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Two Dimensional Infrared (2D-IR) Spectroscopic Studies of the Viscoelastic Behavior of Liquid Crystalline Polyurethanes

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Summary: Dynamic infrared dichroism techniques have been used to study a complex side chain liquid crystalline segmented polyurethane. The obtained dynamic spectra were analyzed using two dimensional infrared techniques (2D-IR) that allow the easier interperation of the dynamic response of this system. Side chain mesogens are monitored by the cyano tag at the end of the molecule while the hard segments can be viewed in the 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 segments and the smectic layers change orientation as the applied strain is increased from low to high strains. In addition, we show further evidence for the coupling of the mechanical deformation behavior of the smectic layers and the hard domains and identified two primary relaxation times in this system.

Introduction

A new class of materials that offers the potential to couple the optical changes brought on by liquid crystal alignment to applied mechanical strains is side chain liquid crystalline polyurethanes. 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. The possibilities of forming

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conformal coatings that are deformable offers the potential for electro-optic or responsive coatings and sensors.[1,2]

Two-dimensional infrared correlation spectroscopy (2D-IR) pioneered by Noda and coworkers has provided a powerful tool for vibrational spectroscopists studying the response of materials to an external perturbation. [3,4] 2D-IR spectra are generated as the product of a pair-wise correlation between the time-dependent fluctuations of IR signals that occur during dynamic IR experiments. The development of the generalized correlation spectroscopy theory eliminated the requirement that the perturbation has a sinusoidal waveform and thus extended this method to the analysis of time-resolved spectra derived from a perturbation of any arbitrary waveform.[5,6] The dynamic spectrum can be defined as

$$\bar{y}(\nu,t)=\begin{cases} y(\nu,t)\rightarrow\bar{y}(\nu) & \text{for } T_{min}\le t\le T_{max} \\ 0 & \text{otherwise} \end{cases} \qquad (1)$$

where $\bar{y}(\nu,t)$ is the spectral intensity variation observed as a function of a spectral variable ν over an interval where the external variable t ranges from T_{min} to T_{max}. The external variable t can be time, or another physical perturbation such as temperature, applied strain, etc. The reference spectrum, $\bar{y}(\nu,t)$ is defined as

$$\bar{y}(\nu)=\frac{1}{T_{max}-T_{min}}\int_{T_{min}}^{T_{max}} y(\nu,t)dt \qquad (2)$$

The formal definition of the generalized 2D correlation spectrum may be written as

$$\Phi(\nu_1,\nu_2)+i\Psi(\nu_1,\nu_2)=\frac{1}{\pi(T_{max}-T_{min})}\int_0^{\infty}\overline{Y}_1(\omega)\bullet\overline{Y}_2^{*}(\omega)d\omega \qquad (3)$$

where $\Phi(\nu_1,\nu_2)$ is the synchronous correlation spectrum and $\Psi(\nu_1,\nu_2)$ is the asynchronous correlation spectrum. $\overline{Y}_1(\omega)$, the forward Fourier transform of the spectral intensity variation $\bar{y}(\nu_1, t)$ may be expressed as

$$\overline{Y}_1(\omega)=\int_{-\infty}^{\infty}\bar{y}(\nu_1,t)e^{-i\omega t}dt \qquad (4)$$

and the conjugate of the Fourier transform $\overline{Y}_2^{*}(\omega)$ for the spectral intensity variation $\bar{y}(\nu_2, t)$ is expressed as

$$\overline{Y}_2^{*}(\omega)=\int_{-\infty}^{\infty}\bar{y}(\nu 2,t)e^{+i\omega t}dt \qquad (5)$$

Further details of the methods of calculation of 2D correlation spectra may be found in a recent paper by Noda.[7]

The synchronous correlation spectrum provides an indication of simultaneous spectral intensity changes as a result of the perturbation. The synchronous spectrum is characterized by the presence of peaks (autopeaks) along the diagonal line defined by $\nu_1 = \nu_2$ and by the presence of cross-peaks. These *autopeaks* indicate which transition dipoles, and thus functional groups, have an orientational response to the perturbation. The sign of the autopeaks is always positive. The off-diagonal peaks (*cross peaks*) indicate the degree to which dipoles respond in phase or simultaneously with each other and, from their sign, the relative reorientation of these dipoles. In contrast to the autopeaks, the signs of cross peaks can be either negative or positive. The existence of a positive cross peak is an indication that the two corresponding dipole moments reorient parallel to each other. On the other hand, when the sign of the synchronous cross peak is negative, this indicates mutually perpendicular reorientations. It is interesting to note that the synchronous correlation map is symmetric with respect to the diagonal. Strong autopeaks are an indication of spectral bands that respond strongly to the applied perturbation.

In contrast, different kinds of information can be obtained by the inspection of the asynchronous correlation map. The function Ψ is a measure of the degree of independence between the reorientation behavior of the corresponding dipole moments. Furthermore, the asynchronous 2D correlation spectrum has no diagonal peaks and produces cross peaks only to the extent that two transition dipoles reorient out of phase with each other. The signs of the asynchronous cross peaks give the relative rates of response of the two contributing dipoles. The asynchronous correlation map is antisymmetric with respect to the diagonal, thus making the upper half of the map the mirror image of the lower part.

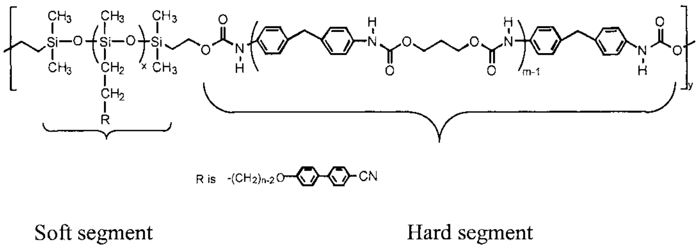
The details of interpretation of frequency correlation maps result from the properties of the corresponding functions, Φ and Ψ. Therefore, in addition to spectral resolution enhancement due to the incorporation of the second dimension, 2D IR spectra can provide information about the relative reorientation of transition dipole moments and the relative rates of inter- and intra-molecular conformational relaxations. The big advantage of the 2D IR technique is the fact that the deconvolution of highly overlapped absorption bands is based on physical arguments instead of mathematical data manipulation techniques (e.g. curve fitting analysis, Fourier self-deconvolution etc.). Overall, it has to be kept in mind that the original dynamic spectra provide all the information found in the 2D spectra. Therefore, even though the two dimensional correlation highlights important features of the dynamic data, it has to emphasized that the S/N of the original data controls the quality and appearance of the 2D data.

2D-IR is especially powerful in studies of polymer reorientation in response to applied perturbations. There have been several papers that have focused on liquid crystalline polymers (LCPs).[8,9] One of the earliest applications of 2DIR studied the kinetics of reorientation of a uniaxially aligned nematic liquid crystal (4-pentyl-4'-cyanobiphenyl) under the influence of an external a.c. electrical field. [10,11] In that study, the synchronous 2D correlation showed that the rigid core of the nematic molecule reorients as a unit. The asynchronous correlation provided preliminary evidence that the pentyl chain may reorient more rapidly than the core.

2D IR correlation analysis has been used to study the orientation and the mobility of a ferroelectric liquid crystal dimer during switching under an electric field.[12] A study of the segmental mobility of a ferroelectric liquid-crystalline polymer (FLCP) in the Sc* phase under the influence of an electrical field, revealed that the mesogen reorients together with the terminal group attached to it and a fragment of the spacer.[13] The remaining part of the spacer and the main chain of the FLCP do not participate in the reorientation. Two-dimensional correlation analysis of polarization angle-dependent infrared spectra of a ferroelectric liquid crystal with a naphthalene ring in the smectic-C* phase revealed the relative orientation of the alkyl chain, mesogen, and chiral segments.[14] The 2D analysis not only identified which groups are involved in hindered rotations about the long molecular axis but was also able to distinguish bands from the chiral part from those in the non chiral portion of the molecule.

Results and Discussion

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.



The static spectrum of the side-chain liquid crystalline polyurethane is shown in Figure 1. The dynamic spectrum is shown in Figure 2. As previously reported[15], the bisignate signature observed in the nitrile band of the quadrature dynamic spectrum indicates the existence of two distinct populations. One population consists of ordered mesogens within the smectic layers and was assigned to the lower wavenumber band at 2224 cm^{-1}. The other population, assigned to the band at 2229 cm^{-1}, comprises those mesogens that exist in the soft segment matrix and are not involved in the formation of smectic layers. In addition, three distinct bands at 1726, 1710 and 1700 cm^{-1} are observed in the carbonyl region. These are assigned to the free carbonyls (1726 cm^{-1}) in the hard segments, slightly less ordered carbonyls at the interface between the hard and the soft segment 1716 cm^{-1}and the hydrogen-bonded carbonyls in the hard segments (1701cm^{-1}).

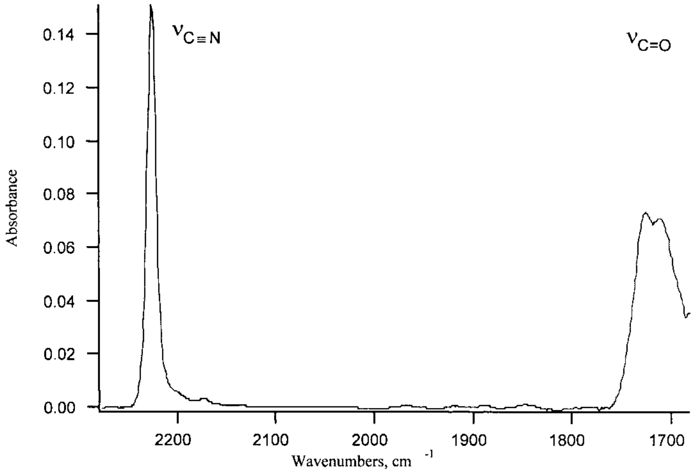


Figure 1: Static spectrum of the side-chain liquid crystalline polyurethane.

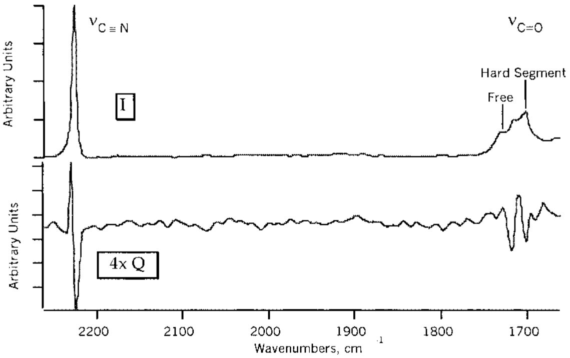


Figure 2: In-phase and 90 degree out of phase dynamic FT-IT spectra of the side-chain liquid crystalline polyurethane.

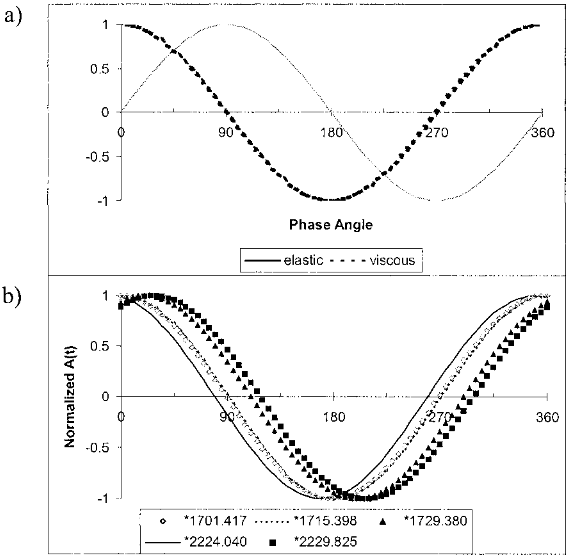


Figure 3: a) Perfectly elastic and perfectly viscous response curves. b) Dynamic dichroic response of polyurethane.

We also observe a positive in-phase response for all three bands. A positive response correlates with a perpendicular alignment of the hard segments since 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. 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

Figure 3a 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 3b depicts the actual variations of the different bands of interest with applied strain. All 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 dependant 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.

The synchronous correlation map for the spectral region from 2300 cm^{-1} to 1690 cm^{-1} is shown in Figure 4. Strong autopeaks are observed at 2225 cm^{-1} and at 1705 cm^{-1}, whereas positive cross peaks are also observed in the same map. The presence of the strong autopeaks indicate that both the mesogens (CN band) and the hard segments (CO band) respond to the applied strain. The positive cross peaks confirm that the mesogens and the hard segments respond to the applied strain at similar rates.

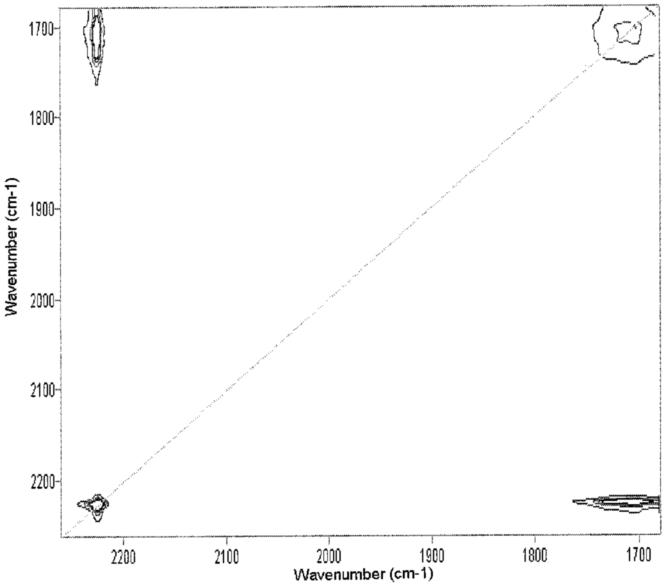


Figure 4: Synchronous correlation map of the –CN and –CO spectral regions.

In the asynchronous 2D correlation plot, the existence of several populations of ordered and less ordered species is implied by the presence of cross peaks for the mesogens and the hard segments in the asynchronous correlation spectrum. The expanded view of the CO region shown in Figure 5, shows the power of 2D IR correlation spectroscopic technique. By drawing asynchronous correlation squares between the three sets of cross peaks, the presence of four bands (1702, 1710,1718 and 1728 cm^{-1}) can be distinguished. In the earlier work, three distinct bands were fit to the broad carbonyl band. These were ascribed to the free carbonyls (1728 cm^{-1}), the H-bonded carbonyls in the hard segments (1701 cm^{-1}) and a set of more loosely H-bonded carbonyls at 1718 cm^{-1}. The 2DIR correlation provides evidence for two populations(1710 and 1718 cm^{-1}) of slightly less ordered carbonyls at the interface between the hard and soft segments, in addition to the free carbonyls at 1728 and the H-bonded carbonyls at 1701 cm^{-1}. The signs of the cross peaks reveal that the band at 1701 cm^{-1}, the H-bonded carbonyls in the hard segments, responds to the applied strain before the bands at 1710 cm^{-1} and 1718 cm^{-1}.

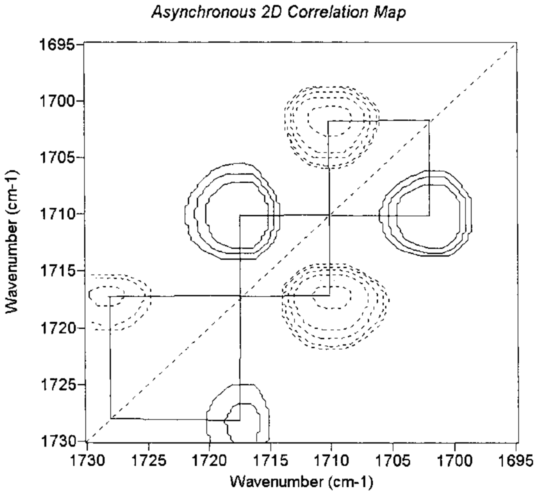


Figure 5: Asynchronous correlation map of the –CO region.

Finally, the 2DIR correlation is in excellent agreement with the results from the dynamic infrared data for the nitrile band region. Specifically, the presence of the cross peak in the CN region (Fig. 6) confirms the two populations of mesogens implied by the bisignate in the dynamic spectrum. The signs of the two cross peaks show that the free mesogens (2229 cm^{-1}) respond to the strain before the less ordered groups at 2224 cm^{-1}.

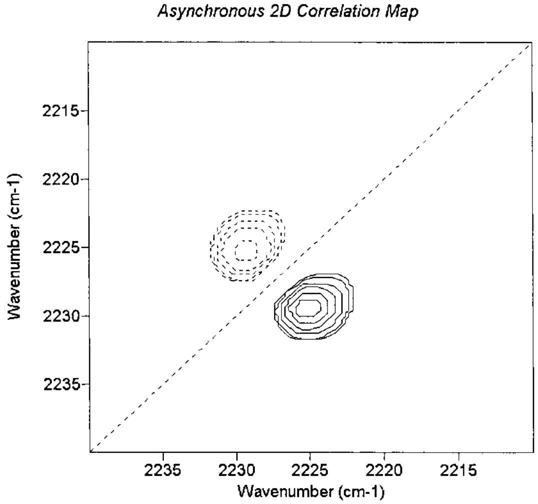


Figure 6: Asynchronous correlation map of the –CN region.

Conclusion

The advantages of 2DIR correlation spectroscopy to resolve highly overlaped bands has been clearly shown in these experiments. Where curve fitting the dynamic spectra for the urethane carbonyls can identify the presence of three highly overlapped bands, the asynchronous 2DIR reveals four bands further refining the concept of the loosely H-bonded carbonyls. For the CN bands, 2DIR was shown to be in excellent agreement with the conclusions drawn from consideration of only the dynamic spectra. Overall, we were able to elucidate two different response patterns in this complex macromolecular system. The smectic layers and the hard domains appear to respond sluggishly at similar rates, while the "free" mesogens and the "lone" hard segments both re-orient in a more elastic manner.

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