

ARTICLES

A Study of the Viscoelastic Behavior of Novel Side Chain Liquid Crystalline Polyurethanes Using Dynamic Infrared Spectroscopy**Bindu R. Nair, Vasilis G. Gregoriou, and Paula T. Hammond****Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139**Received: November 9, 1999; In Final Form: March 14, 2000*

Side chain liquid crystal polyurethanes are a new class of materials designed to exhibit mechano-optic properties. This paper reports phase modulated dynamic Fourier transform infrared spectroscopy (FT-IR) experiments performed to study the response of these materials to sinusoidal mechanical perturbations. In dynamic FT-IR, the viscoelastic reorientation of various segments of the macromolecule can be monitored as a function of the applied strain. For the polyurethane under study, the cyano band is used to follow mesogen movements, and the urethane carbonyl is used to track the hard segment. We present evidence for two types of hard segments: those involved in hydrogen bonding within hard domains, and those found in “lone” hard segments in the soft matrix. We also present evidence for two types of mesogens: those found in smectic layers, and those not involved in smectic ordering at the hard domain interface. The hard domains and the smectic layers have strong viscous components to their mechanical response. The “free” mesogens and the “lone” hard segments, on the other hand, exhibit a more elastic response.

Introduction

Side chain liquid crystalline polyurethanes are an exciting new class of materials developed in our group that offers the potential to couple the optical changes brought on by liquid crystal alignment to applied mechanical strains. Our interest is in creating thermoplastic elastomers, for which mechanical orientation may be achieved using classic plastic processing techniques, to induce changes in liquid crystal orientation. Such thermoplastic elastomers have been designed to exhibit the mechano-optic properties of liquid crystalline cross-linked systems that have been studied by numerous researchers.^{1–3} The possibilities of forming conformal coatings that are deformable offers the potential for electrooptic or responsive coatings and sensors. Other researchers have demonstrated using both ill-defined⁴ and well-defined^{5–11} A–B and A–B–A block copolymers to obtain microphase segregated liquid crystal polymers. We have chosen the approach of designing segmented copolymers with liquid crystals pendant to a low T_g siloxane soft segments; these materials are the only reported elastomers with the responsive LC blocks above their glass transition temperature at room temperature.¹² Processing could be used to orient LC domains in these materials, thus inducing the formation of ordered monodomains in an elastomeric matrix. The resulting films should exhibit a range of properties including piezoelectricity, mechano-optic response, and electrorheological behavior. Because these materials are polyurethanes with the classic film-forming properties associated with this class of copolymers, they show potential as coatings for sensors or transducers.

The side chain liquid crystal segmented polyurethane examined here consists of liquid crystal functionalized polysiloxane soft segments and traditional MDI/butane diol hard segments

as opposed to LC segments in the diisocyanate or chain extender of the hard domain. The hard segments create a network of “physical crosslink” junctions in the liquid crystalline matrix that can transduce applied strains. To create a successful mechano-optic material, an effective conduit for the transfer of strain from the hard segments to the LC phase is desirable. In our copolymer systems, we have reported a coupling between the hard domains and the smectic liquid crystalline layers in the soft domains, as the mesogens respond to both thermal¹² and mechanical¹³ activation.

In addition to sensors, actuators, and other devices that require a mechano-optic response, the low molecular weight series of these materials show promise as viscoelastic damping systems. Damping traditionally occurs near the glass transition temperature of a polymeric material for cases in which the ratio of energy stored to energy dissipated by the material reaches a minimum. In this viscoelastic regime, the frequency of the damped vibration coincides with the molecular motions occurring within the polymer. Interpenetrating networks (IPNs) are the state of the art in damping materials because a broad temperature or frequency range of damping can be achieved through a new series of coupled molecular motions that provides additional paths to disperse energy. The segmented liquid crystal thermoplastic elastomers (LCTPEs) should also exhibit a multitude of characteristic frequencies from the various segments of the macromolecule, as well as from coupled interactions.

To obtain some insight into the viscoelastic nature of this material, we employ dynamic infrared (IR) spectroscopy techniques to study the polyurethane. Dynamic infrared spectroscopy is defined as the use of infrared spectroscopy to monitor a time-dependent process.¹⁴ Because the time scale of the excitation/de-excitation process is of the order of 10^{-13} s or

less, changes in the IR spectrum can be used to monitor the dynamics of slower processes, within the practical limits of the speed of the detector and electronics, and the strength of the signal. Dynamic spectroscopy can be divided into experiments that use the impulse-response technique (“time-resolved” spectroscopy) and those that use synchronous modulation techniques (“phase-resolved” spectroscopy). In the first case, the dynamic response to a perturbation is monitored as an explicit function of time; in the second case, the phase and magnitude of the response with respect to that of the perturbation are measured.

Dynamic infrared spectroscopy has been used successfully in the study of the molecular and submolecular (functional group) origins of the macroscopic rheological properties of organic polymers. The responses of a variety of polymer films to modulated mechanical fields have been examined.¹⁵ Composite films of isotactic polypropylene and poly(γ -benzyl-L-glutamate),¹⁶ uniaxially drawn poly(ethylene terephthalate) (PET),¹⁷ polyethylene,¹⁸ poly(methyl methacrylate),¹⁹ polystyrene,²⁰ Kraton,²¹ and Nylon 11²² are some of the examples that have appeared in the recent literature. Time-resolved dynamic IR experiments that have been performed on nematic liquid crystals^{23,24} to gain insight into the difference in reorientation behavior between small molecule liquid crystals and side chain liquid crystal polymers under the influence of an electric field. Ober, Brehmer, and co-workers have studied liquid crystal block copolymers in electric fields using time-resolved techniques to determine the dynamics of electroclinic switching during the application of the field.²⁵ Other studies of interest include phase-modulated experiments on polyurethanes, which established that hydrogen bonds in polyurethanes are especially sensitive to the stretching of the material.²⁶

In our experiments, we wish to study the coupled interactions of liquid crystals and the polyurethane backbone. Further insight into the viscoelastic behavior of this material should be useful for both the mechano-optic and the damping applications envisioned for this material.

Theory

A synchronous modulation experiment is the study of the anisotropy in a sample as a function of a sinusoidally applied perturbation. In general, IR absorption is caused by the coincidence of the electric field vector of an IR beam and the dipole transition moment of a molecular vibration. An IR band that is anisotropic will have different absorbances depending on the direction of the polarized IR beam; the absorbance is maximized when the electric field is perfectly parallel to the transition moment of the molecule. In general, the degree of anisotropy can be described by the dichroic difference, $\Delta A(v)$, which is defined as the difference in absorbance of a band as probed by polarized infrared radiation.

When a small amplitude sinusoidal strain perturbation is applied along one of these polarizer directions, the dynamic dichroic difference can be calculated. This difference is considered the sum of a quasi-static component and a dynamic component

$$\Delta A(v,t) = \Delta \bar{A}(v) + \Delta \tilde{A}(v,t) \quad (1)$$

The quasi-static component is nothing more than the traditional dichroic difference described above and includes strains that may have been introduced into the system as residual orientation from the sample preparation techniques. The dynamic component, on the other hand, is induced exclusively by the small amplitude perturbations on the sample. The small mechanical vibration of amplitude $\hat{\epsilon}$ and fixed angular frequency

ω_s can be described by the following equation

$$\tilde{\epsilon}(t) = \hat{\epsilon} \sin(\omega_s t) \quad (2)$$

The time dependent response of the IR band absorbance to this periodic stretching can be described in terms of the dynamic component of the dichroic difference. The response is a sinusoidal function with the same periodicity as the applied strain field, ω_s , an amplitude of $\hat{\Delta A}(v)$ and a phase lag, $\beta(v)$, as follows

$$\Delta \tilde{A}(v,t) = \hat{\Delta A}(v) \sin[\omega_s t + \beta(v)] \quad (3)$$

Equation 3 can be rewritten by employing trigonometric identities as the sum of two orthogonal components

$$\Delta \tilde{A}(v,t) = \Delta A'(v) \sin(\omega_s t) + \Delta A''(v) \cos(\omega_s t) \quad (4)$$

where $\Delta A'(v)$ and $\Delta A''(v)$ are related to the amplitude and phase angle by

$$\begin{aligned} \Delta A'(v) &= \hat{\Delta A}(v) \cos[\beta(v)] \\ \Delta A''(v) &= \hat{\Delta A}(v) \sin[\beta(v)] \end{aligned} \quad (5)$$

$\Delta A'(v)$ and $\Delta A''(v)$ are the in-phase and 90° out-of-phase spectra, respectively. The in-phase spectrum is the response to the instantaneous extent of strain. The orthogonal (90°) out-of-phase (also known as quadrature) spectrum is proportional to the viscous response to the strain.

A step-scan FT-IR experiment, which permits the separation of the time of the experiment (applied perturbation) from the time of data collection, is used to collect the in-phase and out-of-phase spectra. In such an experiment, the dynamic spectra, $\Delta A'(v)$ and $\Delta A''(v)$, can be considered as the difference between two static spectra collected at the peaks of the applied strain cycle.²⁷

These quantities measure the viscoelastic behavior of the IR bands in question and are analogous to the data acquired from classic viscoelasticity measurement devices such as dynamic mechanical analysis (DMA). In DMA experiments, an elastic storage (E') and a viscous loss (E'') modulus can be deconvoluted from the complex modulus (E^*). The ratio of loss to storage moduli ($\tan \delta$) is the most often reported quantity to describe degree of viscoelasticity in a system.

Experimental Section

LCP Compound. The polyurethane under investigation is a segmented copolymer with hard segments of MDI/butane diol. The soft segments are polysiloxanes with a cyano-biphenyl mesogen attached to each repeat unit via an eight-methylene spacer. The soft polysiloxane backbone ensures that the liquid crystal is free to move in this low T_g environment; LC mobility is further enhanced by the choice of the long spacer used to decouple the mesogen from the polymer main chain. The structure of this macromolecule, as well as a predicted morphology, is presented in Figure 1. The hard segments form hard domains ($T_g = 88$ °C), and the soft continuous domains are in the smectic A phase over the entire liquid crystalline temperature range ($T_g = -4.7$ °C; $T_{\text{clearing}} = 104.2$ °C). The polyurethane is synthesized by reacting two moles of diisocyanate and one mole chain extender to form a hard segment for every soft segment macrodiol. The soft segment consists of 16 to 20 repeat units of siloxane resulting in a soft segment molecular weight between 4200 and 5500 g/mol. The weight fraction of liquid crystal units in the resulting polyurethane is high, approximately 90 wt %.

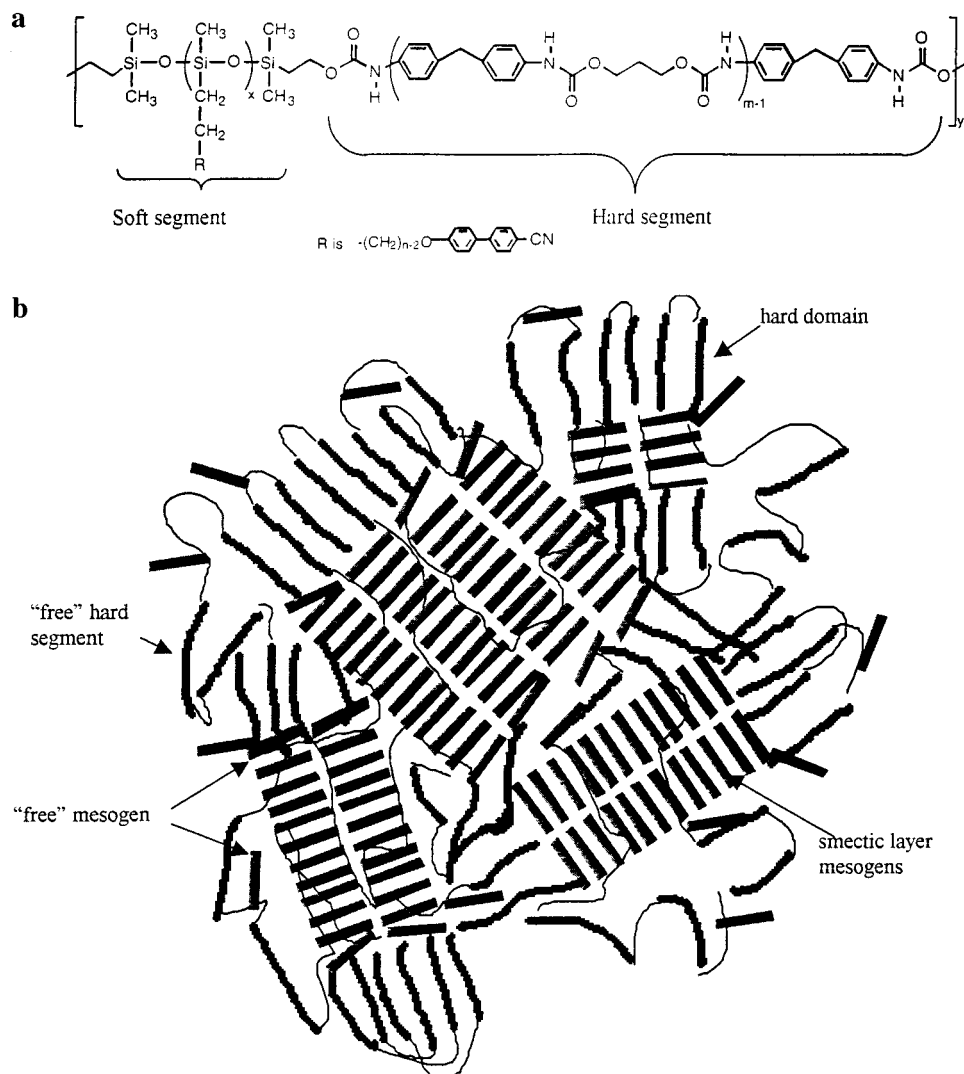


Figure 1. (a) Chemical structure of side chain liquid crystalline polyurethane. (b) Polyurethane morphology cartoon.

The synthesis and characterization of this material has been reported elsewhere.¹² Samples were prepared by solvent casting a thin film of material onto a Teflon substrate from a 50/50 mixture of DMAc and THF. Peel tests and immersion in water, as well as examination of the stretched sample under optical microscopy, suggests that the adhesion of the sample to the substrate is not compromised by mechanical deformation.¹³

Dynamic FT-IR Spectroscopy. Polymer dynamic rheology experiments were conducted with a Nicolet Magna-IR 860 step-scan FT-IR spectrometer and a Manning Applied Technology polymer modulator, which was mounted directly on a base plate inside the sample compartment. A Moletron wire-grid polarizer was placed before the sample allowing only infrared radiation polarized parallel to the stress direction to reach the sample. A low pass optical filter was placed after the sample to filter off the light above 3950 cm^{-1} or 1950 cm^{-1} . The spectra were collected at a resolution of 8 cm^{-1} wavenumber in less than 1 h.

The Magna-IR 860 spectrometer employs a piezo interferometer that utilizes a set of piezoelectric transducers to actuate the phase modulation on the fixed mirror. The stepping of the moving mirror, position holding, dynamic alignment, and phase modulation are all controlled digitally by the digital signal processors. The sinusoidal signal that drives the polymer modulator is also generated internally by the same circuit that generates the signal for the phase modulation. This design has

the added advantage that the phase modulation and the sample modulation by the stretcher are synchronized, which reduces the sampling error and improves the signal-to-noise ratio significantly. The polymer modulator is mounted directly on a base plate inside the sample compartment without any additional vibrational isolation.

The polymer dynamic rheology experiments described in this paper were conducted with a phase modulation frequency of 400 Hz and phase modulation amplitude of $3.5\lambda_{\text{HeNe}}$. This modulation amplitude is chosen to cover the entire mid-IR spectral region and to enhance the modulation efficiency in the fingerprint region. The modulation of applied strain by the dynamic stretcher was 25 Hz with an amplitude of $50\text{ }\mu\text{m}$. This small amplitude of oscillation ensures operation in the viscoelastic regime. Furthermore, at low oscillation amplitudes, the effect of sample thinning on IR band absorbances is negligible when compared to the effect of the dynamic signal. All of the data collection and processing, including the demodulation of the phase modulation and sample modulation frequencies, are carried out by the digital signal processors and other internal electronics of the spectrometer.

To check the validity of these data and the performance of the spectrometer, control experiments with isotactic polypropylene films were conducted under similar conditions. The results for isotactic polypropylene are virtually identical to those

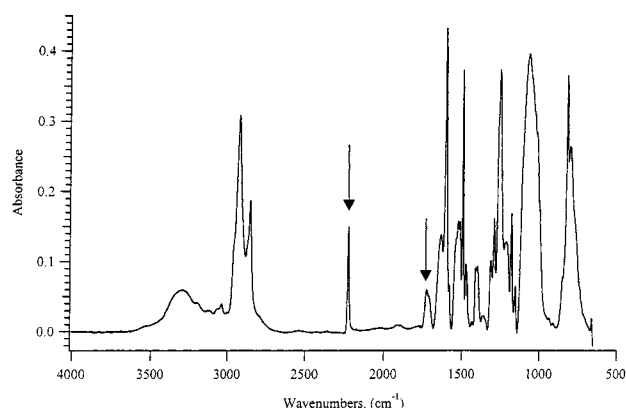


Figure 2. Static FT-IR of polyurethane sample. Arrows indicate bands of interest.

TABLE 1. Compilation of Key FT-IR Bands

wavenumber (cm ⁻¹)	assignment	macromolecular component
2224 (s)	CN stretch vibration	smectic layer mesogen
2229 (w)	CN stretch vibration	free (nematic) mesogen
1730 (s)	amide I stretch (no H-bonding)	free hard segment
1716 (s)	amide I stretch (H-bonding)	hard domain interface
1701 (s)	amide I stretch (H-bonding)	hard domain

in the literature except these data could be obtained with much shorter data collection times.²⁷

The sample was clamped in the polymer modulator such that the film was taut. The macroscopic static strain (ϵ) was not determined, although it is in the range of less than 1%. We are confident that the material is in the linear viscoelastic regime at these low amplitudes of oscillation because dynamic rheological experiments performed on a similar LC polyurethane at 1% strain indicated a sinusoidal variation of both stress and strain satisfying the conditions for linear viscoelasticity.²⁸

Results and Discussion

Static Spectra and Band Assignments. Figure 2 shows the FT-IR spectrum of the liquid crystalline polyurethane under investigation. The different bands in this sample have been previously assigned.¹³ Table 1 is a compilation of the bands discussed in the rest of this paper. In the static spectrum, there is one clear band at 2225 cm⁻¹ that we assign to the cyano group in the mesogen. Thus, when analyzing the dynamic spectra, this frequency will be used to follow the rearrangement of the mesogen. We use the urethane carbonyl region to identify the movement of the hard segments. There are three bands in the urethane carbonyl region. We assign these bands to carbonyls with different degrees of hydrogen bonding. The 1701 cm⁻¹ band is assigned to carbonyls that engage in hydrogen bonding within hard domains. Slightly less ordered carbonyls at the interface between the hard and the soft segment have a stretching frequency of 1716 cm⁻¹. The urethane carbonyls of those hard segments that are not found in hard domains, but rather exist in the soft segment matrix are known as "lone hard segments"; they are not hydrogen bonded and have their IR signature bands at 1730 cm⁻¹.

It is to be noted that the carbonyl dipole does not lie along the molecular axis of the hard segment. Using simple geometry arguments, the urethane carbonyl can be assumed to be 79° off the hard segment axis.²⁹ Qualitative comments on the reorienta-

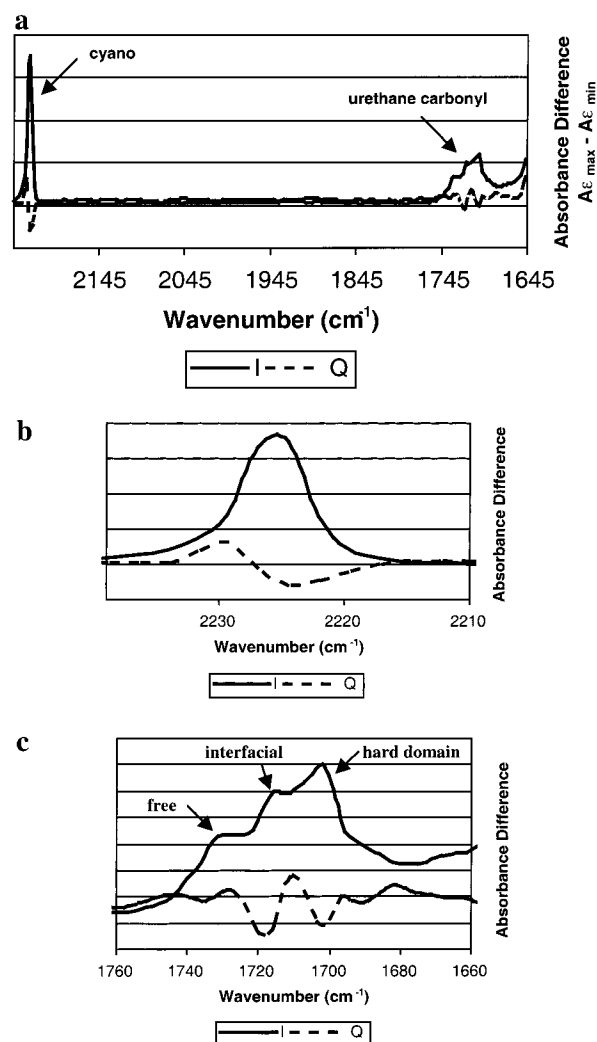


Figure 3. (a) In-phase (I) and in-quad (Q) spectra. Of special note is strength of elastic response as compared to viscous. (b) In-phase and out-of-phase response of cyano band region magnified. (c) In-phase and out-of-phase response of the urethane carbonyl region magnified.

tion of the hard segment will assume an orthogonal relationship between the carbonyl dipole and the hard segment.

In-Phase and Out-of-Phase Dynamic Spectra. As discussed in the theory section, the in-phase response of a material to a cyclic strain field is proportional to the extent of strain. Thus, this component is the elastic component of the total material response. The quadrature spectrum, on the other hand, which is strain rate dependent, is related to the viscous component of the total response. The spectra were collected with the polarizer parallel to the direction of strain. At each step of the step scan, both in phase (0°) and out-of-phase (90°) spectra were recorded. The difference spectra, which measures the difference between the stretched and the relaxed sample, will show a positive increase in intensity when molecules align with the direction of stress, whereas molecules aligning perpendicular to the applied stress will show a negative or decrease in intensity.²⁷

Figure 3a shows both the in-phase and the out-of-phase response of the side chain liquid crystalline polyurethane to the applied cyclic strains. From Figure 3a, it is clear that the in-phase response is much stronger than the quad response. Furthermore, we can see that the ratio of elastic to viscous component is much higher in the cyano band than in the urethane band. The cyano bands are indicative of the mesogen that are found in the soft segment. Because the soft segment is above its T_g of -4 °C, we would expect the mesogens to respond

TABLE 2. Reorientation of Macromolecule under the Elastic and Viscous Components of the Applied Strain

moiety	elastic component	viscous component
free mesogens	parallel ^a	parallel
smectic mesogens	parallel	perpendicular
free hard segment	slightly perpendicular	none ^b
hard domains	perpendicular	parallel

^a Cannot be resolved in in-phase spectrum. ^b No significant variations in out-of-phase spectrum

rapidly to the imposed stress. The urethane bands, on the other hand, can be found in the hard domains that are below their T_g of 88 °C. We therefore expect the response of the urethane band to be more viscous.

Figure 3, parts b and c, shows the expansions of the cyano and the carbonyl regions, respectively, of the spectra in Figure 3a. On the basis of our interpretation of the data found in this section, we have assigned the elastic and viscous orientation of the different parts of the macromolecule as summarized in Table 2. The remainder of this section is a discussion of these assignments.

In Figure 3b, for the cyano band, we observe a strong, positive in-phase response. Thus, the data tells us that the mesogens are aligning parallel to the direction of the strain. Previous experiments performed on this material show that at low strains, mesogens align along the direction of the stress.¹³

We find that the cyano band shows a bisignate signature in the quad spectrum. When a band exhibits such a shape in the dynamic spectra, there are two possible explanations. The first is that the band shifts to a new position during the deformation process. The other potential cause of this phenomenon is that the original band is representative of more than one population that respond to the perturbation in different ways. For instance, if one response is parallel to the deformation and the other perpendicular, the resulting dynamic spectrum will show a bisignate.

It is therefore possible to attribute the bisignate in the quadrature spectrum of the cyano band to the existence of two distinct populations. One population consists of the mesogens existing in smectic layers. We can assign the lower wavenumber (lower energy) band of 2224 cm^{-1} to cyano groups within the smectic layer. IR stretching absorption frequencies of a bond are proportional to the square root of the Hookian force constant of the bond. When the $-\text{CN}$ bond is placed in an environment that diffuses its strong dipole, such as the smectic layer with interlocking antiparallel mesogens (as previously demonstrated for this material¹²), the force constant for each dipole is reduced, and the frequency of vibration is lowered.³⁰ The higher wavenumber population (2229 cm^{-1}) is assigned to the $-\text{CN}$ groups that are not involved in the formation of smectic layers and, therefore, are less ordered.

As we can see in Figure 3b, the quad spectrum has a positive component in the higher wavenumber band (free mesogens) and a negative component in the lower wavenumber band (smectic layers). The latter suggests that the viscous response of the ordered smectic layers is to align the mesogen perpendicular to the direction of stress. This reorientation of the mesogen leads to the smectic layers aligning parallel to the direction of the stress. Previous work by Zhao^{31–33} suggests that the smectic layer can be considered a mechanical entity that likes to align along a mechanical field. Our previous experiments on this material show that at an elongation of 40% strain, the average mesogen orientation switches from parallel to the strain field to perpendicular to the field.¹³

The higher wavenumber population on the other hand shows a positive quadrature peak. This population consists of “free” mesogens that are not involved in smectic layers. The quad response of this small population suggests that since these mesogens do not exist in smectic layers, the viscous component of the stress continues to align the free mesogens continue along the direction of applied strain. It is of interest to note that these “free” mesogens can only be observed in the viscous response because this population cannot be resolved in the in-phase spectrum. It is possible that these mesogens are found near the viscous hard domains, at which the smectic layers are least perfect, and that the hard domain interfaces slow the response time of these liquid crystals.

Figure 3c shows the carbonyl region of the dynamic spectra. We observe a positive in-phase response for all three bands. A positive response correlates with a perpendicular alignment of the hard segments because the carbonyl dipole is orthogonal to the hard segment axis as discussed above. Of special interest is the observation that, despite the expected elastic behavior of the free carbonyls within the soft matrix, they show only a small, positive dichroic difference. Previous work suggests that the free carbonyls respond elastically parallel to the applied stress field.^{13,29,34} It is therefore possible that there is a parallel (or negative) alignment of the free hard segments that is masked by the convolution of the free urethane bands with the hydrogen bonded urethane bands.

The carbonyl region of the quad spectrum shows the strongest viscous responses in the entire material for reasons discussed above. The “free” carbonyls at 1730 cm^{-1} , which are not found in the sluggish hard domains, are the only carbonyls without much activity in the quad spectrum. These carbonyls primarily show an elastic response suggesting that the hard segments embedded in the soft matrix, and denied hydrogen bonding interactions with its neighbors, orient with the flexible soft segment. This observation is consistent with the widely accepted models of polyurethane reorientation behavior presented by Bonart et al.³⁵ and expanded by Cooper et al.^{29,34}

The “free” or non-hydrogen bonded carbonyls do not show much viscous response. On the other hand, the hydrogen bonded carbonyls do show a strong negative band. Thus, the data indicates that the viscous component of the stress induces the hard segments to reorient parallel to the direction of stress. Bonart³⁵ proposed a model for MDI/butane diol polyurethanes wherein hard segments align perpendicularly to the stretch direction at low strains. This orthogonal orientation is attributed to the long direction of the hard domain acting as a mechanical unit to orient within the stress field. In a number of studies,^{29,34} a spherulitic superstructure of the hard domains was considered to be responsible for this negative orientation; however, in our material, we have not seen any evidence of crystallinity of the hard domains. The hard segment length and volume fraction probably results in paracrystalline order rather than fully crystalline hard domains. At high strains of greater than 300%, the polyurethane hard domains underwent slip and deformation with hydrogen bonding now occurring between hard segments aligned parallel to the direction of strain. At this reorientation strain, the chains have undergone permanent deformation, and the material has lost mechanical reversibility.

Viscoelastic Response of the SCLCP. Using the identities developed in the theory section (equation 4), we can use the in-phase and in-quad spectra to create plots of the dynamic response $\Delta A(\nu, t)$ as a function of both wavenumber and phase angle. Figure 4 and Figure 5 show the cyano and the carbonyl regions, respectively. These figures allow us to visualize how

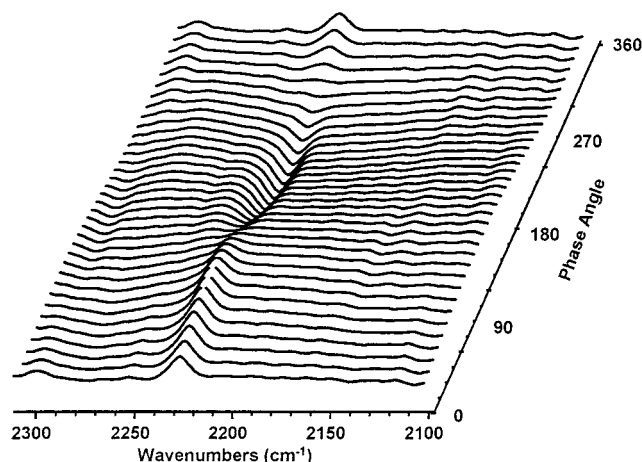


Figure 4. CN band as a function of wavenumber and phase angle. This graph was compiled using linear combination methods described in the theory section from $\Delta A'(\nu)$ and $\Delta A''(\nu)$.

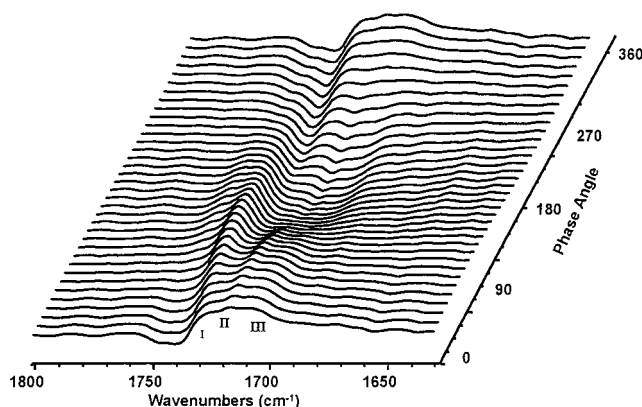


Figure 5. Carbonyl band as a function of wavenumber and frequency. Graph compiled in same manner as Figure 4.

the bands are affected during each cycle of applied strain. Because we apply a 25 Hz modulation frequency, the period of each cycle is 40 ms.

Figure 6a is a representation of a perfectly elastic and a perfectly viscous response to an externally applied oscillatory strain. The elastic component is exactly in-phase with the sinusoidal variation, whereas the viscous component has a phase lag of exactly 90° . Figure 6b depicts the actual variations of the different bands of interest with applied strain. Thus, this figure is a series of cross sections of Figures 4 and 5 at the IR frequencies of interest. All of the curves have been normalized, such that their amplitude is 1.0 in order to represent them on the same scale. The data shows that all the bands have some phase lag when compared to the perfectly elastic response. There are two categories of responses based on the phase lags suggesting that there are two rates of time dependent behavior that can be found in the material. The “free” hard segments and the “free” mesogens appear to respond at the same rate. These curves are clearly viscoelastic within the time frame of this experiment (40 ms). The second group of responses can be found in the hydrogen bonded hard segments that are indicative of the hard domains, and the mesogens in smectic layers. This response is 90° out-of-phase, indicating that the hard domains exhibit a perfectly viscous response within the time frame of this experiment.

We are thus able to elucidate two different response patterns in the complex macromolecular system under investigation. The smectic layers and the hard domains appear to respond slug-

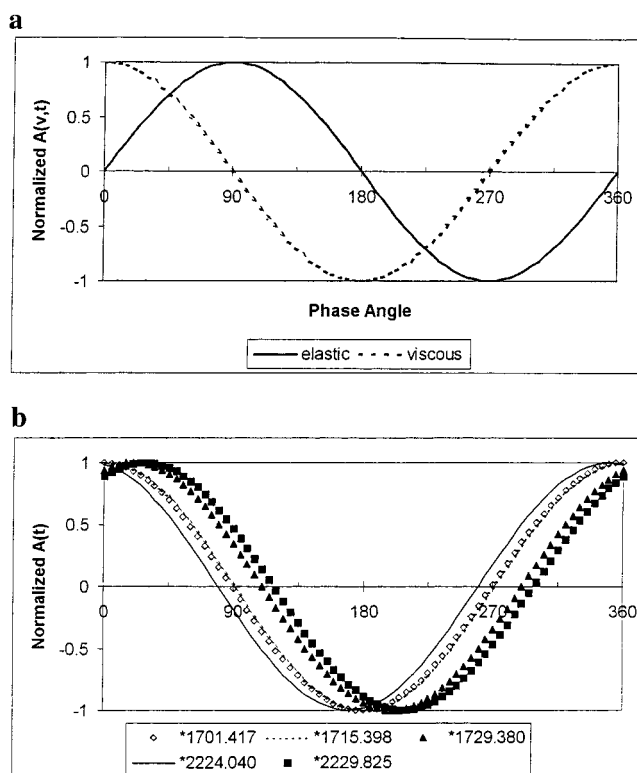


Figure 6. (a) Perfectly elastic and perfectly viscous response curves. (b) Dynamic dichroic response of polyurethane created by compiling cross sections of Figures 4 and 5.

ishly at similar rates, whereas the “free” mesogens and the “lone” hard segments both reorient in a more elastic manner.

Summary

Dynamic infrared dichroism techniques have been used to study a complex side chain liquid crystalline segmented polyurethane. The side chain mesogens are monitored by the cyano tag at the end of the molecule, whereas the hard segments can be viewed in carbonyl spectral region. A study of the different parts of the macromolecule leads to an understanding of the elastic and the viscous orientation behavior of the polymer. We find that the elastic component of the strain aligns smectic layers parallel and hard domains perpendicular to the direction of strain. The viscous strain component, on the other hand, induces a perpendicular smectic layer and parallel hard domain orientation behavior. These observations are consistent with a model proposed in earlier work that the hard domains and the smectic layers change orientation as the applied strain is increased from low static strains, which are characterized primarily by reversible elastic behavior, to high strains, at which permanent deformation occurs.

We have further presented evidence for the presence of mesogens that are not found within the ordered smectic layers. Finally, we have shown further evidence for the coupling of the mechanical deformation behavior of the smectic layers and the hard domains and identified two primary relaxation times within this system.

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