

FT-IR studies of side chain liquid crystalline thermoplastic elastomers

B.R. Nair, V.G. Gregoriou, P.T. Hammond*

Department of Chemical Engineering and The Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

Received 22 March 1999; received in revised form 18 June 1999; accepted 22 June 1999

Abstract

Side chain liquid crystalline polyurethanes are a new class of materials that show promise for mechanooptic applications. The rich morphology afforded by these materials also provides a chance to understand the interplay between polyurethane morphology and liquid crystalline ordering. In this paper, we study the response of a polyurethane with liquid crystals pendant to the soft segments to an applied strain using fourier transform infrared (FT-IR) linear dichroism. We find that this complex material follows the trend established in the literature for both side chain liquid crystalline homopolymers and segmented polyurethanes. At low strains, the soft segments align with strain inducing an orientation in “lone” hard segments. Up to strains of 40%, the LC mesogens align with the strain field and the hard segments in hydrogen bonded domains align perpendicular to the field. At strains above 40%, we find a rearrangement of the ordering that result in smectic layers and the hard segments aligning parallel to the field. A model is proposed to represent these findings, and reflections on the cooperative movement of the different macromolecular components of the polyurethane are offered. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline side groups; Side chain liquid crystalline polymer; Fourier transform infrared linear dichroism

1. Introduction

Side chain liquid crystalline elastomers are a promising set of materials that couple the response of liquid crystals and elastomeric networks to applied stress fields [1]. The elastomer acts as a matrix through which stress is transferred to the liquid crystalline side groups (LCs), which respond to the applied mechanical field with alignment. These materials present a great deal of promise as sensors, actuators, and electromechanical elements with the high strain range and reversibility of rubbery polymers; some potential applications include viscoelastic damping systems, robotic tactile arrays, or mechanooptic sensors. The use of these materials in sensor or actuator applications is highly dependent on the ability to transduce mechanical stresses and deformations through the orientation of the liquid crystalline network, and consequently to the final properties of these materials.

Side chain liquid crystalline polymer (SCLCP) networks were first synthesized by Finkelmann [2]. These covalently crosslinked systems exhibit a number of interesting mechanooptic properties, as demonstrated by several researchers [3–10]; however, some limitations include the

fact that covalent crosslinks reduce the mobility of the liquid crystalline mesogens to respond to mechanical fields [8]. Also, the intractable nature of these thermoset materials prevents the use of common plastics processing techniques in the formation of macroscopically ordered films. We have recently synthesized a new series of liquid crystalline thermoplastic elastomers that contain physical, rather than chemical crosslink points [11]. The liquid crystalline group in these materials is a side chain functional group on the soft segment, rather than a component in the hard segment, as in earlier systems [12–14]. These segmented copolymers can be processed using traditional thermoplastic processing methods to form uniform films or fibers. These systems represent a new direction in the development of ordered liquid crystalline elastomers, and may provide new solutions to the challenges of producing responsive networks of side chain liquid crystalline polymers.

Fundamental to establishing and exploiting the potential of these novel materials is the understanding of the structure–property relationships encountered in liquid crystalline segmented copolymer systems. In the rich morphology afforded by these materials, the underlying question of how to engineer the mechanooptic response can be addressed in part from an understanding of the response of the various parts of the macromolecular LC network to applied strain. We have chosen to study the molecular level

* Corresponding author. Tel.: +1-617-258-7577; fax: +1-617-258-5766.
E-mail address: hammond@mit.edu (P.T. Hammond).

response of a LC soft segment polyurethane to applied strains using Fourier transform infrared (FT-IR) linear dichroism.

Both segmented polyurethanes and SCLCPs have been extensively studied by IR dichroism techniques. Bonart used the FT-IR in conjunction with wide-angle X-ray scattering to create a model describing the reorientation behavior of polyurethanes as a function of the strain [15]. Cooper and co-workers [16,17] performed a series of studies using the FT-IR to enhance this molecular model; Hsu et al. have also contributed significantly in this area [13,18–21]. In the area of molecular reorientation with strain of side chain liquid crystalline polymers, Zhao and coworkers [22–24] have been extremely active. Our side chain liquid crystalline elastomer shows elements of both polyurethane and liquid crystalline orientation.

2. Experimental

2.1. Side chain LC polyurethane

The details of the synthesis of the side chain liquid crystalline polyurethane used in this study have been published elsewhere [11,25]. This material is a segmented copolymer with MDI/butanediol hard segments and side chain liquid crystalline siloxane soft segments. The polymer exhibits a smectic A phase over the entire liquid crystalline range as verified by optical microscopy between crossed polarizers on a Kramer Scientific Leitz DMRX microscope in transmission.

At room temperature, the segmented copolymer is above its soft segment T_g (-4.7°C) permitting movement of its liquid crystalline phase, but below the T_g of the hard segment (88°C).

2.2. Static linear dichroism

Infrared dichroism is a tool often used to measure the anisotropy in the orientation of a functional group within a sample. This anisotropy can be caused by processing conditions, or by the application of fields on the sample (e.g. temperature or mechanical fields). Our experiments study the effect of strain on a segmented polyurethane system.

The static infrared spectroscopic data were collected on a Nicolet 550 Series II FT-IR spectrometer equipped with an MCT/A detector at 2 cm^{-1} spectral resolution. A wire-grid infrared polarizer (SpectraTech Corporation, Stamford, CT) that allows plane polarized light to reach the sample was placed in the infrared beam.

Stretching experiments were performed using a static stretcher designed and machined for this purpose which allows elongation of the sample up to 200% of its initial length at room temperature. A sample was clasped between a stationary jaw and a jaw that was controlled by a micrometer. Uniaxial strains were induced in the sample by

pulling the upper jaw in a controlled fashion with the micrometer.

Free-standing polyurethane films are too thick to be within the range of the Beer–Lambert Law, and saturate key vibrational bands in the transmission IR spectra. In order to examine films thin enough for FT-IR analysis, samples were prepared by casting the polyurethane on a thin poly(tetrafluoroethylene) substrate (Du Pont De Nemours & Co) from 50/50 THF/DMAc. The Teflon™ substrate was used for these experiments as a support for the thin polyurethane film to provide it with enough integrity to be held by the jaws of the stretcher. Substrates for IR dichroism measurements have been used previously in the literature [22,24,26,27]; therefore, there is a precedent for use of this technique. Adhesion of the polyurethane to the Teflon™ substrate was maintained upon testing with tape peel tests and immersion in water.

We are satisfied that there is minimal slippage between the sample and the film on stretching, and the samples viewed under the optical microscope in reflectance at $400\times$ indicated no signs of cavitation. Further, the distance between marks placed on the sample before mechanical deformation increased with strain. The sample width decreased with increasing strain, suggesting that there is conservation of volume, and that the sample is in uniaxial tension.

The use of infrared dichroism involves the orientation of the sample and the subsequent measurement of the absorbance of key vibrational bands parallel and perpendicular to the orientation direction. The dichroic ratio R is defined as

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

where A_{\parallel} and A_{\perp} are the absorbances measured with the radiation polarized parallel and perpendicular to the stretching direction. The value of R can range from zero (where there is no absorption in the perpendicular direction) to infinity (no absorption in the parallel direction). For random orientation, $R = 1$. A useful parameter for determining the orientation is the so-called order parameter, S , which is expressed by the following equation:

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (2)$$

where θ is the angle between the draw direction and the local molecular axis. This orientation function can be related to experimentally measured quantities, such as the dichroic ratio R of the absorption band according to the following equation:

$$S = \frac{(R - 1)(R_0 + 2)}{(R_0 - 1)(R + 2)} \quad (3)$$

where $R_0 = 2 \cot^2 \alpha$ is the dichroic ratio for perfect alignment. The variable α is the angle between the dipole direction and the molecular axis of the segment of the molecule under consideration; α varies from 0 (dipole along

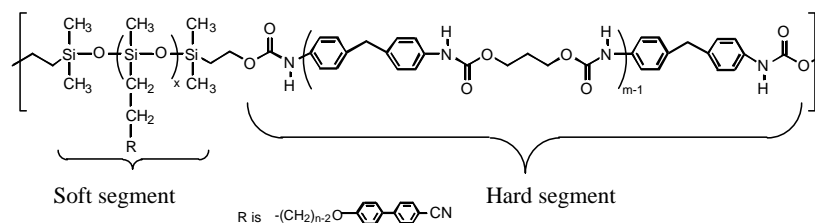


Fig. 1. Molecular structure of side chain liquid crystalline polyurethane.

molecular axis) to $\pi/2$ (dipole perpendicular to molecular axis). The order parameter, S , may vary from $-1/2$ to 1 indicative of perfect perpendicular to perfect parallel orientation of the molecule or molecular segment. In the absence of any orientation, $S = 0$. Recent reported studies point out that this model [28,29] is not sufficient to explain the observed behavior of many real systems. Violations to the model have been noticed in both static systems and systems that undergo dynamic deformations [30,31]. Nevertheless, this model can adequately explain the qualitative behavior of uniaxial systems and will be used here.

For this work, dichroic ratio data were collected by stretching two different samples. For the first sample, a polarizer placed parallel to the direction of stretch was placed between the sample and the detector. A strain was applied and the FT-IR spectra were collected. The same procedure was carried out on a separate sample with the polarizer perpendicular to the stretch direction. The ratio of the parallel to perpendicular absorbance at each strain value was calculated. Since the two samples used in the experiment were of different film thicknesses due to the solvent casting technique used, we normalized the ratios by setting the 0% strain dichroic ratio to 1.0 for all the vibrational bands that we studied. To ensure that this assumption is valid, we performed this experiment on a single sample changing the polarizer from parallel to perpendicular at each strain point and recording two different spectra for each experimental point. Using this method, the trends described for each of the bands in Section 3 can be reproduced, and random orientation at 0% strain can be confirmed. The dichroic ratio of an unstretched polyurethane cast on the Teflon™ substrate was 1.0, indicating that there was no orientation of the sample induced by the solvent casting on the support. However, we choose to present the data compiled from the two different experiments, because absorptions from water vapor can be best avoided if the chamber is not opened during the experiment.

In order to ensure that our reported trends are not a manifestation of the Teflon™ substrate, we performed dichroic ratio calculations on the baseline absorbances for each of the polyurethane bands studied on a bare Teflon™ substrate. We found that these ratios were close to 1.0 throughout the strain range, indicating that changes in peak absorbance heights reported are not a consequence of the experimental technique.

Orientation function graphs were generated by using Eq.

(3) and the measured dichroic ratios. A transition moment direction (α) of 0° was assumed for the cyano band while the carbonyl band was assumed to have an angle of 79° [17]. The carbon–nitrogen bond of the cyano bond is sp hybridized, resulting in a linear geometry for this bond. It was assumed that the normal vibrational mode of the cyano dipole lies exactly along the molecular axis of the liquid crystalline moiety. The dichroic ratio, R , of the cyano band therefore maps the structure factor, S , of the mesogen to the strain. When studying the alignment of the hard segment, the issue is slightly more complicated. Simple ester carbonyls are often assumed to be 60° off the molecular axis in the literature as the carbon is sp^2 hybridized [24]. The 79° angle is arrived at by taking into account the geometry of the entire urethane linkage with respect to axis of the hard segment. For this reason, the orientation function curves of the hard segment do not necessarily follow the trend of the dichroic ratio. It should be recognized that variation in the transition moment direction (α) of greater than 10° is required to significantly affect the orientation function [16].

3. Results and discussion

3.1. Molecular architecture and structure

The polyurethane investigated here is a segmented copolymer of flexible polysiloxane soft segments with pendant liquid crystalline cyano-biphenyl moieties and MDI hard segments [11]. The molecular structure of this macromolecule is shown in Fig. 1. The heterogeneous nature of this segmented copolymer precludes the possibility of finding a single solvent system for the material. A solvent system which includes a non-polar solvent for the siloxane soft segment and a polar, H-bonding solvent for the urethane hard segments such as 50/50 mixtures of THF/DMAc or $\text{CH}_2\text{Cl}_2/\text{DMSO}$ are therefore necessary for casting films. A result of this lack of a single solvent system is the inability to perform gel permeation chromatography to determine polyurethane molecular weights. An estimate of the size of these macromolecules can be obtained from intrinsic viscosity measurements performed at 40°C in 50/50 THF/DMAc. Based on findings in the previous literature [32], our system, with an intrinsic viscosity of 0.4 dl/g, is of relatively low molecular weight.

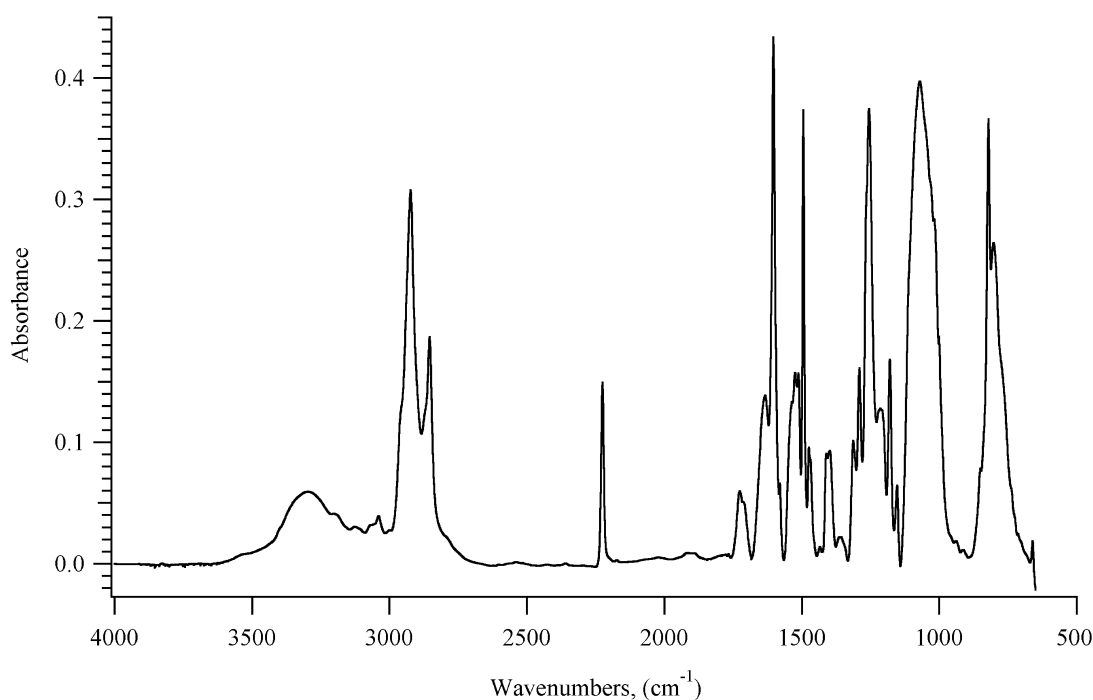


Fig. 2. FT-IR spectrum of liquid crystalline polyurethane.

Our segmented copolymer system is designed to utilize the thermodynamics of phase segregation to produce an environment that can couple applied strain fields to liquid crystalline mobility. LC mesogens are attached to a flexible

Table 1
FT-IR peak assignments in polyurethane

Wavenumber (cm ⁻¹)	Assignment	Uniquely identifies
3309 (m)	NH stretching	Hard segment
3070 (wm)	CH aromatic stretch vibration	
3036 (wm)	CH aromatic stretch vibration	
2924 (s)	CH ₂ asymmetric stretch vibration	Mesogen
2854 (s)	CH ₂ asymmetric stretch vibration	
2225 (s)	CN stretch vibration	
1728 (s)	Non H-bonded urethane	Hard segment
1709 (s)	H-bonded urethane	Hard segment
1643 (m)		
1605 (s)	C–C aromatic stretch vibration	
1524 (s)		
1493 (s)	C–C aromatic stretch vibration	
1470 (s)	CH ₃ asymmetric deformation	
1431 (m)	Amide II	Hard segment
1412 (s)	Amide	Hard segment
1362 (m)	Amide	Hard segment
1311 (s)	CH aromatic in-plane deformation	
1292 (s)	CH aromatic in-plane deformation	
1257 (vs)	Phenyl-O stretching	Mesogen
1200 (m)		
1180 (s)	CH aromatic in-plane deformation	
1068 (vs)	Si–O–Si stretching	Soft segment
941 (wm)		
822 (vs)	CH aromatic out of plane deformation	

siloxane chain; these LC siloxane oligomers are alternated with hydrogen bonding hard segments along the length of the polyurethane chain. Micro-phase segregation of the two types of incompatible segments results in a multiphase polymer network that is physically crosslinked by the aggregation of the hard segments in domains. As these materials are of low molecular weight, the hard domains are only weakly cohesive, and this material behaves more like a viscoelastic gum than a thermoplastic elastomer.

The polyurethane under study is a smectic A side chain LC polymer as determined by SAXS. The polymer is characterized using both NMR and FT-IR spectroscopic techniques. Fig. 2 is the IR spectra of a film of the polyurethane cast from 50/50 THF/DMAc. The spectrum is tabulated with the key peaks identified in Table 1. Table 1 also makes note of the peaks that can be clearly assigned to the different parts of the copolymer. We choose to use the cyano band at 2225 cm⁻¹ as a way of tracking the orientation of the mesogen as it is a clear, unambiguous band.

The amide I carbonyl peak can be resolved into its constituent peaks using a curve fitting method [13,33]. For urethane carbonyls, the lower the frequency of the band, the higher the degree of hydrogen bonding and ordering of the carbonyls. The three peaks identified in Fig. 3 at 1726, 1709, and 1699 cm⁻¹ correspond to free carbonyls, carbonyls at the interface between hard segments and soft segments or in less ordered regions of the hard domains, and ordered hydrogen-bonded carbonyls within the hard domains respectively. Other investigators have ascribed these bands to these types of urethane environments in the literature [13,14]. Similar spectra have been fit using two

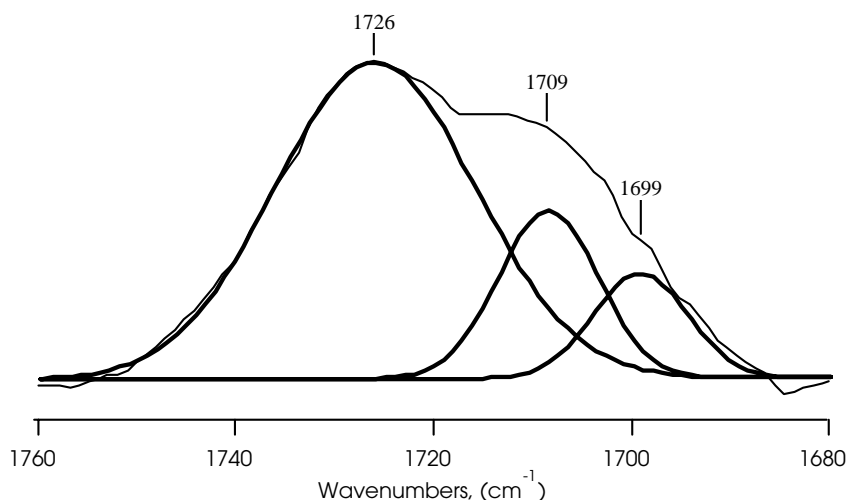


Fig. 3. Amide I carbonyl band resolved into component peaks.

Gaussian curves for the higher wavenumber bands and a Lorentzian for the ordered hydrogen bonded band in order to obtain the “best fit” for their data [13]. We find that we can best fit our data using three Gaussian bands. We assume for the purposes of this fit that adsorption coefficients of the hydrogen bonded bands the same for both H-bonded bands. The ratio of H-bonded to non H-bonded carbonyl adsorption coefficients is assumed to be 1.7 [13].

We are comfortable fitting this curve to three bands because spectra taken of this material when it is subjected to sinusoidal stress fields show each of these bands clearly. Dynamic IR spectroscopy is a tool used to resolve responses of materials to oscillating fields, and to study their viscoelastic properties [34–36]. The results of dynamic response of this material are forthcoming.

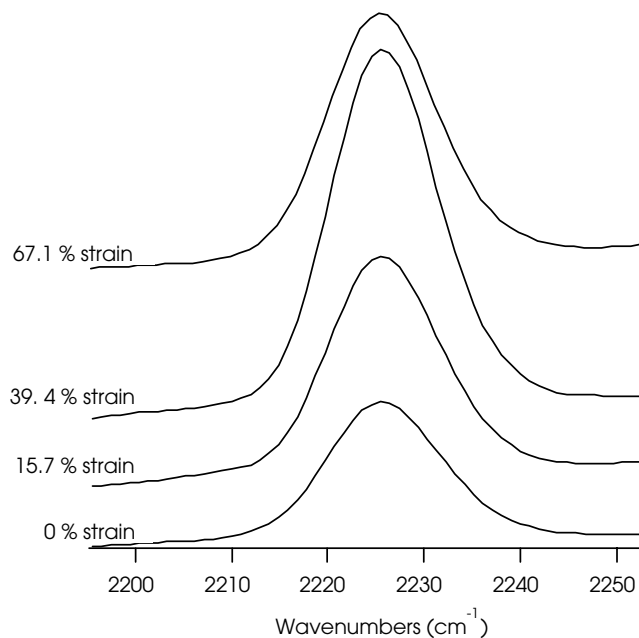


Fig. 4. Parallel polarized cyano bands at 2225 cm^{-1} as a function of strain.

3.2. Dichroic ratio of LC segmented copolymer

Stretching experiments were performed on polyurethane samples as described in Section 2. As the stretching apparatus has only one moveable jaw, and the IR beam was not recentered as the sample was strained, some error may be present due to differences in the region observed during the experiment. For this analysis, we have assumed a uniform strain along the sample; the area covered by the IR beam was sufficiently removed from the jaws to minimize edge effects. Fig. 4 shows the spectra of the 2225 cm^{-1} cyano band polarized parallel to the stretch direction at 0, 15.7, 39.4, and 67.1% strains. The highest degree of orientation along the direction of strain in this sample is found to be near 40% strain. The perpendicularly polarized spectra (not pictured) show a monotonically decreasing peak absorbance with increasing strain that can be attributed to the reorientation of the mesogen along the strain direction. Sample thinning was observed in both parallel and perpendicular orientations. As described in Section 2, we use the dichroic ratio of the parallel to perpendicular absorbances to factor out sample thinning.

The dichroic ratios of the 2225 cm^{-1} cyano band as a function of strain is presented in Fig. 5. We find that there are two different regimes of orientation behavior. At low strains, up to 40% applied strain, the cyano band orients parallel to the stretch direction suggesting that the mesogens initially align with the mechanical field. However, at strains greater than 40%, the mesogens begin to lose their parallel orientation, and the mesogens now begin to align perpendicular to the mechanical field. This behavior can be seen in the peak absorbances in Fig. 4. The parallel band absorption maximizes at 40% strain and then decreases, as can be seen in the 67.1% strain sample.

Fig. 6(a) and (b) show the urethane carbonyl band at selected strains that are polarized parallel and perpendicular to the stretch direction, respectively. As described in Fig. 3,

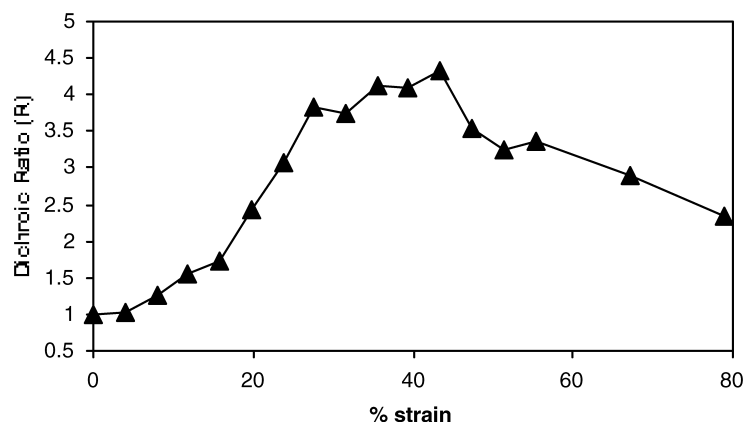


Fig. 5. Dichroic ratio of cyano band (2225 cm^{-1}) as a function of applied strain.

there are three curves that can be fitted to this region of the spectra. However, for the purpose of dichroic ratio computations described in Section 2, these bands cannot be uniquely resolved in the polarized data without analytical resolution enhancement techniques. Therefore, we chose to study the maximum absorption intensity at 1717 cm^{-1} , which represents a convolution of the mechanical responses of both the H-bonded urethane stretch at 1709 cm^{-1} and non H-bonded carbonyls at 1726 cm^{-1} in the segmented copolymer system. The contributions of the 1699 cm^{-1} peak are minimal.

Fig. 7 shows the spectral response of the carbonyl as a function of applied strain. At low strains (less than 8%), there is a sudden drop in the dichroic ratio suggesting a perpendicular orientation of the C=O band with respect to the stretch direction. At medium elongations (10–40%), this initial perpendicular orientation is lost and the carbonyls respond parallel to the applied field. Finally, at high strains (>40% strain), the dichroic ratio decreases again suggesting that carbonyls are beginning to align perpendicular to the field once again. Examination of the spectra in Fig. 6(a) and (b) reveals that the lower frequency (lower wavenumber) shoulder at 1709 cm^{-1} appears to grow relative to the 1726 cm^{-1} peak with increasing strain, suggesting an increase in the number and degree of order of the hard segments within hard domains.

3.3. Orientation function of polyurethane molecular components

As discussed in Section 2, the dichroic ratio merely indicates the orientation of a specific functional group. The alignment of the actual molecular components of the polyurethane such as the hard segment and the mesogen can be followed by the use of the orientation function, S . Table 2 is a tabulation of the order parameter, dichroic ratio, and the average angle between the stress direction and the molecular axis for this sample. Fig. 8 is a depiction of the orientation parameter, S , of both the mesogen and the hard segments. The cyano band is representative of the orientation of the LC

mesogens while the carbonyls are indicative of the orientation of the hard segments of the polyurethane.

From data in Fig. 8, we can see that the mesogens align first parallel and then perpendicular to the field. Previous SAXS and optical microscopy studies of this material [11] show that it is in the smectic A state over its entire LC temperature range. Mesogens initially align with their molecular axis along the direction of strain, resulting in the smectic layers stacked with their long axis perpendicular to the direction of strain. However, at 40% strain, some of the smectic layers begin to undergo shear and re-align parallel to the field, inducing a perpendicular alignment in the mesogens. It has been established by Zhao et al. [23,24] that smectic layers in side chain liquid crystalline polymers are mechanical entities that can be acted on by applied mechanical fields.

The plot in Fig. 8 tracks the reorientation of the hard segments as a function of the externally applied mechanical field. We visualize two different hard segment populations; the first population consists of the “lone” hard segments that are embedded in the soft siloxane matrix, while the second population includes the hard segments that are intermolecularly hydrogen-bonded in hard domains.

Fig. 8 suggests three different regimes of behavior for the hard segment. At 0% strain, both populations of hard segments are randomly oriented, giving a net orientation factor of 0. Between 0 and 8% strain, the population of lone hard segments undergoes orientation initially, while the remaining hard segments in the mechanically cohesive hard domains remain randomly arranged. For this reason, the lone segments dominate the orientation factor at low strains. It has been established that the lone segments, which are characterized by non-hydrogen bonding bands (1728 cm^{-1}), are representative of the movement of the soft, rubbery domains [20]. As we are unable to directly measure the peak heights of saturated Si–O bands to describe soft segment orientation, we can assume that the lone hard segment reorientation is representative of the soft segment movement. These hard segments are fairly independent of the arrangement of the LC layers at low

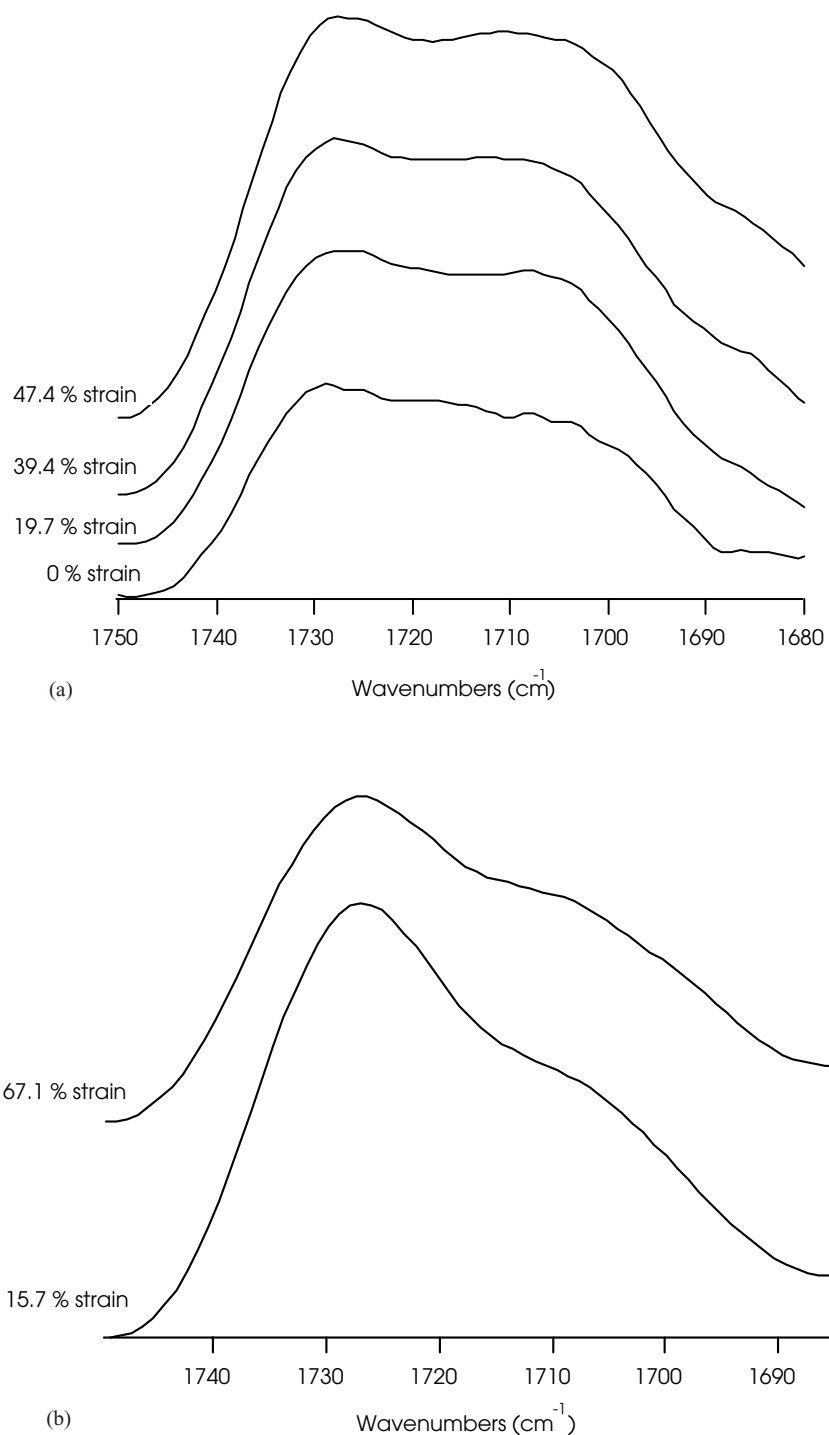


Fig. 6. Carbonyl band with polarizer placed (a) parallel and (b) perpendicular to the direction of the strain.

strains. At this strain range, the “lone” segments align elastically with the applied strain resulting in a sharp increase in the orientation function.

The alignment of the hydrogen bonded hard domains dominates the convoluted carbonyl response at higher strains, as these components also begin to orient in the strain field. From 8 to 40% strain, the orientation function of this band decreases with strain, indicating a net perpendicular

alignment of the hard segments. At higher strains, the orientation function increases again, suggesting that the hard segments are now aligning with the field. Many researchers have seen this type of negative to positive orientation shift in polyurethanes at low strains [15,17]. Bonart and co-workers [15] proposed the widely accepted model that the perpendicular alignment of the hard segments result from an alignment of the long axis of the aggregated hard domains

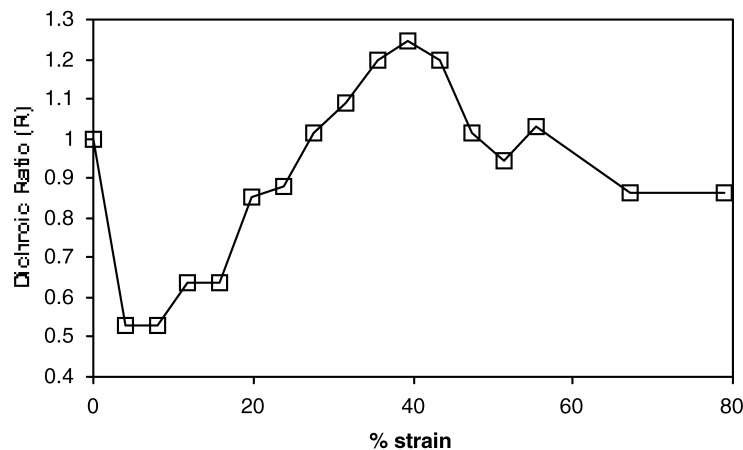


Fig. 7. Dichroic ratio of urethane carbonyl band (1717 cm^{-1}) as a function of the applied strain.

with the strain field. At extremely high strains, the domains break up, the hard segments align along the strain direction, and the hydrogen bonds are reformed in this new “domain” configuration. The strain at which the hard domains reorient in past studies has been near 300%, which is much higher than the 40% reorientation strain that we observe. However, the low molecular weight nature of this segmented copolymer, coupled with the interactions between the liquid crystalline smectic layers and the hard segment could account for the lower strain value at which reorientation is observed. In earlier studies, it has been found that this reorientation strain is highly dependent on the crystalline nature of the polyurethane hard domains, and in some cases, perpendicular orientation is not observed at all [13,16,17].

Further support for this model can be found in samples

Table 2

Dichroic ratio, structure factor and average angle of disorientation as a function of applied strain

Strain (%)	Cyano band (2225 cm^{-1})			Cyano band (1717 cm^{-1})		
	<i>R</i>	<i>f</i>	θ	<i>R</i>	<i>f</i>	θ
0.0	1.00	0.000	54.7	1.00	0.000	54.7
3.9	1.03	0.009	54.4	0.53	0.416	38.6
7.9	1.25	0.076	51.7	0.53	0.416	38.6
11.8	1.55	0.155	48.6	0.64	0.306	42.8
15.7	1.74	0.198	47.0	0.64	0.306	42.8
19.7	2.44	0.324	42.2	0.85	0.118	50.1
23.7	3.07	0.408	38.9	0.88	0.094	51.0
27.6	3.83	0.485	35.9	1.01	-0.009	55.1
31.6	3.73	0.477	36.2	1.09	-0.065	57.4
35.5	4.13	0.510	34.8	1.20	-0.139	60.6
39.4	4.10	0.508	34.9	1.25	-0.171	62.1
43.4	4.33	0.526	34.2	1.20	-0.139	60.6
47.4	3.55	0.459	36.9	1.01	-0.009	55.1
51.3	3.23	0.427	38.2	0.94	0.042	53.0
55.3	3.37	0.441	37.6	1.03	-0.022	55.7
67.1	2.89	0.387	39.7	0.86	0.108	50.5
79.0	2.33	0.307	42.8	0.86	0.108	50.5

where we fit Gaussian curves to the amide I carbonyl band. We were able to successfully fit the spectra in Fig. 6(b)), for the carbonyl bands polarized perpendicular to the stretch direction at 15.7 and 67.1%. We choose these two points since they are above and below the transition strain of 40% when the hard segments go from a parallel to a perpendicular arrangement. For the 15.7% strain sample, we find that the free carbonyls at 1726 cm^{-1} contribute 58.3% of the total area, while the hydrogen bonded carbonyls at 1709 and 1699 cm^{-1} contribute 26.7 and 15.0%, respectively. In the 67.1% sample, the relative areas are 48.7, 34.0 and 17.3% for the free and two H-bonded carbonyls. As mentioned earlier, the shoulder at lower wavenumber is more pronounced in the more highly strained sample. The increase in the H-bonded fraction suggests that as strain is applied, the original hard segments break up to arrange in more highly ordered domains aligned such that the segments are along the direction of stress. The population of lone hard segments appears to decrease as they become incorporated into ordered domains. This sort of breakup and re-ordering has been observed by other researchers in common segmented polyurethanes [15,17].

3.4. Interdependence of the orientation behavior of LC layers and hard segment domains

An interesting feature of Fig. 8 is the observation that the reorientation of the smectic layers and the hard domains occur at the same strain. We have shown in a previous paper that the polyurethane hard segment thermally stabilizes the smectic phase [11]. In these studies, polysiloxane oligomers with only nematic phases (three methylene unit spacers between the siloxane and the LC mesogen) formed smectic phases below the dissociation temperature of the hard segment when placed in the polyurethane. For those polysiloxane oligomers with both smectic and nematic phases (eight methylene spacers), the nematic phase did not occur in the polyurethane. We have also observed that

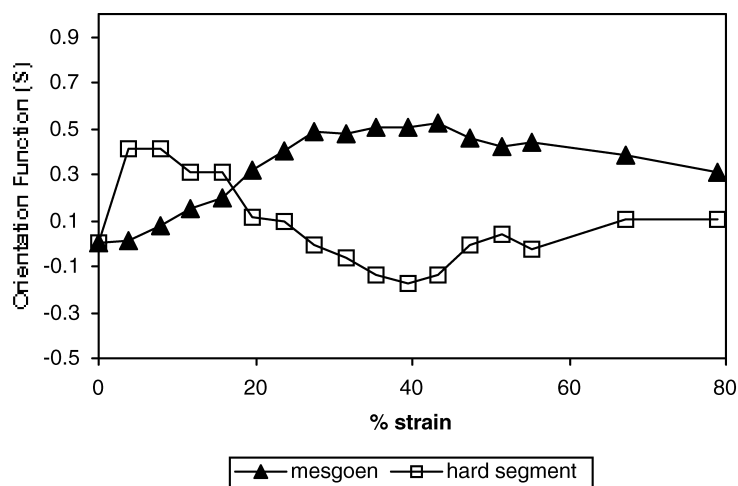


Fig. 8. Structure factor as a function of applied strains demonstrating the orientation behavior of the mesogenic groups and the hard segments.

for a polyurethane that has both a smectic and a nematic phase, the onset of the nematic phase is the same as the temperature at which the hard segments dissociate. Thus, we have established that the behavior of the hard domains and the LC smectic layers seem to be correlated.

The results of the IR stretching experiments confirm that the smectic layer and the hard segment orientations must be cooperative. Fig. 9 is a schematic of a proposed model that is consistent with the results of our experiments on the

polyurethane with eight methylene spacers. The picture at 0% strain suggests that the hard domain interface acts as an anchoring surface for the smectic layers, with the smectic layers perpendicular to the long axis of the hard domains. The configuration of the soft siloxane backbone is shown to be relatively decoupled from the arrangement of LC layers. The eight methylene spacer groups connecting the mesogens to the siloxane main chain are expected to allow independent arrangements of the main chain and side group at the lower strain levels.

As strain is applied to the randomly oriented polyurethane, the lone hard segments align with the stress field almost instantaneously (see Fig. 9, upper right). The hard domains containing hydrogen bonded hard segments align and rotate due to torsion at intermediate strains from approximately 8–40%, with their long axis perpendicular to the direction of strain (Fig. 9, lower left). At this point, the smectic layers rearrange so that the individual mesogens are parallel to the stress field, and the smectic layers are perpendicular to the strain direction. It has been observed that fibers drawn from main chain liquid crystalline homopolymers in the smectic LC phase also contain smectic layers perpendicular (i.e. individual mesogens parallel) to the strain direction [37]; in this case the mesogen is thought to be the primary mechanical element which drives orientation of the system in the LC phase, despite potentially unfavorable arrangements of the homopolymer main chain. Similar factors may also be the cause of the observed transverse orientation of the LC smectic layers in the LC siloxane polyurethane system. At higher strains (above 40% strain), however, the hard domains and the smectic layers undergo shear, breakup and re-alignment such that they are parallel to the stress direction (see Fig. 9, lower right). This re-arrangement, which appears to be cooperative, involves effectively two interdependent mesophase systems—the polyurethane hard domains and the smectic LC phase. At 40% strain and higher, the polymer main chain

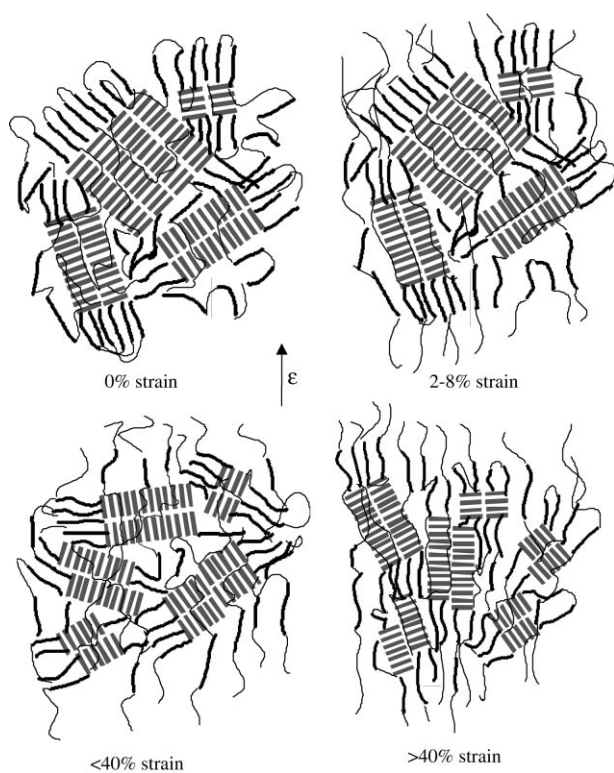


Fig. 9. Proposed model of cooperative deformation of hard segments and smectic layers as a function of strain.

exists in its extended state along the direction of stress; thus at very high strain levels, molecular level re-orientation results in extension of the main chain of both segments. It is interesting to note that throughout the re-orientation process, the relative arrangements of the LC and hard segments within domains remained the same. The transverse anchoring of the LC layers with respect to the hard domains is maintained, despite the shearing and re-ordering processes of both the liquid crystalline and polyurethane morphologies. This interdependence suggests that the deformation behavior of these novel materials may involve cooperative motions of the two phases, driven by LC anchoring interactions at the interface and the connectivity of the hard and soft segment main chains.

4. Conclusions

FT-IR dichroism studies of a new side chain liquid crystalline siloxane polyurethane were used to determine the relative orientations of the hard segments and LC mesogens during deformation. Dichroic ratios and orientation functions were determined for a series of strain levels in a uniformly strained sample. It has been determined that upon the application of tensile strain, the lone hard segments within the soft segment continuous phase are the first elements to orient within the applied mechanical field. The hard segments incorporated into hydrogen bonded domains and the LC smectic layers undergo re-orientation and alignment above approximately 8% strain, initially aligning perpendicular to the stress direction. At strains above 40%, both the LC smectic layers and hard segments re-orient parallel to the stress direction. A model has been proposed which addresses the deformation of these LC soft segment polyurethanes, and compares these results to those found for more traditional polyurethane materials. It has been found that the re-orientation of the hard domains and the LC mesogens are coupled, and are thought to be cooperative in nature.

Acknowledgements

The authors gratefully thank the National Science Foundation Polymer Program for funding under Grant No. DMR-9526394, and the MIT Center for Materials Science and Engineering Seed Grant No. DMR-9400334. We would further like to thank S. Rodman of Polaroid Corp for her help with some of the figures.

References

- [1] Davis FJ. *J Mater Chem* 1993;3:551–62.
- [2] Finkelmann H, Kock H-J, Rehage G. *Makromol Chem, Rapid Commun* 1981;2:317–22.
- [3] Brehmer M, Zentel R. *Macromol Chem Phys* 1994;195:1891–904.
- [4] Benne I, Semmler K, Finkelmann H. *Macromol Rapid Commun* 1994;15:295–302.
- [5] Brand HR, Kawasaki K. *Macromol Rapid Commun* 1994;15:251–7.
- [6] Hikmet RAM. *Macromolecules* 1992;25:5759–64.
- [7] Kupfer J, Finkelmann H. *Makromol Chem, Rapid Commun* 1991;12:717–26.
- [8] Mauzac M, Nguyen HT, Tournilhac FG, Yablonsky SV. *Chem Phys Lett* 1995;240:461–6.
- [9] Meier F. *Macromol Rapid Comm* 1990;11:599–605.
- [10] Vallerien SU, Kremer F, Fischer EW. *Makromol Chem, Rapid Commun* 1990;11:593–8.
- [11] Nair BR, Osbourne MAR, Hammond PT. *Macromolecules* 1998;31:8749–56.
- [12] Eiichi A, Koide N. *Liq Cryst* 1993;14:1645–54.
- [13] Tang W, MacKnight WJ, Hsu SL. *Macromolecules* 1995;28:4284–9.
- [14] Sun S-J, Hsu K-Y, Chang T-C. *J Polym Sci, A Polym Chem* 1995;33:787–96.
- [15] Bonart RJ. *Macromol Sci, B Phys* 1968;2:115–38.
- [16] Estes GM, Seymour RW, Cooper SL. *Macromolecules* 1971;4:452–7.
- [17] Seymour RW, Allegrezza AE, Cooper SL. *Macromolecules* 1973;6:896–902.
- [18] Nitzsche SA, Hsu SL, Hammond PT, Rubner MF. *Macromolecules* 1992;25:2391–6.
- [19] Tao HJ, Meuse CW, Yang XZ, MacKnight WJ, Hsu SL. *Macromolecules* 1994;27:7146–51.
- [20] Lee HS, Hsu SL. *J Polym Sci, B Polym Phys* 1994;32:2085–98.
- [21] Tao DJ, Rice DM, MacKnight WJ, Hsu SL. *Macromolecules* 1995;28:4036–8.
- [22] Zhao Y, Lei H. *Polymer* 1994;35:1419–24.
- [23] Zhao Y. *Polymer* 1995;36:2717–24.
- [24] Zhao Y, Roche P, Yuan G. *Macromolecules* 1996;29:4619–25.
- [25] Nair BR, Hammond PT. *Abstr Pap Am Chem Soc* 1998;216:U171 (Part 3, Aug. 23, 1998).
- [26] Marcott C, Dowrey AE, Noda I. *Anal Chem* 1994;66:1065A.
- [27] Palmer RA, Manning CJ, Chao JL, Noda I, Dowrey AE, Marcott C. *Appl Spectrosc* 1991;45:12.
- [28] Frasier RDB. *J Chem Phys* 1953;21:1511.
- [29] Stein RS. *J Appl Phys* 1961;32:1280.
- [30] Cael JJ, Dalzell W, Trapani G, Gregoriou VG. *Pittsburgh Conference in Analytical Chemistry and Applied Spectroscopy, Abstract #1204, March 1997.*
- [31] Noda I, Dowrey AE, Marcott C. *Polym Prepr* 1984;5:167.
- [32] Papadimitrakopolos F, Hue SL, MacKnight WJ. *Macromolecules* 1992;25:4671–81.
- [33] Papadimitrakopolos F, Sawa E, MacKnight WJ. *Macromolecules* 1992;25:4682.
- [34] Kischel M, Kisters D, Strohe G, Veeman WS. *Eur Polym J* 1998;34:1571–7.
- [35] Siesler HW. *Makromol Chemi—Macromol Sym* 1992;53:89–103.
- [36] Gregoriou VG, Palmer RA. *Macromol Chem Macromol Symp* 1995;94:75.
- [37] Tokita M, Osada K, Kawauchi S, Watanabe J. *Polym J* 1998;30:687–90.