LA-UR--98-508

Title:

Analysis of Polyurethane Elastomer Using
Thermal 2D FT-1R

CONF-980314--

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Form No. 836 R5
ST 2629 10/91

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Analysis of a Polyurethane Elastomer Using Thermal 2D FT-IR,
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Introduction: Polyurethane-polyester elastomers contain hard and soft domains which give these materials unique structural and elastic properties and lead to their use in various applications. It is desirable to characterize the molecular-level interactions giving rise to the two domains and to use this information to monitor chemical changes which take place in the polymer as a function of exposure to agents known to effect structural changes. Infrared spectroscopy has been used to study polymeric structures, including polyurethane elastomers,¹ as the vibrational absorption bands characteristic of different functional groups are sensitive to changes in their chemical environment. One difficulty in the application of infrared spectroscopy to complex chemical systems has been the ambiguity of interpretation due to the limitations of different deconvolution techniques. Noda's development of a 2D correlation method² provides a means by which convoluted spectral information, such as that arising from the two domains of elastane, can be resolved as a function of some perturbation. We present here a thermal 2D FT-IR study of elastane.

Experimental: Elastane[®], obtained from B.F. Goodrich, has the form $[(CH_2)_4OOCNH(C_6H_4)CH_2(C_6H_4)NHCOO]_m[(CH_2)_4OOC(CH_2)_4COO]_n$. Samples were prepared by casting a dilute MEK solution of the polymer onto 13mm x 2mm BaF₂ windows. Sample thickness yielded a maximum absorbance under 1.6 absorbance units.

Samples were mounted between two BaF₂ windows in an aluminum block cell containing a cartridge heater and connected to a temperature controller. The temperature ($\pm 0.1^\circ\text{C}$) was monitored through a Type K thermocouple placed next to the sample in the temperature cell. Sixteen spectra were collected with a Nicolet 20SXB FTIR spectrometer at approximately equal temperature intervals from 35 to 80 °C. 128 scans were measured with a resolution of 4cm⁻¹. 2D plots were calculated using the MathCad (Mathsoft) software package.

Results: The absorption spectra are shown as a function of temperature in Figure 1. Synchronous (real) and asynchronous (imaginary) components of the cross-correlation analysis of this data, from 1500 to 1800 cm⁻¹, are shown in Figures 2 and 3, respectively.

Figure 1: Sixteen infrared absorption spectra of estane at temperatures ranging from 35 to 80 °C. Each spectrum is an average of 128, resolution 4 cm^{-1} , referenced to air and baseline corrected for the presence of atmospheric water.

Discussion: The spectra in Figure 1 reflect the molecular-level changes which give rise to a hard-segment ordering transition in the 60-80°C temperature range. The 2D plots of the 1500-1800 cm^{-1} region, Figures 2 and 3, illustrate the usefulness of the analysis technique. Intensity arises in the 2D plots for a pair of vibrations whose responses to the perturbation are correlated in specific ways. For example, a positive feature in the synchronous plot occurs for two bands which are simultaneously changing and in the same direction (i.e. both increasing); a negative feature indicates bands which are simultaneously changing

Figure 2: Synchronous correlation plot of estane, 1500 to 1800 cm^{-1} ; shading indicates negative contours.

Figure 3: Asynchronous correlation plot of estane, 1500 to 1800 cm^{-1} ; shading indicates negative contours.

but in an opposite direction (one increasing, one decreasing). The 1500 to 1800 cm^{-1} region contains three spectral features: the $\nu(\text{C}=\text{O})$ at 1720 cm^{-1} (both hard and soft domains), the $\nu(\text{C}=\text{C})$ at 1600 cm^{-1} , and the $\nu(\text{C}-\text{N})$ plus $\delta(\text{N}-\text{H})$ at 1535 cm^{-1} . Changes are seen in N-H hydrogen bonding as the temperature is raised (data not shown); we expect to see these changes in the $\nu(\text{C}=\text{O})$ region as well, and also expect to resolve the C=O contributions from the hard and soft domains. Note that in the $\nu(\text{C}=\text{O})$ region of the synchronous plot, the band has clearly been resolved into three frequency components, while the $\nu(\text{C}-\text{N})$ plus $\delta(\text{N}-\text{H})$ region of the synchronous plot has given rise to two distinct components; the asynchronous plots of these regions show further complexity. Correlations of these modes with that of the phenyl $\nu(\text{C}=\text{C})$ mode is also clearly observed. By assessing the cross correlations through the entire frequency range, it is possible to assign spectral components and to interpret their behaviors with confidence.

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