

Two-Dimensional Correlation Infrared Analysis (2D-IR) Based on Dynamic Infrared Spectroscopy Used as a Probe of the Viscoelastic Behavior of Side Chain Liquid Crystalline Polyurethanes

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Dynamic infrared dichroism techniques were employed in the study of a complex side chain liquid crystalline segmented polyurethane. The dynamic spectra obtained were further analyzed using two-dimensional correlation infrared spectroscopy (2D-IR) that facilitates an easier interpretation of the dynamic response. The behavior of the side chain mesogens is monitored by the cyano tag at the end of the molecule while the hard segments response is found in the carbonyl spectral region. This study of the different parts of the macromolecule leads to the understanding of the elastic and the viscous orientation behavior of the polymer under conditions of dynamic strain. In particular, 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. The utilization of two-dimensional infrared spectroscopy made possible the discovery of the presence of paracrystalline hard segment “domains” within this material that have slightly different viscoelastic responses. All of 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. Finally, we show conclusive evidence for the coupling of the mechanical deformation behavior of the smectic layers and the hard domains and identified the two primary relaxation times in this system.

Introduction

A new class of materials that allow the coupling of the optical changes brought on by liquid crystal alignment to applied mechanical strains is side chain liquid crystalline polyurethanes. The design and fabrication of thermoplastic elastomers, for which mechanical orientation may be achieved using classic plastic processing techniques to induce changes in liquid crystal orientation, is of high importance to the modern polymer industry. Such thermoplastic elastomers have been designed to exhibit the mechano-optic properties of liquid crystalline cross-linked systems. These materials could be ultimately used in the manufacturing of electrooptic or responsive coatings, sensors and transducers using conformal coatings as the building block.^{1,2} These segmented copolymers have liquid crystals pendant to a low T_g siloxane soft segments. These materials are the only so far reported elastomers with the responsive liquid crystalline part above their glass transition temperature at room temperature.

As was stated earlier, the appealing feature of these materials is the opportunity to manufacture them using classic polymer processing techniques and could be used to orient the liquid crystalline domains in these materials. The result would be the formation of ordered monodomains in an elastomeric matrix. Therefore, it is anticipated that the resulting films should exhibit

a range of interesting properties including piezoelectricity and mechano-optical response. In these materials, the hard segments create a network of physical rather than chemical cross-link junctions. These cross-links result in the ability of the material to transduce applied strains. To create a successful mechano-optic material, an effective conduit for the transfer of strain from the hard segments to the liquid crystalline phase is desirable, either by thermal or mechanical means.

An additional aspect of the importance of these materials is that they show promise as viscoelastic damping systems. Damping generally is found near the glass transition temperature of a polymer when a minimum is observed for the ratio of the energy stored to the energy dissipated by the material. Interpenetrating networks (IPNs) are the best suited damping materials due to the broad temperature and/or frequency range of damping that can be attained. In addition to these materials, segmented liquid crystal thermoplastic elastomers (LCTPEs) should also in principle display a variety of characteristic frequencies from the various parts of the macromolecule.

Dynamic infrared spectroscopy has been used successfully in the study of the molecular and submolecular origins of the macroscopic rheological properties of polymeric materials.^{3–7} In the experiments reported here, our goal is to elucidate the coupled interactions of liquid crystalline moieties with 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. Therefore, the application of two-dimensional infrared correla-

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tion techniques to these dynamic data can be proven extremely useful in uncovering subtle responses that otherwise will be hidden in the complexity of the dynamic infrared data.

Theory of Two-Dimensional Infrared Spectroscopy

Two-dimensional infrared correlation spectroscopy (2D-IR) is a technique originally introduced by Noda and co-workers that has become a powerful tool for vibrational spectroscopists studying the response of materials to an external perturbation.^{8,9} Two-dimensional infrared maps are created as the product of a pair-wise correlation between the time-dependent fluctuations of infrared signals that occur during dynamic infrared experiments. The recent 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.^{10,11} Wang and Palmer have recently presented a detailed review of generalized 2D spectroscopy.¹² The dynamic spectrum can be defined as

$$\tilde{y}(\nu, t) = \begin{cases} y(\nu, t) - \bar{y}(\nu) & \text{for } T_{\min} \leq t \leq T_{\max} \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

where $\bar{y}(\nu, t)$ is the spectral intensity variation observed as a function of a spectral variable 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 $\bar{y}(\nu)$ is defined as

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

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

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

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

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

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

$$\tilde{Y}_2^*(\omega) = \int_{-\infty}^\infty \tilde{y}(\nu_2, t) e^{+i\omega t} dt \quad (5)$$

Further details of the methods of calculation of 2D correlation spectra may be found in a recent paper by Noda.¹³

In particular, the *synchronous correlation map* provides an indication of simultaneous spectral intensity changes as a result of the perturbation. This map 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. In contrast, when the sign of the synchronous cross peak is negative, the indication is that we observe 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 reorientational behavior of the corresponding dipole moments. Furthermore, the asynchronous 2D correlation map has no diagonal peaks and produces cross peaks only to the extent that two transition dipoles reorient out of phase with each other. The corresponding signs of the asynchronous cross peaks give the relative rates of response of the two contributing dipoles. Therefore, 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 . In that respect, in addition to spectral resolution enhancement due to the incorporation of the second dimension, two-dimensional correlation maps can provide information about the relative reorientation of transition dipole moments and the relative rates of inter- and intramolecular conformational relaxations. The big advantage of this 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 these maps. Therefore, even though the two-dimensional correlation highlights important features of the dynamic data, it has to be emphasized that the S/N of the original data controls the quality and appearance of the produced correlation maps.

Two-dimensional infrared correlation analysis is especially powerful in studies of polymer reorientation in response to applied perturbations. There have been several papers that have focused on liquid crystal materials and liquid crystalline polymers (LCPs).^{14,15} One of the earliest applications of two-dimensional spectroscopy monitored 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.^{16,17} 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. The importance of the work lies in the fact that the separate responses of the different parts of the molecule were captured for the first time and in that sense this work was the prelude to the results reported here.

In addition, two-dimensional infrared correlation analysis has been used to study the orientation and the mobility of a ferroelectric liquid crystal dimer during switching under an electric field.¹⁸ 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.¹⁹ The remaining part of the spacer and the main chain of the FLCP do not participate in the reorientation. Two-dimensional correlation analysis of

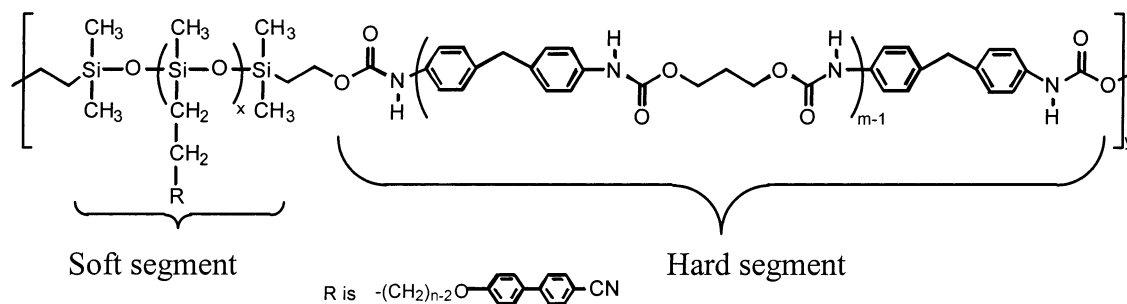


Figure 1. Structure of the side chain liquid crystalline polymer.

polarization angle-dependent IR 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.^{20,21} The two-dimensional correlation 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 nonchiral portion of the molecule.

Experimental Section

Compound Synthesis. The details of the synthesis of the side chain liquid crystalline polyurethane used in this study have been published elsewhere.²² 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). Figure 1 shows the structure of the side chain liquid crystalline macromolecule.

Infrared Experiments and Two-Dimensional Correlation Maps. 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 plane polarizes the infrared light was placed in the propagation direction of the beam. Free-standing polyurethane films are too thick and as a result saturation of important infrared absorption bands occurs in the transmission spectra. Therefore, thin films were prepared by casting the polyurethane on a thin Teflon substrate from a 50/50 THF/DMAc solution. The integrity of the adhesion of the polyurethane to the Teflon substrate was tested with tape peel tests and immersion in water and was found very satisfactory.

The dynamic step-scan 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 the sample compartment's base plate. Again, a wire-grid polarizer was placed before the sample allowing only infrared radiation polarized parallel to the stress direction to reach the sample. This time, a low-pass optical filter was placed after the sample to filter off the light above 3950 cm^{-1} . The inclusion of the optical filter improves substantially the appearance of the dynamic spectra and should be preferred. The spectra were collected at a resolution of 8 cm^{-1} in a period of less than 1 h.

The polymer dynamic rheology experiments described in this paper were conducted with a phase modulation frequency of 400 Hz and phase modulation amplitude of $3.5\lambda_{\text{HeNe}}$.²³ The

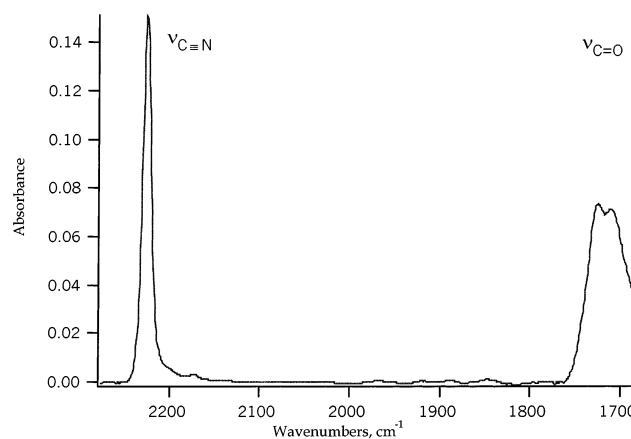


Figure 2. Static spectrum of the side-chain liquid crystalline polyurethane.

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 which is key to the success of these types of experiments. Furthermore, at low oscillation amplitudes, the effect of sample thinning on the infrared bands is negligible when compared to the effect of the dynamic signal 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 in the literature except these data could be obtained with much shorter data collection times.²⁴

The 2D correlation spectra were generated using KG2D, a macro program using ArrayBasic for Grams/386 (Thermo-Galactic, Inc., Salem, N. H.) written by Y. Wang (Kwansei Gakuin University).

Results and Discussion

The static spectrum of the side-chain liquid crystalline polyurethane is shown in Figure 2. The different bands in this sample have been assigned in an earlier work.²² There are two main spectral regions of interest to the dynamic work. The first region is the cyano region that shows a 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 with respect to the external applied mechanical strain. The other spectral region of interest is the carbonyl region between 1740 and 1700 cm^{-1} . We use this spectral region to identify in a direct manner the movement of the hard segments as well as the movement of the soft segment in an indirect manner. Specifically, there are three bands in the urethane carbonyl region. We assign these

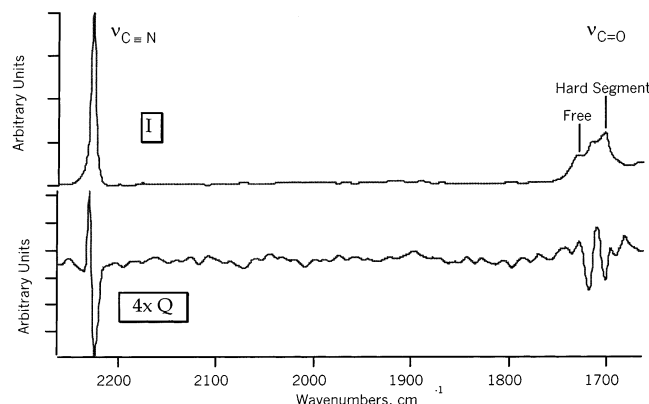


Figure 3. In-phase and 90° out-of-phase dynamic FT-IT spectra of the side-chain liquid crystalline polyurethane.

bands to carbonyls with different degrees of hydrogen bonding. The 1701 cm^{-1} band is assigned to carbonyls that engage in hydrogen bonding within the hard domains. Slightly less ordered carbonyls, probably 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 infrared signature bands at 1730 cm^{-1} . These later species allow us to follow the response of the soft matrix as well.

The dynamic spectrum is shown in Figure 3. As previously reported,²³ the bisignate observed in the nitrile band of the quadrature spectrum is indicative of the existence of two distinct populations within the polymer morphology. 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. On the other hand, in the carbonyl region three distinct bands at 1726, 1710, and 1700 cm^{-1} are observed. However, the dynamic spectra are very complicated in this region. Therefore, the use of two-dimensional correlation infrared spectroscopy can be of great help in a situation like this.

Before we move to the two-dimensional analysis, the data in Figure 4 give us a good indication of the existence of two distinct relaxation mechanisms in the system. Specifically, Figure 4a 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 4b 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. However, there are two distinct categories of responses based on the phase lags suggesting that there are two primary 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 (25 Hz^{-1} = 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

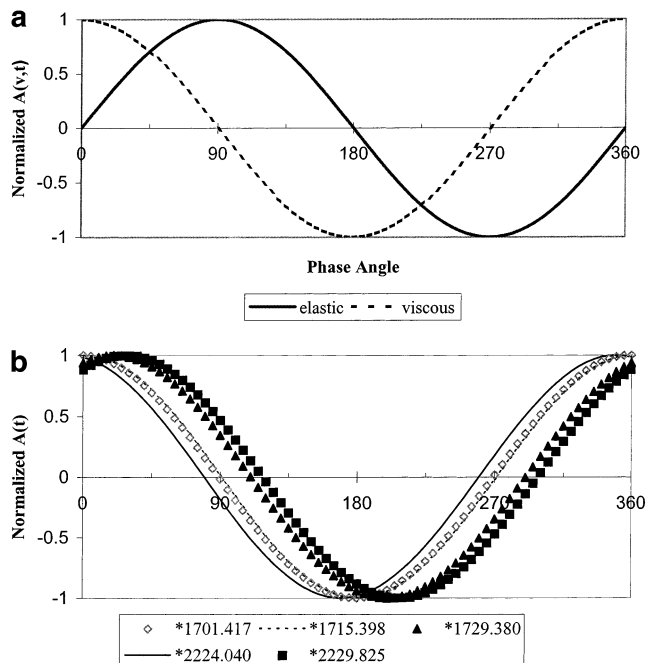


Figure 4. (a) Perfectly elastic and perfectly viscous response curves. (b) dynamic infrared response of polyurethane (1701 ordered hard segments, 1715 less-ordered hard segments, 1729 “free” hard segments, 2224 ordered mesogens, and 2229 “free” mesogens).

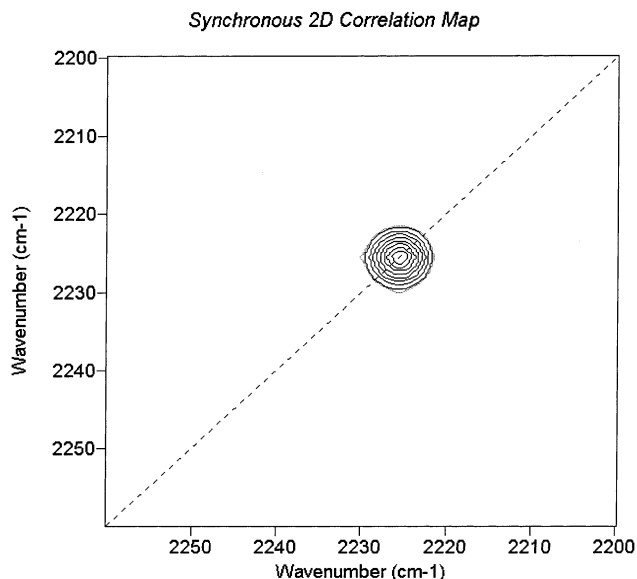


Figure 5. Synchronous correlation map of the $-\text{CN}$ spectral region.

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 to 1690 cm^{-1} shows strong autopeaks at 2225 cm^{-1} and at 1705 cm^{-1} , whereas positive cross peaks are also observed in the same map (figure not shown). The presence of the strong autopeaks indicates that both the mesogens (CN band) and the hard segments (CO band) respond to the applied strain. Figure 5 and Figure 6 depict the synchronous correlation maps for the two spectral regions (cyano region and carbonyl region) respectively. In addition, the positive cross peaks between the features at the two distinct regions confirm that the mesogens and the hard segments respond to the applied strain at similar enough rates.

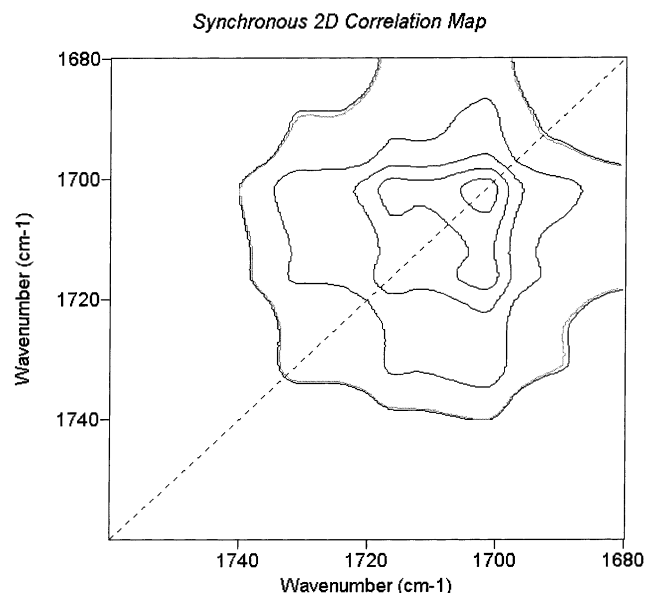


Figure 6. Synchronous correlation map of the -CO spectral region.

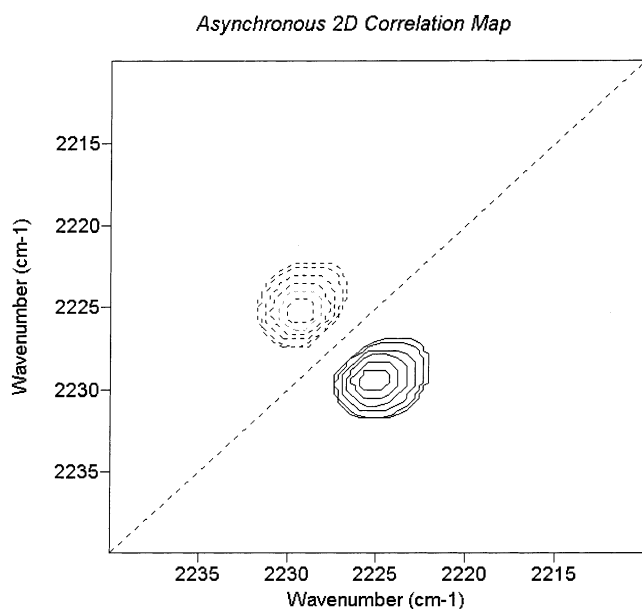


Figure 7. Asynchronous correlation map of the -CN region.

In the asynchronous 2D correlation plots, 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. For instance, the two-dimensional correlation data are 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 in Figure 7 confirms the presence of 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} . This is another indication that a rapid orientation of the flexible soft segment, that includes the free mesogens, takes place at the early times of the cyclic deformation.

Finally, the expanded view of the CO region, shown in Figure 8, shows the power of the two-dimensional infrared 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 work²³ three distinct bands were fit to

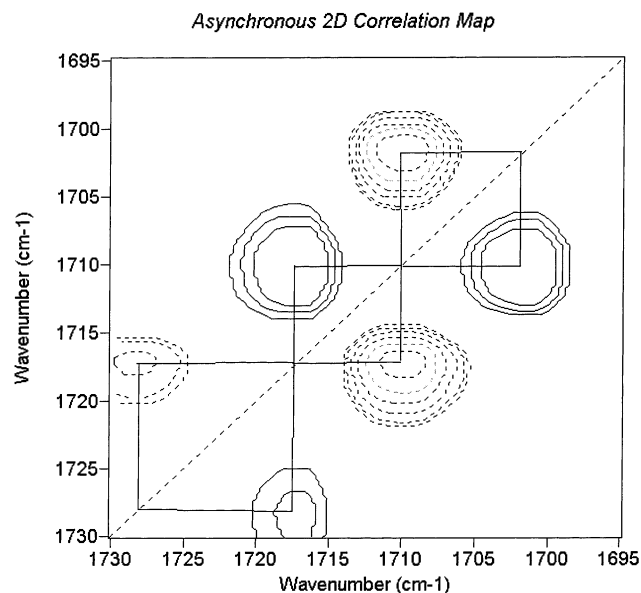


Figure 8. Asynchronous correlation map of the -CO region.

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 two-dimensional correlation map 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 and 1718 cm^{-1} . Therefore, the power of the technique is clearly demonstrated in this example since it is very difficult to make this observation by looking only at the dynamic spectra.

This observation implies that there are probably hard segment "domains" within this material that have slightly different viscoelastic responses. It is well-known that crystalline hard segments do not orient in the same way as noncrystalline hard segments in static elongation experiments. Even though no direct evidence of fully crystalline hard domains was observed for this material, the presence of paracrystalline order is highly suspected. In our studies, the application of two-dimensional correlation analysis showed that the reversible orientation of both the crystalline-like and noncrystalline regions at these low strains takes place at different time scales. With regards to the "crystalline" hard segments, lamellar type structures have been proposed in the past with the long direction of the domain perpendicular to the hard segment backbone.²⁵ Our results show that the orientation of the paracrystalline type takes place with the long axis of the domains moving toward the direction of the mechanical fields, thus resulting in a perpendicular orientation of this type of hard segment. Due to the low deformation amplitude, we expect that these domains remain intact during the entire process with no observable breaking up of the paracrystallites. Overall, these hard segment crystalline-type "domains" exhibit a viscoelastic response which is more elastic in nature than the predominant strongly hydrogen bonded carbonyls but not as elastic as the free carbonyls.

Summary

The advantages of two-dimensional correlation infrared (2D-IR) spectroscopy to resolve highly overlapped 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 2D-IR map reveals four bands further refining the concept of the loosely H-bonded carbonyls. For the CN bands, 2D-IR 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 reorient in a more elastic manner.

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