrogen-bonded carbonyl band found in many noncrystalline 24TDI-based polyurethanes.[18] Figure 10 plots the spectra of 24TDI/HD and 24TDI/BHHBP in two annealing states. The carbonyl region differs significantly between highly annealed 24TDI/BHHBP and the two other spectra. The carbonyl region of the unannealed sample of 24TDI/BHHBP most resembles that of the amorphous 24TDI/HD. There is, however, some evidence of three carbonyl bands. A careful examination of the carbonyl region of 24TDI/HD also provides evidence for the existence of these bands. Figure 11 presents a plot of the carbonyl region of 24TDI/HD along with the second derivative and a Fourier self-deconvoluted[26] spectrum of this region. Discernable bands are seen at 1735, 1717, and 1695 cm^{-1}. It is thus tempting to assign these bands to the structures observed in 24TDI/BHHBP. Since no crystallinity is exhibited in 24TDI/HD, the small band intensity at 1717 cm^{-1} and relatively broad bandwidth are consistent with the lack of specific conformations in this noncrystalline system. Caution in placing too much emphasis in these manipulated spectra must be exercised, however, as artifacts can easily be introduced by these procedures.

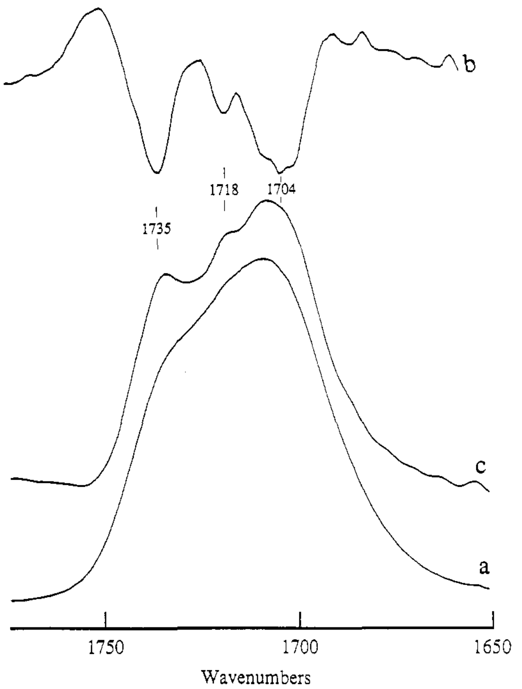


Figure 11. Infrared spectra of the carbonyl region of 24TDI/HD: (a) normal absorbance spectrum, (b) second derivative spectrum, and (c) Fourier self-deconvoluted spectrum.

Thus far, attention has focused on changes observed in the carbonyl region. These bands are most sensitive to changes in the environment of the 24TDI unit. It was also noted that several other bands exhibit changes upon an increase in the annealing temperature. The amide II band, located at 1535 cm^{-1} in unannealed samples, shows the development of a high-frequency shoulder at 1554 cm^{-1} upon annealing. In 24TDI/HD this band does not exhibit a high-frequency shoulder. In the model compound 24TDI/$MeOH_2$, the amide II band also displays two components at 1546 and 1537 cm^{-1} in its crystalline phase and a single band at 1529 cm^{-1} in the isotropic phase at 170 °C. By comparison, 26TDI/$MeOH_2$ has only one band in the amide II region in its crystalline phase at 1524 cm^{-1}. This vibrational mode is associated with in-plane bending of the N–H as well as contributions from the stretching motion of the carbonyl and C–N bond. It is thus not surprising that the same type of splitting behavior is exhibited as the carbonyl itself, again providing evidence for a difference in the conformations of the two urethane linkages in the 24TDI unit.

The band at 1475 cm^{-1} also has a shoulder at 1470 cm^{-1}. These bands are of mixed assignment, possibly due to methylene bending modes or biphenyl C–H in-plane bending. In 24TDI/HD, the 1470-cm^{-1} band is absent and the 1475-cm^{-1} band is weak. Thus the 1470-cm^{-1} band is most likely due to biphenyl-related vibrations. The weak intensity of the 1475-cm^{-1} band in 24TDI/HD is due, in part, to the fact that there is only one hexamethylene chain per monomer repeat, whereas in 24TDI/BHHBP, there are two. This doublet is also observed in the isotropic

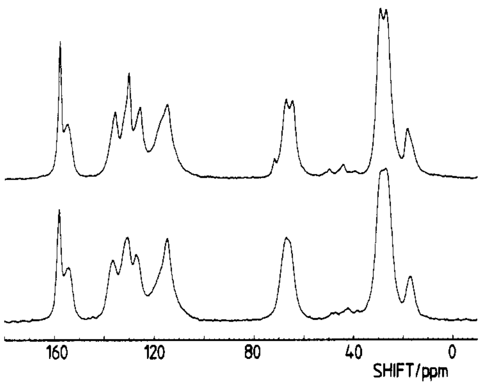
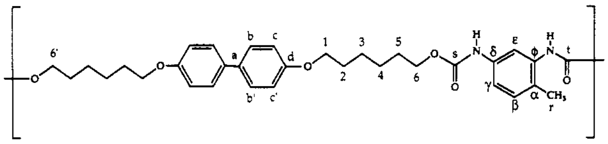


Figure 12. ^{13}C NMR CP spectra for annealed (top) and unannealed (bottom) 24TDI/BHHBP polyurethane at room temperature. Line assignments are presented in Table II.

phase of BHHBP[27] but not in its crystalline phase which contains a chain in the all-trans conformation. It thus appears reasonable to associate the new band with an increase in the number of gauche type linkages in the spacers during development of the crystalline phase of the polymer.

Attempts by infrared spectroscopy to gain further insight into the nature of the conformations of the methylene sequences and the biphenyl group proved difficult. NMR spectroscopy proved to be more tractable for such an examination. Additionally NMR was used to investigate the molecular motion of the various moieties of 24TDI/BHHBP. The solid-state ^{13}C NMR spectrum of 24TDI/BHHBP polyurethane is shown in Figure 12 along with the spectrum of a sample which had previously been annealed at 174 °C for 24 h after slow heating from room temperature. The previous study demonstrated that a slow heating rate and annealing at high temperatures increased both the degree of crystallinity as reflected in the total melting enthalpy and the degree of crystal perfection as reflected by the melting temperature.[11] For the annealed sample used in the present investigation, the melting enthalpy and melting temperature were measured to be 42 J g^{-1} and 178 °C, respectively, which may be compared with values of 32 J g^{-1} and 170 °C for the unannealed material. In view of these observations it is reasonable to attribute the greater resolution of the annealed sample compared to the as-received sample to its increased crystallinity and conformational regularity, which reduce isotropic chemical shift dispersion.

Table I
^{13}C NMR Chemical Shift Data for 24TDI/BHHBP Polyurethane[a]



	solid	solution		solid	solution
1	67.1	67.3	a	130.0 (±0.9)	132.1
2	29.2	28.6	b/b′	125.5	127.1
3	26.9	25.2	c/c′	114.7	114.7
4	26.9	25.2	d	157.8	157.7
5	29.2	28.6	α	125.5 (±1.7)	125.1
6	64.6	64.1	β	130.0	129.5
6′	64.6	64.0	γ	114.7 (±2.0)	114.7
r	18.2	17.1	δ	135.6	136.5
s	154.8	154.3	ϵ	114.7 (±2.0)	114.7
t	154.8	153.6	ϕ	135.6	137.2

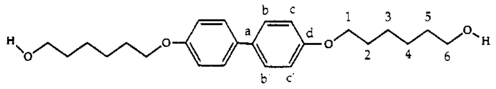
[a] For composite solid-state lines the values in parentheses indicate the estimated offset from the central line position where applicable.

Table II
^{13}C Chemical Shift Data for BHHBP and 24TDI/MeOH$_2$

	BHHBP			24TDI/MeO$_2$	
	solid	solution		solid	solution
1	67.1	67.4	α	129.7	125.5
2	30.8	28.7	β	131.3[b]	130.1
3[a]	25.7	25.4	γ[a]	118.8	114.8
4[a]	28.9	25.2	δ	136.5[b]	136.4
5	35.2	32.4	ϵ[a]	118.8	114.9
6	62.7	60.6	ϕ	136.5[b]	137.1
a	129.0	132.2	r	15.9	17.0
b/b′	124.9	127.1	s	156.7[b]	154.1
c/c′	110.6/116.3	114.8	t	156.7[b]	153.4
d	157.3	157.7	u	52.5	51.5
			v	51.8	51.4

[a] Line assignments are tentative owing to the small shift difference of neighboring lines. [b] Lines exhibit structure possibly owing to nonaveraged ^{13}C–^{14}N (I = 1) interactions.[16]

BHHBP



24TDI/MeOH$_2$

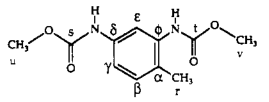


Table I presents ^{13}C NMR spectral assignments for the annealed sample along with solution data for comparison. Considerable overlap exists between lines from the biphenyl and TDI ring carbons in the aromatic region. Assignments are, therefore, based on model compound studies (Table II) of BHHBP[27] and 24TDI/MeOH$_2$ and identification of various protonated and nonprotonated carbons using SC and DD pulse sequences. Line assignments for the BHHBP model compound given in Table II have been previously discussed in relation to its crystalline structure.[27] Attention is drawn only to the large splitting of the C and C′ of the biphenyl mesogen occupying the ortho ring positions with respect to the oxygen-bonded biphenyl carbons. This splitting is attributed to a locked conformation of the alkoxy substituent in or close to the biphenyl plane resulting in an upfield shift of the ortho ring carbon closest to the alkoxy group and, conversely, a downfield shift for the carbon occupying the other ortho position. A similar splitting has been noted in solid dimethoxybenzene[28,29] and in a variety of polyester compounds.[30,31] Assignments for the other model compound, 24TDI/MeOH$_2$, presented in Table II are based on known substituent effects for benzene derivatives[32] and, in the case of the solid-state spectrum, by identifying protonated and nonprotonated carbons using SC and DD pulse sequences. These assignments are consistent with an earlier solution study of a similar model compound.[33]

Returning to consideration of the polyurethane spectrum, the broad high-field line centered at ca. 115 ppm is a composite line with contributions from the protonated C and C′ of the biphenyl and the protonated γ and ϵ lines of TDI. There is no evidence of splitting for the protonated biphenyl carbons in this region at ambient temperatures. This observation suggests a fixed locked planar conformation does not exist for the biphenylalkoxy group as found in BHHBP at room temperature. The line at ca. 126 ppm is attributed to the protonated b/b′ ring carbons of the biphenyl. Between 126 ppm and the next lower field line at 130 ppm, indications of a rather broad nonprotonated carbon line are found using the DD sequence.

This line is tentatively attributed to the methylated TDI ring carbon. The line at 130 ppm is found by SC and DD experiments to have contributions from both protonated and nonprotonated carbons which, by analogy with the model compounds, are attributed to the protonated β carbon of the TDI ring and the nonprotonated bridging biphenyl carbons. The lines at still lower fields are all nonprotonated and lack the composite structure of the other lines. In order of decreasing field strength, these lines are attributed to the nitrogen-bonded TDI carbons, the carbonyl carbons, ad the oxygen-bonded biphenyl carbon.

On the basis of model compound studies, line assignments for the alkoxy, aliphatic, and methyl carbons are straightforward. It is interesting to note that while the resonances of the 1/6 and 2/5 carbons are comparable in the solid state or solution, the resonances of the inner methylene pair 3/4 are shifted ca. 1.7 ppm downfield in the solid relative to their solution. This occurrence is reminiscent of observations by Uryu and co-workers[30,31] for melted and resolidified thermotropic polyesters having alkyl spacers. They reported small differences between the solid-state and solution spectra of these polyesters for all of the methylene carbons except the central pair, for which the resonances occurred at an appreciably lower field in the solid state as compared to solution. By considering spectra from samples subjected to different thermal treatments, it was concluded that the relative deshielding of the central carbon pair of the alkyl spacer was due to introduction of a gauche conformation in the alkyl spacer at the central methylene pair. Such a conformation leads to an increased shielding of carbons which are directly bonded to the central carbon pair via the so-called γ-gauche effect[34,35] but leaves the central carbon pair relatively unaffected. In solution, rapid trans-gauche configurational jumps can occur easily, causing all carbons to experience some γ-gauche shielding interactions. In comparison to the solid state, the central methylene pair will resonate at a lower field. Although previous analysis is primarily based on comparison of the spectra from the melted and resolidified polyesters to other samples considered to have an all-trans alkyl configuration, the same arguments should be applicable in the present study for comparison of annealed semicrystalline polyurethane and its solution spectrum. The measured shifts are consistent with the existence of a gauche conformer at the central position of the alkyl spacer in annealed polyurethane. This interpretation is consistent with X-ray data reported previously.[12]

Variable-temperature ^{13}C NMR studies on unannealed polyurethane were performed to obtain information about the various molecular motions present. An earlier study of BHHBP has utilized spectral editing SC and DD pulse sequences, which are generally less time consuming than NMR relaxation time studies via ^{13}C NMR spectroscopy, to obtain information about reorientational motions.[27] Preliminary investigations performed at selected temperatures indicated that the information gained through use of the SC sequence over a wide temperature range was minimal by comparison with information gained from the CP and DD pulse sequences. Detailed variable-temperature measurements were therefore limited to the acquisition of CP and DD spectra. Spectra obtained using CP and DD pulse sequences are shown as a function of temperature in Figures 13 and 14, respectively. For CP spectra, there is a general tendency for the spectral resolution to increase with increasing temperature, which probably reflects the partial averaging of the isotropic chemical shift distribution for the various carbon species resulting from small-scale molecular motions at elevated temperatures. For temperatures above the glass transition temperature, 95 °C, it is expected that the spectral resolution may be increased due to extensive motions in the noncrystalline regions for the semicrystalline material.

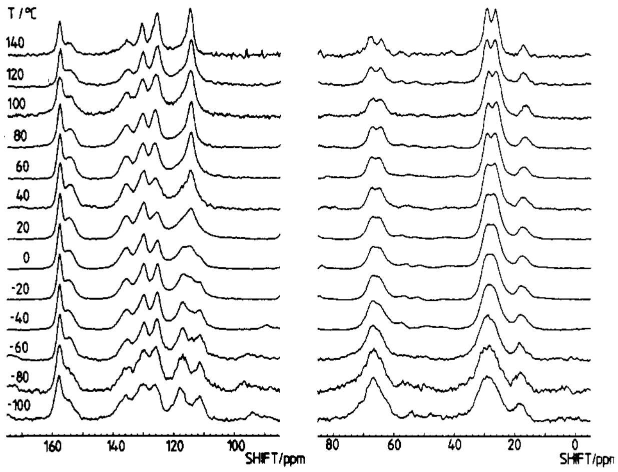


Figure 13. ^{13}C NMR CP spectra for 24TDI/BHHBP polyurethane at various temperatures from −100 to +140 °C.

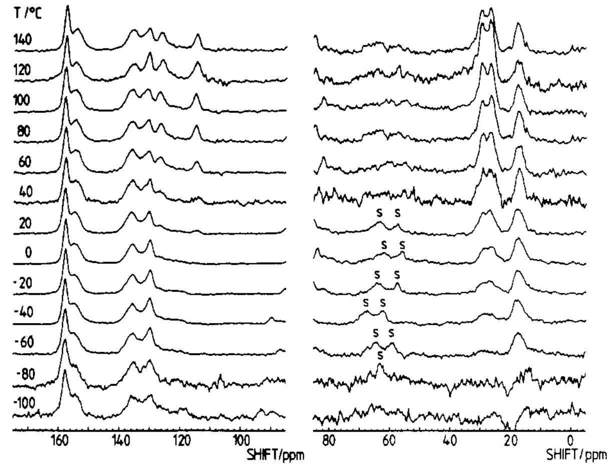


Figure 14. ^{13}C NMR DD spectra for 24TDI/BHHBP polyurethane at various temperatures from −100 to +140 °C. S denotes peaks which arise solely from spinning side bands.

It is also readily apparent that a splitting of the broad resonance centered at ca. 115 ppm occurs at the lowest temperatures, in direct contrast to spectra obtained at room temperature. The splitting of this resonance, which has contributions from the protonated biphenyl carbons c and c′ and the protonated TDI carbons γ and ϵ, is analogous to the splitting of the c/c′ carbons observed previously in crystalline BHHBP at room temperature.[27] This indicates that the alkoxy group 1 is locked in the biphenyl plane at low temperatures in this polyurethane. The lower field component of this doublet thus has contributions from the c′ biphenyl carbon, which is furthest removed from the alkoxy carbon 1, and from the γ and ϵ carbons of TDI. The higher field component, on the other hand, is due only to the biphenyl carbon c which is closest to the alkoxy carbon. As temperature is increased above ca. −40 °C, the intensity is observed to increase at the central position of this doublet with a concomitant decrease in the intensity of the outer peaks until the doublet is completely replaced by the line growing at the central position.

The variable-temperature DD spectra shown in Figure 14 do not contain cleanly resolved peaks, and, in fact, only nonprotonated carbon resonances are clearly visible. The question of whether or not the methyl resonance is really suppressed at the lowest temperatures is difficult to determine due to poor resolution. Normally methyl groups behave as freely reorienting rotors down to very low temperatures[36] and would be expected to survive a dipolar dephasing sequence. In the present case, the adjacent urethane group on the TDI ring may provide some steric restriction to free rotation and thus shift the activation of fast methyl rotation to higher temperatures. The methyl resonance can be clearly resolved only in spectra obtained above −80 °C where methyl groups are undergoing rapid reorientation about a 3-fold symmetry axis.

At ca. −40 °C the resonance arising from the inner protonated methylenes (carbons 2–5) of the alkyl chain can be determined, indicating that some motional averaging of the ^{13}–^{1}H interaction is occurring. This is in contrast to the behavior observed in crystalline BHHBP at room temperature where a dipolar dephasing delay of 50 μs was found sufficient to extinguish all methylene carbon lines from the spectrum.[27] The intensity of these methylene carbons in the DD spectra increases with increasing temperature. At 20 °C the carbon resonances from the protonated biphenyl carbons b/b′ at 127 ppm and from the collapsed c/c′ carbon pair at 115 ppm can be just barely resolved. The intensity of these carbons increases rapidly with a further increase of the temperature until ca. 120 °C. It appears that most of the intensity of these protonated carbons survives the 50-μs dephasing period of the DD sequence, indicating a significant reduction in the strength of the ^{13}C–^{1}H interaction and suggesting that the reorientational motion of the biphenyl group is responsible for the reduction in the interaction strength—possibly consisting of free rotation or a combination of ring flips and large-angle vibrations.[27]

Observation of the CP and DD variable-temperature studies suggests a number of motional processes exist below the glass transition in this polyurethane. It may reasonably be assumed that the same biphenyl motion process is responsible for the collapse of the c/c′ doublet at low temperatures in the CP spectra and the appearance of the b/b′ and collapsed c/c′ carbon resonances in the DD spectra at higher temperatures. At low temperatures, the biphenyl and alkoxy groups are locked in a planar configuration. With increased temperature, biphenyl reorientation about the oxygen–phenyl bond becomes possible, causing the ca. 6 ppm shift difference between the c and c′ carbons. Any reorientational motion with correlation time $\tau_C < 0.5$ ms which can cause and interchange the c and c′ carbon positions can thus achieve a collapse of the c/c′ doublet. At still higher temperatures, the increased rapidity of the reorientational motions eventually becomes sufficient ($\tau_C < 3$ μs) to smear the ^{13}C–^{1}H interactions, causing the appearance of the b/b′ and c/c′ carbon resonances in the DD spectra.

The fact that spectral lines consistent with collapsed and uncollapsed c/c′ carbon pairs coexist at low temperatures does not necessarily imply the existence of two distinct biphenyl populations. An interpretation using a model originally derived by Resing[28,29] to account for ^{1}H relaxation of water in heterogeneous media[37–39] may be reasonable. Another model has been adopted by Jones and co-workers[40,41] to interpret ^{2}H NMR line shape. One assumes in this model that the biphenyls exist at different sites and are characterized by a distribution of motional correlation times. Some of the phenyls are characterized by correlation times such that $\tau_c < 0.5$ ms, the critical correlation time required to collapse the c/c′ doublet, while the remainder are characterized by correlation times with $\tau_C > 0.5$ ms. With a temperature increase, the distribution of correlation times shifts to shorter time scales so that the relative proportion of collapsed c/c′ pairs increases at the expense of the resolved c/c′ doublet until all of the c/c′ pairs exhibit collapsed line shapes. The fact that there is no evidence for doublet structure of the c/c′ pairs at temperatures above 20 °C indicates that reorientational motions of the biphenyl are effective in both crystalline and noncrystalline regions of this semicrystalline polyurethane.

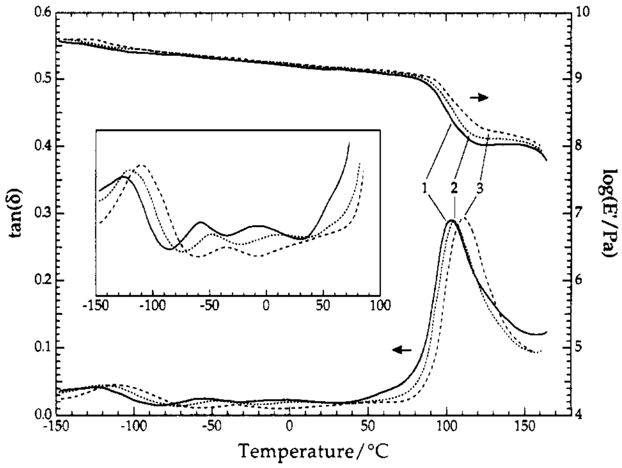


Figure 15. Dynamic mechanical loss tangent (tan δ) and modulus (E') vs temperature data for 24TDI/BHHBP polyurethane. The inset shows an expanded view of the low-temperature tan δ data. Recorded at 0.33 Hz (1), 1 Hz (2), and 3 Hz (3).

It is apparent that at least some of the inner methylene carbons (carbons 2–5) can undergo reorientational motions of sufficient rapidity to reduce the effectiveness of the ^{13}C–^{1}H interaction. Whether these motions occur in both the crystalline and amorphous phases cannot presently be determined with great certainty. The fact that the relative alkyl/phenoxy carbon intensity ratios observed at 20 °C for DD spectra from annealed (0.13) and unannealed (0.12) polyurethanes are comparable would support the hypothesis that such motions can indeed occur in both phases. If such motions do occur in the crystalline region, then the presence of gauche conformations in the alkyl spacer may be important in providing the opportunity for conformational jumps.

A striking feature of this study is the absence of evidence for motion associated with alkoxy carbons 1 and 6 despite the rather convincing evidence found for motion of the biphenyl and inner methylene carbons. In view of the data obtained for the existence of a gauche linkage at the center of the hexamethylene spacer, it is tempting to interpret this behavior in terms of a three-bond $tg^{+}t \leftrightarrow tg^{-}t$ motion.[42] Evidence for extensive motion in TDI linkages is also lacking, although this is not as surprising in view of the possibility for extensive hydrogen-bonding interactions between urethane groups and also, unlike the biphenyl, that the TDI groups lack a molecular axis for reorientation which is also a symmetry axis.

A number of workers have demonstrated that motions observed via NMR spectroscopy can be related to the dynamic mechanical response of the material.[36,43] In view of the NMR evidence associated with subglass molecular relaxation processes, dynamic mechanical measurements were conducted to determine whether these molecular relaxations were mechanically active. DMTA measurements were therefore performed over a wide temperature range from −150 °C up to the onset of crystal melting at

Table III
Relaxation Map Data for 24TDI/BHHBP Polyurethane

		temperature/°C						
		DMTA			NMR			
assignment	$-\log(\tau_2/\mathrm{s})$	0.32	1.28	2.28	3.28	4.90	4.99	ΔE/kJ·mol^{-1}
C		−125.0	−119.5	−110.0			−50.0	80
B		−57.5	−48.0	−36.5	−30.0	10.0		78
A		−7.0	10.5					44
T_g		99.5	105.0	109.5				

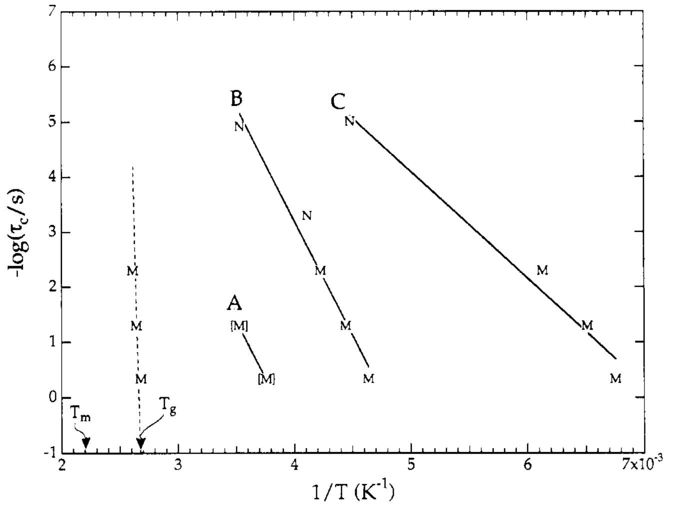


Figure 16. Transition map illustrating the various relaxation processes observed in 24TDI/BHHBP polyurethane. Points denoted N and M are from NMR and mechanical data, respectively. Brackets denote relaxations which are weak and therefore tentative.

ca. +155 °C. Previous DMTA studies were primarily concerned with the behavior of this material at glass transition or higher temperatures.[13] Figure 15 presents the DMTA loss tangent and modulus data for the polyurethane as a function of temperature. Although the glass transition in the 90–110 °C region is clearly observed, a number of lower temperature relaxation processes are also apparent. These are referred to as A, B, and C in order of decreasing temperature. Of these, A is the weakest and only apparent for data recorded at 3 and 0.33 Hz. C is the most active mechanically.

To correlate these transitions with relaxation processes identified by NMR, mechanical and NMR relaxation data (Table III) were compared as shown in Figure 16. The loci A–C drawn in Figure 16 are fit to the Arrhenius equation for which activation energies are presented in Table II. The locus describing the data in the glass transition region, on the other hand, is fit to an empirical WLF type equation[44,45]

$$\ln\frac{\tau}{\tau_0} = -\frac{A(T-T_0)}{B+T-T_0}$$

with parameters $A = -13.5$, $B = 50$ °C, $\log(\tau_0/\mathrm{s}) = 0.85$, and $T_0 = 95$ °C. From the transition map it may be seen that the relaxation denoted A does not correlate with any of the processes apparent in the NMR study nor does it appear to have been identified in previous studies of simpler polyurethane systems.[46] The origin of this relaxation cannot presently be readily identified. Other sub-T_g relaxations are, however, readily correlated with motional processes identified by NMR. The relaxation denoted C correlates with the motion of the inner methylene carbons of the alkyl spacer which are apparent from the DD spectra. The correlation time for this process was taken to be that required to reduce the strength of the ^{13}C–^{1}H dipole–dipole interaction which is related to the Van Vleck second moment.[47,48] In terms of position and activation energy, the relaxation denoted C is comparable to the γ-relaxation observed in other polyurethane systems[46] and in other polymeric materials such as poly(ε-caprolactone)[49,50] and polyethylene[36,44,51] where it has been identified with a motion of the alkyl spacer. It is therefore gratifying that NMR data independently identifies this relaxation with the methylene carbons of the alkyl spacer.

The remaining mechanical relaxation, B, occurring in the temperature range −60 to −30 °C, correlates well with the biphenyl reorientational motion identified by NMR. It must be noted, however, that this particular mechanical relaxation falls in a temperature region associated with β-relaxation in polyurethane systems[44,46,52] which do not contain biphenyl groups as well as with the β-relaxation in nylons.[36,44] In these polymers the β-relaxation has been attributed to effects associated with small amounts of adsorbed water. Thus, in the present study, it may be concluded that mechanical relaxation is a superposition of the two processes.

Conclusions

In summarizing the results of the infrared and ^{13}C NMR investigations of 24TDI/BHHBP polyurethane, it is apparent that there is a general tendency toward increased conformational regularity as crystallization proceeds. Infrared spectroscopy, in particular, shows that the urethane linkages on the TDI ring adopt different conformations with respect to the ring. The urethane linkage at the para ring position relative to the methyl substituent adopts a planar type conformation which promotes resonance interactions with the ring while the other urethane group at the ortho position adopts a more perpendicular conformation. Infrared and ^{13}C NMR spectroscopy provide additional information concerning the conformation of the hexamethylene spacer which supports the conclusion of an earlier X-ray study which postulated the existence of a gauche conformer at a central position in the spacer.

^{13}C NMR spectroscopy additionally provides extensive information on the various motional processes active in this material. Reorientational motions of the methylene carbons in the spacer set in at quite low temperatures and, on the basis of ^{13}C line intensity data, appear to occur in both crystalline and noncrystalline phases. Reorientational motions of the biphenyl mesogen also set in at quite low temperature, although somewhat higher than motions of the hexamethylene spacer, and also occur in both crystalline and noncrystalline phases. Interestingly, these motions, which are readily correlated with mechanically active relaxation processes, set in at a considerably lower temperature than in mesomorphic BHHBP which does not exhibit any significant motional effects until close to the crystal-mesophase transition above 80 °C.[27] This suggests that, not surprisingly, conformational and packing effects can have an important influence upon activation of these secondary relaxation processes.

In view of the evidence for extensive motion in the biphenyl mesogen and alkyl spacer of 24TDI/BHHBP, it must be assumed that the TDI units which are relatively immobile and capable of hydrogen-bonding interactions play an important role in stabilizing the crystal phase of this polymer. Moreover, the dynamic disorder associated with these motional processes suggests that the crystal phase of 24TDI/BHHBP is perhaps best classified as a condis crystal mesophase as described by Wunderlich and co-workers.[53] The dynamic disorder associated with the crystal phase of this material may also account, at least in part, for the low value of the crystal melting enthalpy reported earlier.[11]

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