Segmented Polyurethane Elastomers with Liquid Crystalline Hard Segments. 3. Infrared Spectroscopic Study

Weiming Tang, William J. MacKnight,* and Shaw L. Hsu

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: Segmented liquid crystalline polyurethanes (LCPUE) have been studied by infrared spectroscopy. The nematic liquid crystalline hard domains act as physical cross-links and can be oriented by the application of mechanical strain. The orientation function achievable in the hard segments results from the combination of mechanical strain and stress-softening. Furthermore, elastic deformation induces the rearrangement of some hard segments in the mesophase into a more ordered packing. High-temperature infrared spectra have been correlated with thermal transitions of the LCPUE, and a liquid–liquid microphase-separated morphology above the isotropization of the mesophase appears to exist.

Introduction

Segmented block copolymers with alternating liquid crystalline hard and amorphous soft segments are a new class of thermoplastic elastomers. Due to the chemical structural differences between the hard and soft segments, a microphase separation occurs, consisting of liquid crystalline hard domains and amorphous soft domains. The liquid crystalline hard domains act as physical cross-links for the network and tend to become macroscopically anisotropic during elongation. Hence, mechanical strain may result in a highly oriented thermoplastic elastomer.[1]

Thermotropic liquid crystalline polyurethanes have been studied for their variable phase behavior and potential application as high-strength fibers.[2–4] In previous studies, Stenhouse et al.[5] obtained an enantiotropic liquid crystalline polyurethane (referred to as LCPU) from 4,4′-bis(6-hydroxyhexoxy)biphenyl with 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate at equal molar ratios. The LCPU has been further investigated by differential scanning calorimetry (DSC), polarized optical microscopy, and wide angle X-ray scattering (WAXS) and clearly exhibits a smectic mesophase. In WAXS studies,[2] an intense and sharp X-ray diffraction at 14.3 Å is observed and assigned to the 004 layer reflection of the LCPU. One additional weak meridional diffraction at 28.8 Å arises from the 002 layer reflection.

The elastomers described here (referred to as LCPUE) are based on this LCPU structure as the hard segment and poly(tetramethylene oxide) as the soft segment. The mesophase in the LCPUE is formed by the aggregation of the liquid crystalline hard segments. This is experimentally proven on the basis of DSC, WAXS, and rheology studies.[1,6] Compared with the smectic mesophase in LCPU, the WAXS pattern shows the disappearance of the sharp low-angle reflection in the LCPUE mesophase. This may be attributed to the fact that the liquid crystalline hard domain structure is perturbed by the polydispersity of the hard segments and the incorporation of low molar mass homologues of the poly(tetramethylene oxide) soft segments. The chemical structure modification results in reduced position correlation in the mesophase by smearing out the layered morphology[7] and consequently leads to a nematic mesophase with an average inter-hard-segment lateral packing of 4.5 Å.

The mechanical properties of this type of segmented block copolymer are strongly dependent upon domain structure and orientation. Hence, it is important to determine how each of the domains deforms during the straining process. Infrared dichroism is a useful method to monitor the orientation behavior of specific polymer chain segments and affords a determination of the degree of domain orientation induced by mechanical deformation.[8]

Infrared spectroscopy is also widely used to study chain–chain interaction and conformational order in polymers.[9,10] The molecular interactions are related to the nature of the phase which determines the relative arrangement of functional groups. Therefore, it is possible to investigate the dependence of the mesophase microstructure on molecular interactions using this technique and much of the interest has focused on the analysis of absorption bands which are involved in hydrogen bonding. Furthermore, mechanical strain improves the lateral packing of the chains and reduces the degree of disorder within the mesophase. This increase in order can be monitored by infrared spectroscopy and WAXS.

Experimental Section

Materials. The polymers were synthesized via solution polymerization. In the first stage of the reaction, a prepolymer was prepared from hydroxy-terminated poly(tetramethylene oxide) (PTMO; M_w = 650, 1000) and the 1:1 mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate at 100 °C. This was followed by chain extension using the mesogen 4,4′-bis(6-hydroxyhexoxy)biphenyl. The resulting polymers, referred to as LCPUE 650 and LCPUE 1000, have 65.1 and 42.3 wt % of hard segments, respectively.

Infrared Spectroscopy. Infrared spectroscopic experiments were performed with an IBM Model 32 Fourier transform infrared spectrometer. Data were collected at 2 cm^{-1} resolution with a minimum of 128 scans. The LCPUE films cast from $CHCl_3$ solution were sufficiently thin to be within an absorbance range where the Beer–Lambert law was obeyed.

The applicability of infrared dichroism to thermoplastic elastomers depends on the availability of characteristic absorption bands in the hard and soft domains with known transition moment vectors. In LCPUE samples, the stretching vibration of the N–H part of the urethane linkage of the hard segments appears at 3286 cm^{-1} and is employed to character-

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* To whom correspondence should be addressed.

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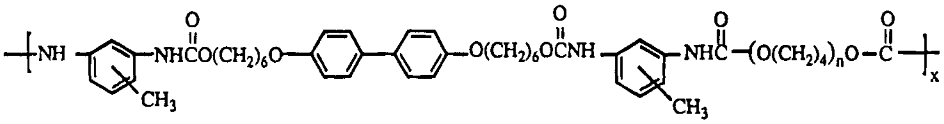

Figure 1. Chemical structure of segmented liquid crystalline polyurethanes.

ize the orientation of hard domains. The asymmetric C−H stretching absorption occurs at 2935 cm^{-1} and is used to describe the orientation of soft domains. A small portion of the methylene groups from the chain extender (Diol-6) and the methyl groups from TDI reside in the hard domains (17% in LCPUE 1000 and 25% in LCPUE 650) but do not affect the CH_2 asymmetric stretching band significantly, so it can be employed as the characteristic band for the soft segment poly(tetramethylene oxide).

The dichroic ratio D for a particular absorption band is defined by

$$D = A_{\parallel}/A_{\perp} \qquad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the peak absorbancies of infrared radiation polarized parallel and perpendicular to the stretching direction, respectively.

The orientation function for the absorbing species can be calculated from

$$f = \frac{(D_0 + 2)(D - 1)}{(D_0 - 1)(D + 2)} \qquad (2)$$

where $D_0 = 2 \cot^2 \alpha$, defined as the dichroic ratio for perfect chain alignment. Here α, the angle between the transition moment of the vibration and the chain axis, is assumed to be 90° for both the N−H vibration and the C−H asymmetric stretching bands in LCPUE samples. The orientation function ranges from a value of −0.5 to +1.0, $f = -0.5$ for perfect chain orientation transverse to the stretch direction, $f = 0$ for random chain orientation, and $f = 1.0$ for perfect orientation in the stretch direction.

The orientation function, f, can be further related to an average angle θ by

$$f = \langle 3 \cos^2(\theta) - 1 \rangle /2 \qquad (3)$$

where θ is the angle between the chain segment and the stretching direction.

Thin LCPUE films were stretched to different strain levels. Polarized and unpolarized IR spectra were recorded 30 min after the deformation had taken place to allow sufficient time to reach orientation equilibrium.

High-temperature infrared spectra were obtained by placing LCPUE films between KBr windows, which were clamped between brass holders in a temperature-controlled cell monitored via thermocouples placed adjacent. The heating rate of the LCPUE sample was controlled as 10 K/min.

Results and Discussion

IR Dichroism. The orientation function−strain curves of hard and soft domains for LCPUE 1000 are shown in Figure 2. Overall there is a clear distinction between the two domain orientations, illustrated by a much higher value for the hard domain.[11] This is largely attributed to the fact that the amorphous PTMO ($M_w = 1000$) is above its T_g and tends to relax toward random conformations after stress is applied. On the other hand, the orientation function of the soft segments increases gradually to 0.20 with the strain, indicating that PTMO undergoes conformational changes leading to chain orientation. The mesophasic hard domain orientation function is found to be positive and reaches its maximum ($f = 0.37$) at 600% strain. From this, one can conclude that the mesophase orients parallel to the stretching direction.

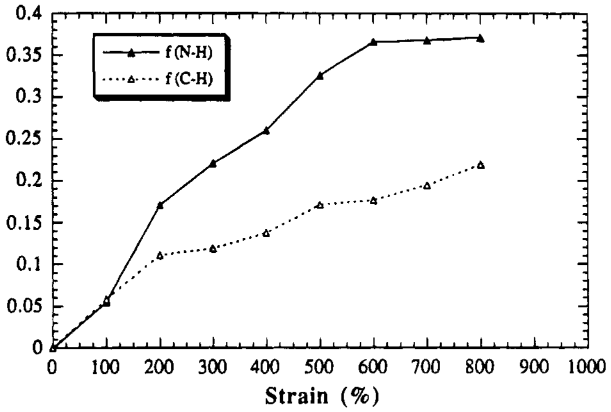

Figure 2. Orientation function−strain curves for LCPUE 1000.

It has been reported, in some types of polyurethane block copolymers, that negative orientation of the hard segments is observed up to 400% strain. Cooper and co-workers[12] compared the orientation mechanisms of amorphous and crystalline hard segment regions in MDI−polyurethane elastomers and found that only crystalline regions showed a transverse orientation at low elongation with respect to the stretching direction. Bonart and co-workers[13,14] correlated this observation with a proposed model. Hard segments were oriented perpendicular to the longer axis of the domain and soft segments were envisioned as being stretched initially to different extents, giving rise to local torques which twisted the hard segments preferentially transverse to the stretching direction and eventually led to parallel alignments at high strains.

In the current LCPUE 1000 sample, no negative orientation values of the hard domains are observed in the range 0%−100% strain. This suggests that the nematic mesophase (hard domain) is oriented in the direction of stretch even at low strains.

The orientation function of the hard domains is used to calculate the average ordering of the nematic mesophase (eq 3). At 0% strain, $f = 0$, indicating that mesophases orient randomly. At 800% strain, $f = 0.37$ and the angle is 40.4° on average between the stretching axis and the local director of the mesophase.

Figure 3 illustrates, in the LCPUE 650 sample, that the orientation of soft segments is little affected by the change of poly(tetramethylene oxide) molar mass. However, the decrease of the hard segment orientation function may be attributed to the morphological difference between the two LCPUE samples caused by the different concentration of soft segments, and the maximum values of the orientation function are strain dependent.

Strain-Induced Reorganization. There are two major regions of the infrared spectrum of LCPUE 1000 which are useful for understanding the reorganization of the nematic mesophase. These are the N−H stretching region from 3100 to 3500 cm^{-1} and the amide I region from 1640 to 1780 cm^{-1}.

Amide I Mode. Figure 4 shows infrared spectra of LCPUE 1000 in the amide I region as a function of

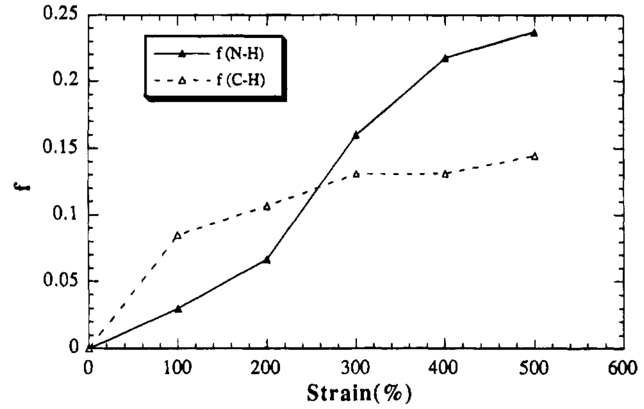

Figure 3. Orientation function–strain curves for LCPUE 650.

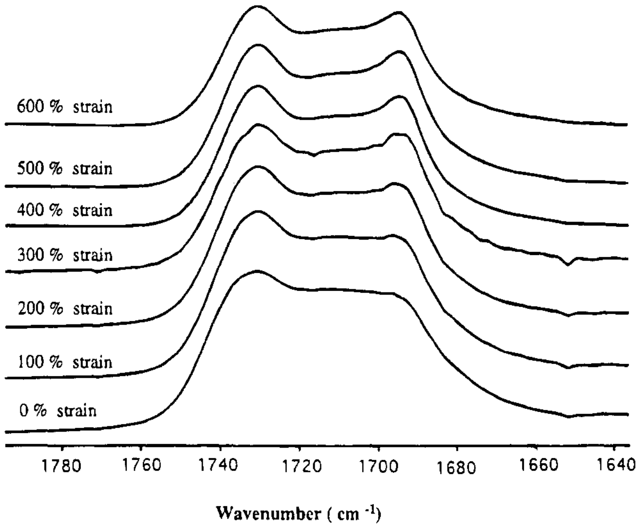

Figure 4. IR spectra of LCPUE 1000 recorded from 0% to 600% strain in the amide I region.

increasing strain. A substantial increase of the intensity of the low-frequency peak at 1692 cm^{-1} is observed during the elongation. It is well-known that the infrared band of H-bonded urethane carbonyls appear at a lower frequency than that of free urethane carbonyls.[15] Furthermore, semicrystalline samples such as polyamides[16] and polyurethanes[9] have been studied, and it has been found that C=O groups in the amide I band are sensitive to the differences in the pattern of hydrogen bonds that determine the relative arrangement of the C=O groups and the degree of dipole–dipole interactions. The amide I band was resolved into its constituents as hydrogen-bonded carbonyl groups in ordered ("crystalline") domains, hydrogen-bonded carbonyl groups associated with disordered ("amorphous") conformations, and non-hydrogen-bonded (free) carbonyl groups.

In LCPUE 1000, thermal analysis and WAXS have previously shown the existence of a mesophase and suggested the reorganization of some hard segments in the mesophase during mechanical strain.[1] IR spectroscopy provides a more detailed technique to study localized microstructural changes taking place during elongation. In Figure 5a, there are three different bands at 1694, 1711, and 1735 cm^{-1} in the amide I region, which correspond to ordered hydrogen-bonded, disordered hydrogen-bonded, and non-hydrogen-bonded free carbonyl groups. Other investigators have also observed carbonyl bands at these frequencies in liquid crystalline polyurethanes and ascribed them to different patterns of hydrogen bonds.[9,17] Here, both ordered and disordered hydrogen-bonded carbonyl groups exist in the mesophase, while the free C=O groups are at the domain interface and/or within the soft segment matrix. In order to analyze the data quantiatively, curve fitting is employed to resolve the amide I mode into its constituents.[16,17]

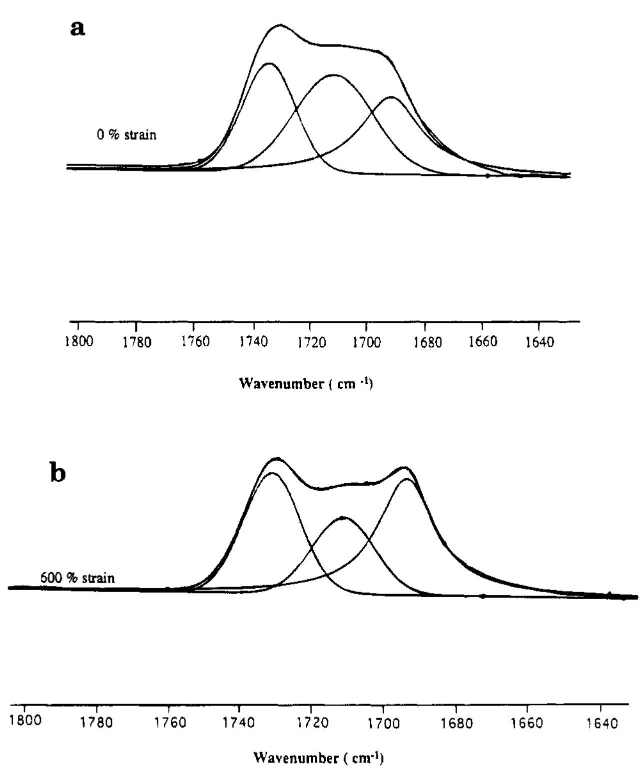

Figure 5. Least-squares curve fitting of the amide I region of LCPUE 1000: (a) at 0% strain; (b) at 600% strain.

The following assumptions are made to permit a logical approach in the procedure of curve fitting:

1. The band shapes of the non-hydrogen-bonded carbonyls and disordered hydrogen-bonded ones are assumed to be Gaussian. Together with these two, a Lorentzian band shape is imposed on the ordered H-bonded carbonyl peak. These assumptions afford a "best fit" of the original curve, and the areas of the deconvoluted peaks are reasonable and consistent with other experimental data.
2. The frequency, band shapes, and band widths of these three bands are assumed to be unchanged at different strains.
3. Curve fitting is limited to the spectral data of the amide I region between 1780 and 1640 cm^{-1}.
4. The absorption coefficients of these disordered hydrogen-bonded and ordered hydrogen-bonded carbonyl bands are assumed to be the same and independent of the strength of the hydrogen bonding. The ratio of the H-bonded/nonbonded carbonyl band absorption coefficients is listed as being 1.7.[18]

Table 1 summarizes the detailed results of the curve fitting of the amide I region in the strain range 0%–600%. At 0% strain (Figure 5a), one can observe that the disordered hydrogen-bonded amide I band from the nematic mesophase occurs at 1712 cm^{-1}, the "free" band at 1735 cm^{-1}, and the ordered band at 1692 cm^{-1}. This is consistent with the results from the previous wide angle X-ray studies. Figure 6a shows the diffuse outer ring at 4.5 Å resulting from the nematic mesophase diffraction. These two types of hydrogen bonding and

Table 1. Curve-Fitting Results of the Amide I Region of LCPUE 1000

	hydrogen bonded											
	ordered			disordered			"free"					
strain, %	ν, cm^{-1}	$W_{1/2}$,[22] cm^{-1}	A_0	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_d	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_f	A_d/A_t	A_o/A_t	A_f/A_t
0	1692	26.1	3.50	1712	39.0	4.18	1735	26.5	5.36	0.32	0.27	0.41
100	1693	22.2	4.22	1711	27.5	2.73	1733	25.8	6.55	0.20	0.31	0.49
200	1694	20.2	4.35	1711	24.8	2.38	1732	26.3	6.94	0.17	0.32	0.51
300	1694	20.3	4.45	1711	25.1	2.12	1732	24.2	7.23	0.16	0.32	0.52
400	1694	18.6	4.61	1711	24.2	2.43	1731	23.4	6.39	0.18	0.34	0.48
500	1694	18.8	4.71	1711	24.6	2.46	1731	22.8	6.10	0.18	0.36	0.46
600	1694	19.6	4.84	1712	24.2	2.40	1732	22.8	6.00	0.18	0.37	0.45

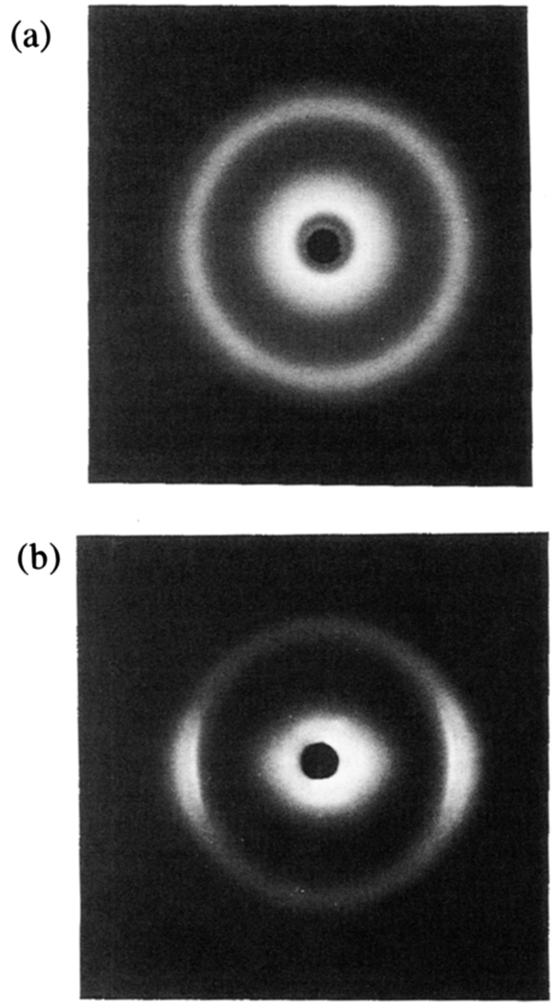

Figure 6. Room-temperature X-ray diffraction patterns: (a) unstretched LCPUE 1000 fiber drawn from the melt; (b) stretched LCPUE 1000 fiber drawn from the melt.

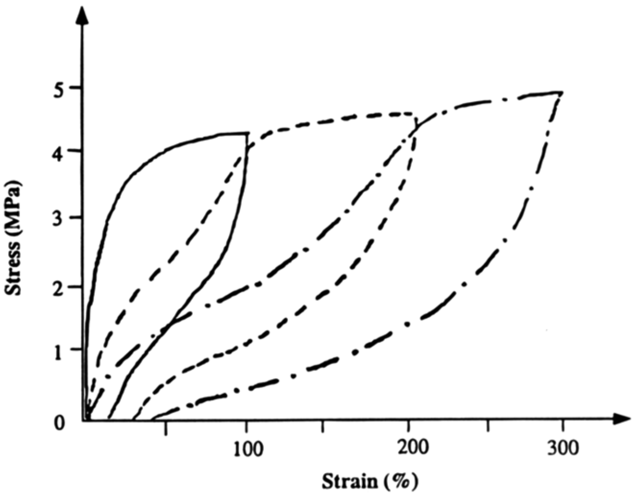

Figure 7. Stress-softening of LCPUE 1000.

other dipolar interactions lead to the aggregation of hard segments and maintain the structural order within the mesophase. However, cocrystallization of the isomeric 2,4- and 2,6-tolylene diisocyanate hard segments does not occur.[5] This means that no thermodynamically stable crystal phase exists in the hard domains.

Upon stepwise increase of the strain to 600% (Figure 5b), the area of the disordered hydrogen-bonded carbonyl band decreases substantially, and the ordered one becomes significantly increased. This suggests that the rearrangement of some hard segments in the mesophase has been achieved. Mechanical strain reduces the disorder in the mesophase by packing the hard segments in a more regular fashion. In Figure 6b, WAXS studies show there are two types of diffraction from the mesophase on the equatorial position. The sharp reflection at 4.5 Å corresponds to the ordered lateral hard segment packing. The diffuse arc reflection at about 4.5 Å relates to the continuing presence of disorder in the nematic mesophase.

On the other hand, in Table 1, the area of the "free" amide I band has increased with strain. This would suggest the disruption of hydrogen bonding in some segregated hard domains, or hard segments pulling out from the hard domains into the soft matrix. This is responsible for the stress-softening effect.

In order to illustrate the stress-softening effect from mechanical hysteresis, LCPUE 1000 film is stretched for the first time to 100%, then the strain is removed, and the sample is restretched to 200%. The stress in the second cycle is lower than that in the first by up to 100%, after which it continues in a manner following the first cycle. In a third cycle, a softening up to 200% is observed due to the previous strain history. While the infrared spectroscopic studies give a molecular interpretation of this phenomenon, Figure 7 shows that the detached hard segments in the soft domains no longer support the stress, giving rise to the observed softening.[19]

N−H Stretching Mode. Figure 8 shows infrared spectra in the range 3100−3600 cm^{-1} as a function of increasing strain. At 0% strain, the spectrum is characterized by a primary band of the hydrogen-bonded N−H stretching vibration centered at 3290 cm^{-1}, and it can be approximated as a single Gaussian curve with a width at half-height of 109.8 cm^{-1}. The band of non-hydrogen-bonded N−H groups only appears at about 3450 cm^{-1} as a small satellite peak. As strain is increased, there is a steady decrease in the width of the hydrogen-bonded N−H stretching band (Table 2). Sandorfy[20] and Molis et al.[21] reviewed the unusual breadth of the hydrogen-bonded N−H stretching mode and concluded that it was due to anharmonic oscillations and disordered phase behavior. Hence, it can be deduced

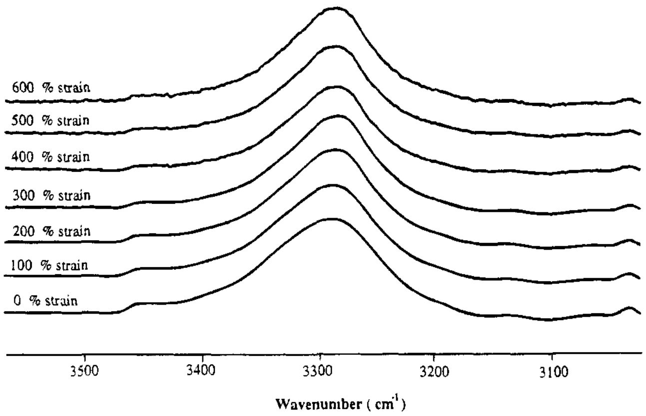

Figure 8. IR spectra of LCPUE 1000 recorded from 0% to 600% strain in the N–H stretching region.

Table 2. Hydrogen-Bonded N–H Stretching Mode of LCPUE 1000

strain, %	frequency, cm^{-1}	$W_{1/2}$, cm^{-1}
0	3286	110
100	3286	100
200	3284	96
300	3283	86
400	3283	86
500	3283	85
600	3283	86

here that the narrowing of the N–H band is another manifestation of the reduction of disorder in the nematic mesophase and phase perfection under mechanical strain.

Temperature-Induced Phase Transition. The phase transition of the nematic mesophase in LCPUE 1000 is manifested by two endotherms separated by an exotherm.[1] The lower temperature endotherm occurs at ca. 101 °C and corresponds to the isotropization of the thermodynamically less stable mesophase. Then, it is followed by the reorganization into the thermodynamically stable mesophase, which isotropizes at ca. 128 °C. IR spectroscopy can be used to monitor the microstructural changes during the thermal processes.

Amide I Mode. Three discernible bands in the carbonyl stretching region are observed for LCPUE 1000 film cast on a KBr cell at room temperature. Consistent with the previous study, the highest frequency component at 1734 cm^{-1} corresponds to carbonyls not involved in hydrogen bonding. The other two components, at 1715 and 1694 cm^{-1}, are due to disordered and ordered hydrogen-bonded carbonyls within the mesophase, respectively.

Figure 9 shows infrared spectra of LCPUE 1000 in the range 1650–1800 cm^{-1} recorded as a function of increasing temperature. It should be noted that the spectra are plotted on an absolute absorbance scale and, consequently, the changes in frequency, breadth, and relative area can be directly compared. The spectrum at 40 °C is characterized by a strong absorbance at 1734 cm^{-1} and two additional broad bands at lower frequencies. When the sample is heated to 126 °C, the disordered hydrogen-bonded carbonyl band decreases in absolute intensity. This observation can be correlated with the low-temperature endothermic transition of the LCPUE 1000 sample, as shown previously. The disordered hydrogen-bonded carbonyl groups originate from the mesophase with less thermodynamic stability.

When the sample is heated to 150 °C, the second stage isotropization occurs. This causes the disappearance of the low-frequency band at 1694 cm^{-1}. The ordered hydrogen-bonded carbonyls are transformed into free carbonyls and/or disordered hydrogen-bonded carbonyls in the amorphous phase. Above 150 °C, the presence of the band at 1715 cm^{-1} suggests that urethane groups can still interact with each other via hydrogen bonding and, indeed, liquid–liquid microphase separation may exist in the isotropic phase.

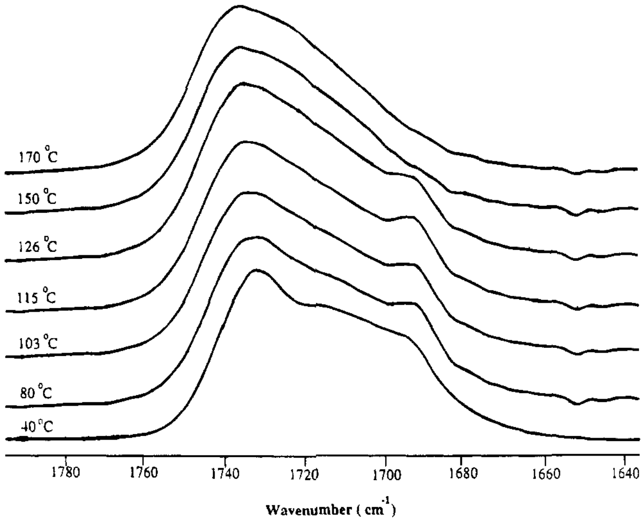

Figure 9. IR spectra of LCPUE 1000 recorded from 40 to 170 °C in the amide I region.

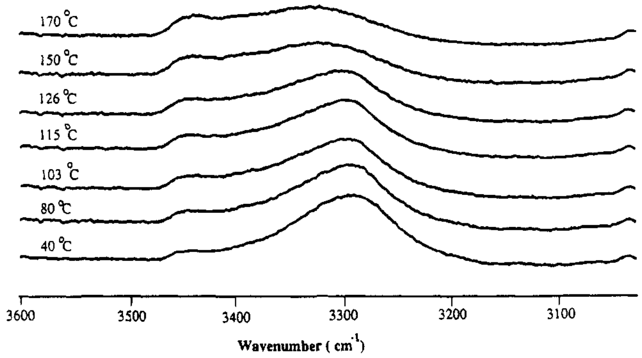

Figure 10. IR spectra of LCPUE 1000 recorded from 40 to 170 °C in the N–H stretching region.

N–H Stretching Mode. Figure 10 shows infrared spectra in the range 3100–3600 cm^{-1} plotted on an absolute scale. As temperature is increased from 40 to 170 °C, the broad hydrogen-bonded N–H stretching band shifts to higher frequency. This can be attributed to the fact that, during the isotropization process, N–H groups dissociate and transform into "free" ones. Coleman and Molis studied the dependence of the N–H absorption coefficient on frequency in amorphous polyamides[18] and polyurethanes,[21] respectively. Their results indicate that the absorption coefficient doubles over the 40 cm^{-1} range from 3360 to 3320 cm^{-1}. The reduction of the total area of the N–H band in LCPUE 1000 is another example of a substantial decrease of absorptivity with increasing N–H stretching frequency.

Summary and Conclusion

In summary of the results of the infrared investigation of LCPUE, it is apparent that mechanical strain tends to orient the nematic mesophase, which acts as physical cross-links of the network, in the direction of stretching.

The amide I mode is well resolved into three constituents corresponding to ordered hydrogen-bonded, disordered hydrogen-bonded, and free C=O. In the unstrained sample, the large amount of disordered hydrogen-bonded carbonyl band is more evidence for the lack of short range positional order in the LCPUE mesophase. Elastic deformation reduces the disorder in the mesophase, shown by a substantial area increase of the hydrogen-bonded amide I band at 1694 cm^{-1}.

The carbonyl stretching and N−H stretching vibrations in the high-temperature IR spectra reflect microstructural changes during thermal transitions. The presence of disordered hydrogen-bonded carbonyl groups above the isotropization transition of the mesophase suggests the existence of liquid−liquid microphase-separated morphology.

Very high values (>0.4) of the hard segment orientation function cannot be attained by straining, and this is largely due to mechanical relaxation accompanying the stress-softening effect.

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(22) The width at half-height of the resolved bands varies with the degree of strain, particularly in the disordered band. This is a common problem when strongly overlapping bands are curve resolved.

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