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Rheo-Optical Fourier Transform IR (FTIR) Spectroscopy of Polyurethane Elastomers*

2. Measurements at Elevated Temperature

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** In memoriam Prof. Dr. Otto Bayer*

SUMMARY

In a preceding paper of this study (SIESLER 1983) the application of rheo-optical FTIR spectroscopy to a series of model polyester urethanes at ambient temperature has been discussed with reference to the phase separation and segmental orientation of these polymers during uniaxial elongation and recovery. Here, the results of variable-temperature FTIR measurements and rheo-optical FTIR investigations at elevated temperature are presented and interpreted in terms of the temperature dependence of hydrogen bonding and structural organization of the hard segments.

INTRODUCTION

With the introduction of a variable temperature cell for rheo-optical FTIR spectroscopy (SIESLER 1982) the potential of this technique has been further expanded to study in more detail the temperature dependence of the mechanical properties of polymers.

Vibrational spectroscopic studies at variable temperature have become an important tool for the characterization of the physical structure of polymers. Especially in combination with DSC measurements short-time spectroscopic FTIR investigations in controlled heating and cooling experiments provide a detailed picture of structural changes as a function of temperature. Any variations of spectroscopic parameters such as intensity, wavenumber position and band shape directly reflect the temperature dependence of the vibrational behaviour of the investigated polymer as a consequence of changes in the inter- and intramolecular interactions and the state of order. Thus, the vibrational spectra of polymers recorded in selected temperature intervals are of special value in studies of melting and recrystallization processes, thermal degradation and hydrogen bonding.

Although the energies of hydrogen bonds are weak (20 - 50 kJ/mol) in comparison to covalent bonds (about 400 kJ/mol) this type of molecular interaction is large enough to produce appreciable frequency and intensity changes in the vibrational spectra of polymers. In fact, the disturbances are so significant that IR and Raman spectroscopy provide the most informative source of criteria for the presence of hydrogen bonds (MURTHY and RAO 1968).

Generally, hydrogen bonding involves the interaction between a proton donating group (R_1-X-H) and a proton acceptor (Y-R_2) and may be described schematically by:

$$R_1\text{-X-H}\cdots\text{Y-}R_2$$

As a consequence of the hydrogen bonding forces the ν(XH) and ν(YR_2)

stretching frequencies will be lowered, whereas the deformation frequencies associated with the motions of the H and Y atoms perpendicular to their X-H and $Y-R_2$ bonds, respectively, will be increased.

Most of the investigations so far reported deal with the observed frequency shift and intensity increase of the $\nu(XH)$ stretching vibration upon hydrogen bonding. Primarily the frequency shift $\Delta\nu(XH)$ has been correlated with various chemical and physical properties of the hydrogen bond. With increasing hydrogen bond strength, for example, the $R_{X...Y}$ distance decreases and this decrease is accompanied by an increase in the difference between the associated $\nu(XH)$ and the nonassociated $\nu(XH)$ stretching frequency. In fact, for a number of different types of hydrogen bonds relationships between $\Delta\nu(XH)$ and $R_{X...Y}$ have been established (PIMENTEL and SEDERHOLM 1956) and in the case of NH...O bonds this relationship is expressed by the following equation:

$$\Delta\bar{\nu} = 0.548 \cdot 10^3\ (3.21 - R) \qquad (1)$$

where $\Delta\bar{\nu}$ is given in cm^{-1} and R in Å. Thus, valuable information regarding the temperature dependence of hydrogen bonding and its influence on the mechanical properties of polymers may be derived from variable temperature measurements and rheo-optical studies at elevated temperature, respectively.

EXPERIMENTAL

The spectra were obtained on a Nicolet 7199 FTIR spectrometer equipped with a Nicolet 1280 64K computer.

The investigated polyester urethanes were synthesized from diphenylmethane-4,4'-diisocyanate, a dihydroxyterminated adipic acid/butane diol/ ethylene glycol polyester (molecular weight 2000) and butane diol as chain extender with polyester:chain extender:diisocyanate molar ratios of 1.0: 2.2:3.4 (a), 1.0:5.4:6.6 (b) and 1.0:7.5:8.7 (c), respectively.

The experimental and instrumental details of the rheo-optical investigations and the sample preparation have been described in the preceding paper (SIESLER 1983). The rheo-optical measurements of this study were performed at 348 ± 0.5 K in the variable-temperature cell of the stretching machine. A separate variable-temperature cell was used to record the FTIR spectra of the individual polyester urethanes without application of stress during heating above the melting point of the hard segments to 500 K. The heating rate was 9 K/min and 25-scan spectra were taken in 30-second intervals with a resolution of 2 cm^{-1}. For the evaluation of these variable-temperature measurements in terms of wavenumber position a peak search routine was developed which automatically determines and subsequently plots the peak maxima of selected absorption bands in a series of spectra taken as a function of temperature.

DSC diagrams of the polyester urethanes were recorded on a Perkin Elmer DSC II instrument with a heating rate of 10 K/min.

RESULTS AND DISCUSSION

The DSC diagrams of the three polyester urethanes between 380 and 500 K are shown in Fig. 1. The observed endotherms with multiple peaks reflect the sequential melting and disruption of the hard segment domains with different degrees of structural organization. The heats of fusion which may be regarded as a measure of the strength of the hard segment crosslinks have been determined from the areas under the entire melting endotherms. Within the composition range studied, increasing the hard segment content resulted in higher ΔH values of 4.8 Jg^{-1} (a), 7.9 Jg^{-1} (b) and 13.7 Jg^{-1} (c). The highest state of order in the hard segment phase of polyester urethane

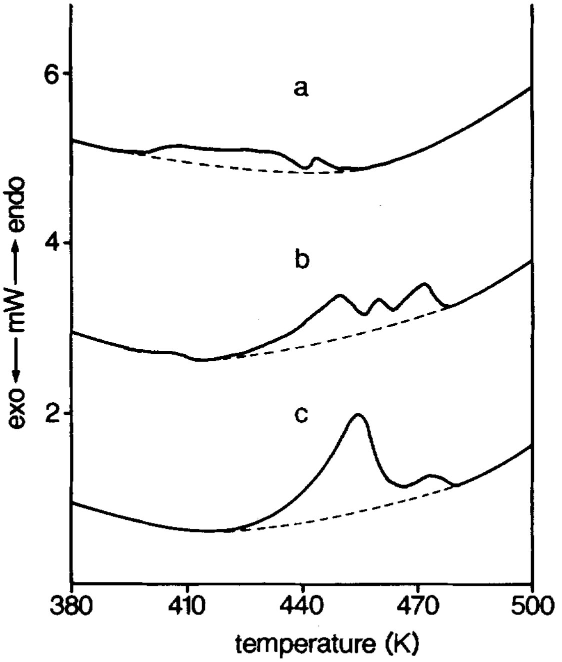

FIGURE 1 DSC diagrams of the polyester urethanes (a), (b) and (c).

(c) is also in agreement with the observation of the 0.75 nm Bragg reflection (BLACKWELL et al. 1981) in the wide-angle X-ray diagram of this polymer. However, the ΔH values representing only about 15% (a), 17% (b) and 25% (c), respectively, of that expected from a model hard segment (CAMBERLIN et al. 1982) demonstrate the significantly reduced hard segment crystallinity of the investigated polyester urethanes.

The FTIR spectra of the polyester urethanes recorded during heating exhibited characteristic temperature-dependent features for the ν(NH), ν(C=O) and δ(NH)+ν(CN) absorption bands as a consequence of changes in hydrogen bonding. As an example the spectra of polyester urethane (c) taken in the 300 - 507 K interval are shown in Fig. 2. While the intense absorption band at 3331 cm^{-1} can be assigned to the ν(NH) stretching vibration of the NH-groups associated through hydrogen bonds [ν_{ass}(NH)], the small shoulder at about 3440 cm^{-1} is characteristic of the ν(NH) vibration of the nonhydrogenbonded NH-groups [ν_{free}(NH)]. Similarly, the ν(C=O) band complex can be separated in a ν_{ass}(C=O) band at 1703 cm^{-1} (primarily contributed from hydrogenbonded urethane carbonyl groups) and a ν_{free}(C=O) band at 1733 cm^{-1} which can be predominantly assigned to nonbonded ester carbonyl groups. With increasing temperature the following spectral changes are observed (SRICHATRAPIMUK and COOPER 1978):

1. The intensity of the ν_{free}(NH) band increases at the cost of the ν_{ass}(NH) band.
2. The peak maximum of the ν_{ass}(NH) band is shifted toward larger wavenumbers.

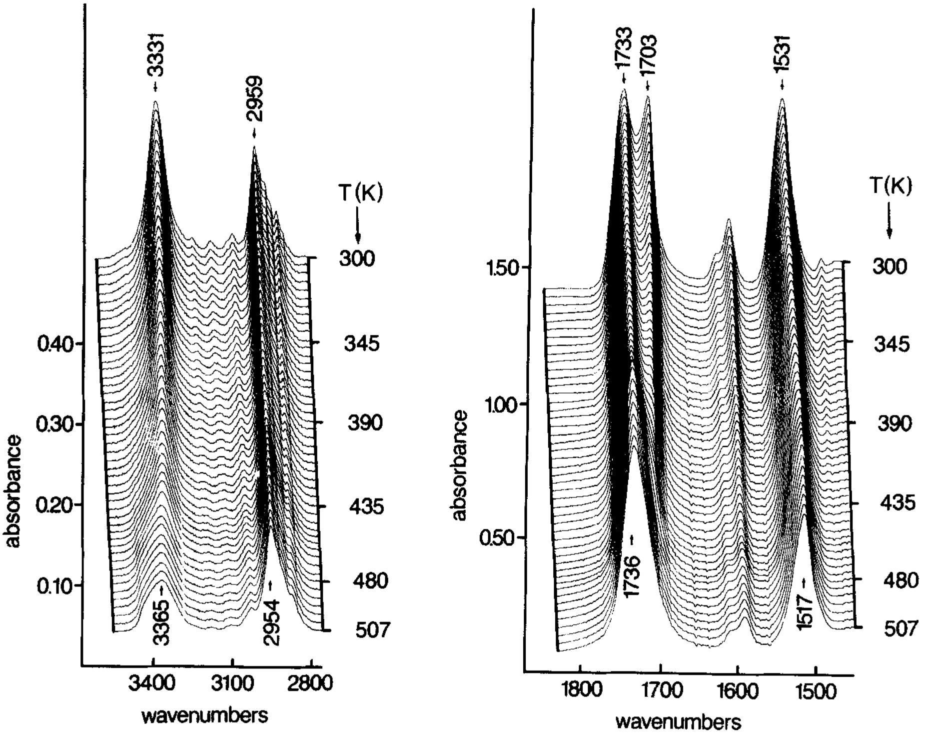

FIGURE 2 FTIR spectra of polyester urethane film (c) recorded in the 2800 - 3500 cm^{-1} and 1400 - 1800 cm^{-1} wavenumber region during heating at 9 K/min from 300 K to 507 K.

3. The half width of the ν_{ass}(NH) band increases considerably with increasing temperature.
4. The ν_{ass}(C=O) band is shifted toward larger wavenumbers and eventually coalesces with the ν_{free}(C=O) band.
5. The δ(NH) + ν(CN) band is shifted toward smaller wavenumbers.

The intensity decrease and increase of the ν_{ass}(NH) and ν_{free}(NH) absorptions, respectively, are indicative of the shift in equilibrium concentration of the hydrogenbonded and nonhydrogenbonded NH-groups. The wavenumber shift and increase in band width of the ν_{ass}(NH) band at higher temperatures are the result of a general weakening of the hydrogen bonds and a concomitant broader distribution of their energies. Similar temperature-dependent spectral changes are also observed for the ν_{ass}(C=O) absorption band. The frequency shift in the vibration of the bonded carbonyl groups, however, is less pronounced than that of the NH-groups because the acceptor atom is certainly less displaced than the hydrogen atom of the donor group. The shift of the δ(NH) + ν(CN) band toward smaller wavenumbers reflects the predicted inverse effect of hydrogen bonding on stretching and deformation vibrations.

In Fig. 3 the peak maximum wavenumbers of the ν(NH) and $\nu(CH_2)$ absorption bands have been plotted as a function of temperature with the aid of

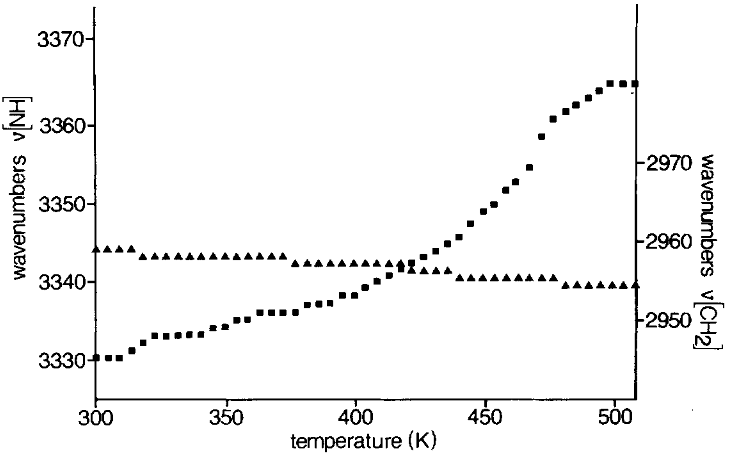

FIGURE 3 Shift of the peak maximum wavenumber of the ν(NH) (■) and ν(CH_2) (▲) absorption bands of the polyester urethane film (c) as a function of temperature.

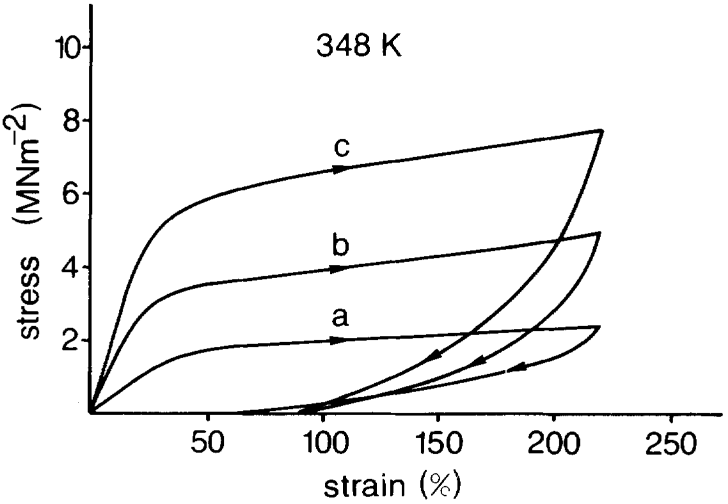

FIGURE 4 Stress-strain diagrams of loading-unloading cycles of the polyester urethane films (a), (b) and (c) at 348 K.

the automatic peak search and plot routine. Drastic frequency shifts can be observed for the ν(NH) band in the 430 K - 490 K melting temperature interval of the hard segments (see also Fig. 1c). With Eq. (1) a concomitant increase of $R_{N...O}$ from 3.01 Å to 3.07 Å can be derived between 300 K and 500 K. In view of the uncertainty of the exact wavenumber position of the ν_{free}(NH) absorption band at about 3440 cm^{-1} the value of 3.01 Å for 300 K is in reasonable agreement with the value of 2.98 Å obtained by X-ray analysis on chemically equivalent model urethanes (BORN et al. 1982).
The corresponding peak maxima plots of the polyester urethanes (a) and (b) differ basically only in that the region of the pronounced wavenumber shift is observed in the temperature interval 390 K - 450 K (a) and 420 K - 490 K (b), respectively. Additionally, between 300 K and 348 K, the experimental

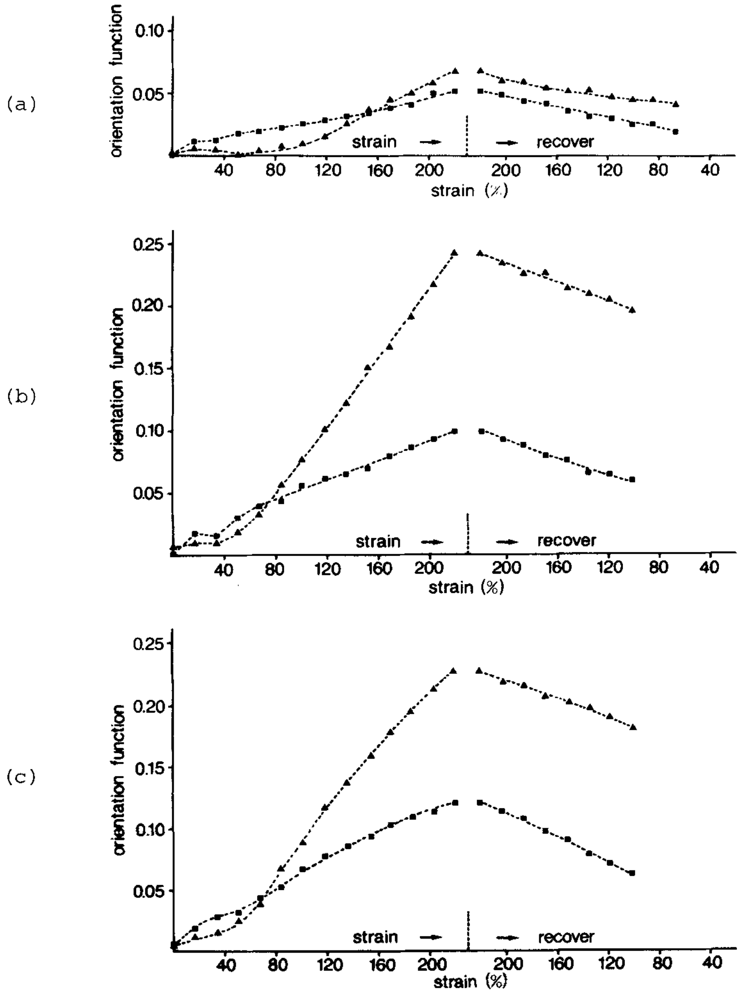

FIGURE 5 Orientation function-strain plot of the hard and soft segments of the polyester urethanes (a) - (c) as monitored by the ν(NH) (▲) and $\nu(CH_2)$ (■) absorption bands, respectively, at 348 K.

temperature of the rheo-optical measurements in the present study, $R_{N...O}$ length increments of approximately 0.01 Å have been determined for the three different polyester urethanes with Eq. (1).

The stress-strain diagrams of the three elastomers measured at 348 K are shown in Fig. 4. The consequence of temperature elevation is a drastic decrease of stress level and initial modulus [5 MNm^{-2} (a), 18 MNm^{-2} (b) and 24 MNm^{-2} (c)]. Furthermore, an increase of extension set [65% (a) and 85% (b)] and an increase and constancy, respectively, of stress hysteresis [68% (a) and 80% (b)] have been evaluated for the low and intermediate hard segment polymers (a) and (b) while a decrease of these parameters was observed for polyester urethane (c) (extension set: 85%, stress hysteresis: 80%) in comparison to the measurements at ambient temperature (SIESLER 1983). Thus, at 348 K extension set and stress hysteresis reach their maximum values already for the polyester urethane (b) with intermediate hard segment content (FERGUSON and KUMAR 1981).

The orientation functions of the hard and soft segments derived from the dichroism of the ν(NH) and ν(CH_2) absorption bands, respectively, in the polarization spectra monitored during the loading-unloading cycles of the different polyester urethanes at 348 K are shown in Fig. 5. Basically, the following structural consequences of the mechanical treatment at 348 K are observed with respect to the measurements at ambient temperature:

a) earlier onset of positive hard segment orientation
b) drastic enhancement of hard segment orientation
c) slight deterioration of soft segment orientation
d) larger retention of hard segment alignment upon recovery to zero stress.

These effects can be predominantly attributed to the temperature dependence of the domain structure in the polymers under examination. Thus, it was indicated (WILKES et al. 1975) that upon heating polyurethanes above about 343 K the degree of domain formation gradually decreases such that more mixing occurs between hard and soft segments. The abovementioned weakening of the hydrogen bonds between 300 K and 348 K will also contribute to an increased disruption tendency of the hard segments upon application of stress. While this enhanced disruption tendency of the hard segments leads to an earlier onset of their more pronounced positive orientation at elevated temperature on the other hand a somewhat lower chain alignment of the soft segments is effected during elongation. Owing to the low crystallization tendency of the involved soft segments strain-induced crystallization does not account for the mechanical behaviour of polyester urethane (c). Therefore, it could be assumed that due to the higher state of order in the hard segments of polyester urethane (c) (see also Fig. 1) the smaller domains are preferentially disrupted during elongation at elevated temperature (BONART and MÜLLER-RIEDERER 1981) resulting in a smaller positive hard segment orientation at maximum elongation than polyester urethane (b) (see Fig. 5). The smaller extension set and stress hysteresis of polyester urethane (c) in comparison to the ambient temperature measurements may be interpreted in terms of a more homogeneous stress distribution in the elongated sample and the improved retractive force of the soft segments at elevated temperature.

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