

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

3. Investigation of NH-Deuterated Specimens

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In memoriam Prof. Dr. Otto Bayer

SUMMARY

In the preceding papers of this study (SIESLER 1983, 1983a) the results of rheo-optical FTIR investigations at ambient and elevated temperature obtained from a series of model polyester urethanes with varying composition have been discussed in terms of the phase separation and segmental orientation of these polymers. The present work demonstrates the potential of this technique applied to NH-deuterated specimens of these polyester urethanes with reference to a more detailed insight into phase separation and the orientation mechanism of the phase-separated hard segments during uniaxial elongation and recovery.

INTRODUCTION

As has been pointed out already polyurethanes are particularly suited to rheo-optical FTIR spectroscopic investigations because they contain functional groups which are predominantly located in specific domains of these polymers. Therefore, the polarization properties of the corresponding characteristic IR absorption bands can be utilized to monitor the orientation of the individual domains during mechanical treatment. In this respect more detailed information becomes available from investigations of NH-deuterated specimens due to the fact that isotope exchange offers a means to differentiate the hard segments into phase-separated species and moieties dispersed in the soft segments or located at domain interfaces.

Among isotope exchange techniques direct deuteration with liquid or gaseous D₂O in combination with IR spectroscopic investigations has been widely applied in studies of polymeric structure (LIANG 1964, DECHANT 1972, SIESLER and HOLLAND-MORITZ 1980). Owing to the mass dependence of the vibrational frequency isotopic substitution reaction will result in frequency shifts of those absorption bands which belong to vibrations of the involved isotopes. The technique, however, is limited to polymers containing loosely bonded protons in NH or OH functional groups (e.g. cellulose, polyamides, polyurethanes) and its applicability to the characterization of molecular order in polymers is based on the fact that hydroxyl and amido groups residing in chain segments of different degree of order are differently exposed to isotopic substitution. Thus, the rate and extent of the exchange reaction will strongly depend on the mechanical and thermal history of the polymer under examination.

Given the applicability of Beer's law and assuming that the reason for a proton not to exchange is due to it being inaccessible to D₂O the percentage of accessible regions (Z) at any stage of deuteration can be determined from the relationship:

$$z = \left[1 - \frac{A_{(X-H)}}{A_{(X-H)_i}} \right] 100(\%) \quad (1)$$

where $A_{(X-H)}$ is the absorbance of an absorption band which can be assigned to a primarily uncoupled X-H vibration and the subscript i refers to the undeuterated sample.

Previous investigations of aliphatic and aromatic polyamides of different degree of crystallinity (SIESLER and HOLLAND-MORITZ 1980) have established a direct correlation between the extent of readily deuterated NH-protons and the percentage of amorphous regions determined by independent methods. In polyurethanes, however, the readily exchanged NH-protons reflect the percentage of small hard segments dispersed in the accessible soft segment phase while the successive region of reduced substitution rate corresponds to the slow penetration of the deuteration agent into larger phase-separated hard segment domains. Therefore, a combination of the deuteration technique and rheo-optical FTIR investigations should provide a more quantitative picture of phase separation and a better differentiation of the individual domain contributions to the overall orientation of the polymer.

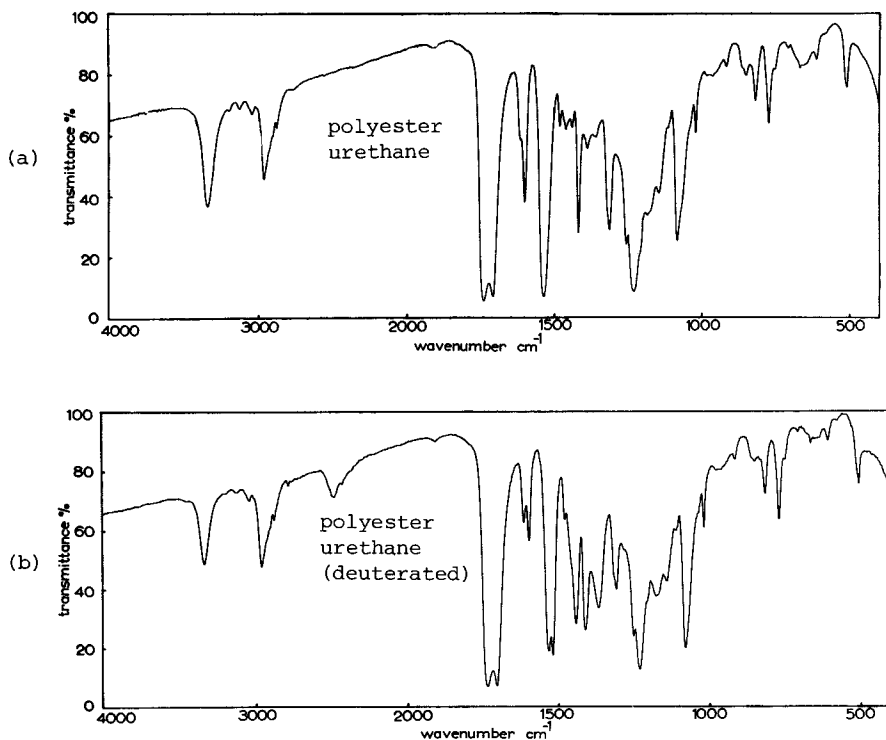


FIGURE 1 IR spectra of an undeuterated (a) and partially deuterated (b) polyester urethane film.

EXPERIMENTAL

The rheo-optical FTIR spectra were obtained at 300 K 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).

The experimental and instrumental details of the rheo-optical measurements and the polymer sample preparation have been described in a preceding paper (SIESLER 1983).

The deuteration procedure and the construction of the deuteration cell have been reported previously (HOLLAND-MORITZ and SIESLER 1976). Basically, the polymer film is mounted in a sealed cell with IR-transparent windows which is kept at a constant temperature of 323 K. Deuterium exchange is induced by saturating dry nitrogen with liquid D₂O prior to flushing the deuteration cell. After five days of deuterium exchange the polymer film is finally transferred to the sample chamber of the stretching machine.

RESULTS AND DISCUSSION

The IR spectra of an undeuterated and partially deuterated polyester urethane (c) film are shown in Fig. 1. The most obvious spectral changes upon deuteration directly reflect those absorption bands which belong to vibrations involving the NH groups. Thus, the H-D isotope exchange results in partial replacement of the $\nu(\text{NH})$ absorption band at 3331 cm^{-1} by a band complex at 2480 cm^{-1} (GARTON and PHIBBS 1982). While the absorption bands at 1703 and 1733 cm^{-1} , essentially attributed to the $\nu(\text{C}=\text{O})$ absorptions of the hydrogenbonded urethane and nonbonded ester carbonyl groups, are almost unaffected by deuteration the bands at 1590 and 1531 cm^{-1} which have been interpreted as $\delta(\text{NH}) + \nu(\text{CN})$ modes (ISHIHARA et al. 1974) decrease in intensity upon substitution of H by D.

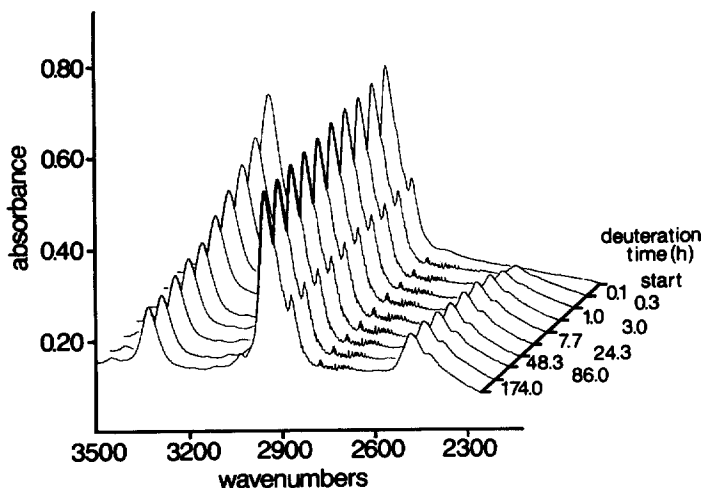


FIGURE 2 FTIR spectra of the polyester urethane (a) film in the $3500 - 2300\text{ cm}^{-1}$ region taken in different time intervals during deuteration.

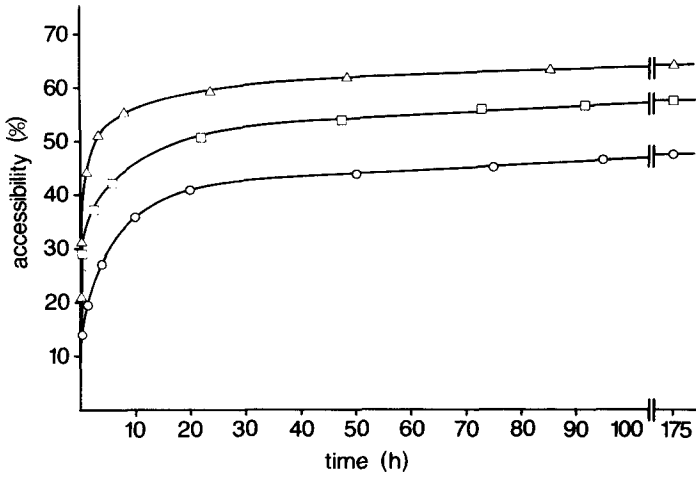


FIGURE 3 Accessibility of the investigated polyester urethane films [(a) Δ , (b) \square , (c) \circ] as a function of deuteration time (see text).

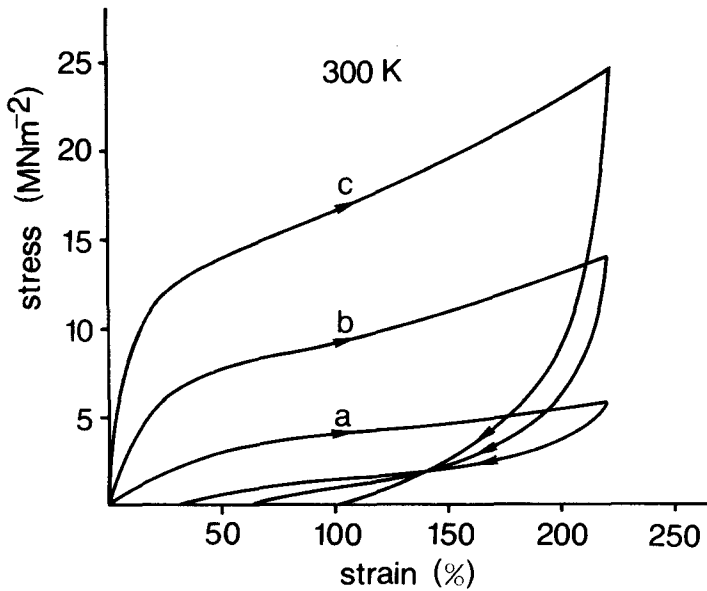


FIGURE 4 Stress-strain curves of loading-unloading cycles of the original and deuterated polyester urethane films with different hard and soft segment composition (see text) at 300 K.

The time dependence of the isotope exchange reaction can be monitored quantitatively by taking IR spectra of the polyester urethane film in regular time intervals during the deuteration progress (Fig. 2) and evaluating the integrated absorbance of the $\nu(\text{NH})$ absorption band with the aid of Eq. (1). The accessibility curves derived in this manner for the three different polyester urethanes are shown in Fig. 3. Principally, the curves can be separated into two portions. Thus, in the region of rapid exchange progress approximately 60% (a), 52% (b) and 42% (c) of the available NH-protons have been substituted by deuterium within 25 hours. At the slightly elevated deuteration temperature of 323 K no significant enhancement of accessibility due to phase mixing has to be taken into account. In analogy to the DSC data of these polyester urethanes (SIESLER 1983a) the different accessibility levels in Fig. 3 clearly demonstrate the improvement of phase separation with increasing hard segment content. Further experimental support of

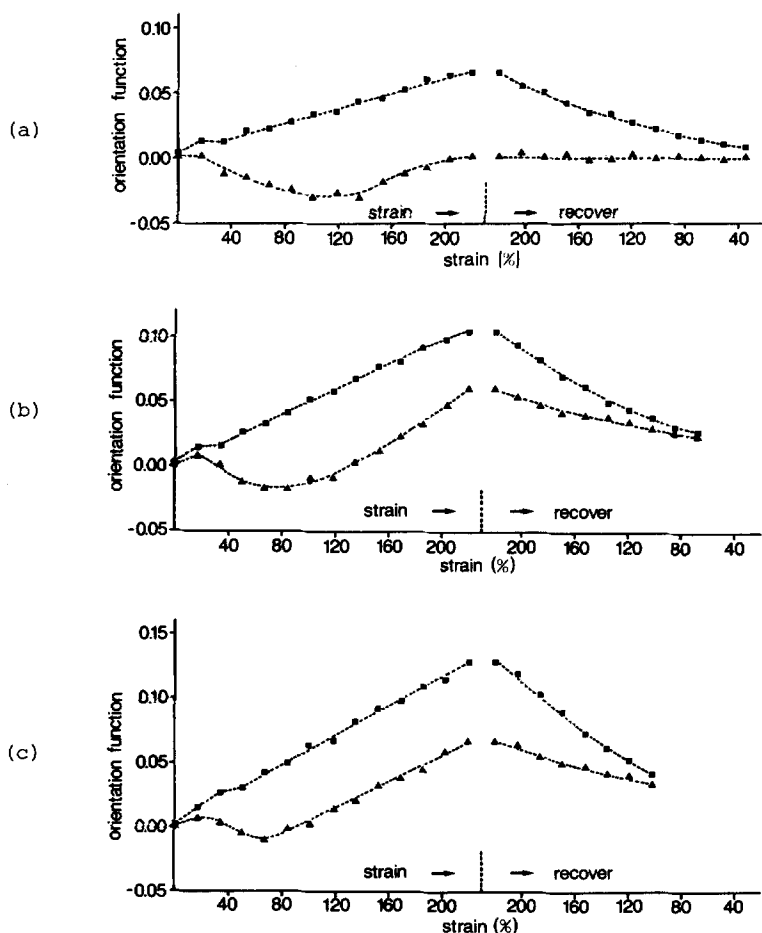


FIGURE 5 Orientation function-strain plot of the hard and soft segments of the deuterated polyester urethanes (a) - (c) as monitored by the $\nu(\text{NH})$ (▲) and $\nu(\text{CH}_2)$ (■) absorption bands, respectively, at 300 K (see text).

the above results can be drawn from deuteration experiments of the same polymers in the 200% drawn state which yield about 5-10% higher accessibility values. This increase of accessibility can be interpreted in terms of the disruption of large hard segment domains into smaller subunits during elongation.

The stress-strain diagrams of the deuterated samples measured at 300 K did not deviate significantly from the corresponding mechanical data of the original undeuterated specimens (Fig. 4).

The orientation functions of the hard and soft segments derived from the dichroism of the $\nu(\text{NH})$ and $\nu(\text{CH}_2)$ absorption bands, respectively, in the polarization spectra monitored during the loading-unloading cycles of the deuterated polyester urethanes at 300 K are shown in Fig. 5. Here, the $\nu(\text{NH})$ orientation function represents the orientation of the inaccessible hard segment domains. According to BONART'S model of segmental orientation in polyurethanes (BONART and HOFFMANN 1982) the pronounced transverse hard segment orientation observable in Fig. 5 is therefore fully consistent with the assignment of the involved urethane groups to phase-separated lamellar domains. As can be readily derived from Fig. 5 the negative orientation of the hard segments does not immediately start with the application of stress. This supports a structural model proposed by VAN BOGART et al. (1979) in which the hard segment domains are partly interconnected. Thus, the interconnections of such a hard segment network have to break up first before any transverse alignment can take place. The shift of the maximum negative orientation to higher strain values in the polymers with lower hard segment content [110% (a), 80% (b) and 70% (c)] is indicative of the delayed onset of the molecular-mechanical stress transfer owing to longer soft segments (BONART and MÜLLER-RIEDERER 1981). Generally, the orientation of the inaccessible hard segments induced during elongation to the maximum experimental strain of 220% has been found much smaller than the total average hard segment orientation of the undeuterated samples (SIESLER 1983). In fact, in the polyester urethane (a) with the lowest hard segment content the lamellar hard segments do not take on a positive orientation at all (Fig. 5). The deuteration technique, therefore, offers the possibility to differentiate the individual contributions to the average hard segment orientation.

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