Polymer Bulletin 9, 382-389 (1983)

Polymer Bulletin

Rheo-Optical Fourier Transform IR Spectroscopy of Polyurethane Elastomers

1. Principle of the Method and Measurements at Ambient Temperature

H.W. Siesler

Bayer AG, Werk Dormagen, Forschung und Entwicklung,
Postfach 1140, D-4047 Dormagen, Federal Republic of Germany

In memoriam Prof. Dr. Otto Bayer

SUMMARY

Rheo-optical FTIR spectroscopy has emerged as an extremely valuable tool to study deformation phenomena in polymeric solids. With the aid of a specially designed stretching apparatus short-time spectroscopic and mechanical data can be obtained simultaneously during the deformation and relaxation of polymers.

Polyurethanes are particularly suited to such investigations because they contain functional groups with characteristic IR absorptions which can be assigned to specific domain locations of the polymer.

Apart from a general introduction to the principle of the technique and its application to polyurethanes the data obtained with a series of three model polyester urethanes of different hard and soft segment content at ambient temperature are discussed in terms of the segmental orientation induced during uniaxial elongation and recovery.

INTRODUCTION

The mechanical properties of polymeric materials are of considerable importance for their engineering applications. In this respect the understanding of the molecular mechanisms involved in polymer deformation is a necessary prerequisite for a reasonable structure-morphology-property correlation.

An extremely powerful method for the study of transient phenomena in polymer deformation and relaxation is rheo-optics which describes the relation between stress, strain and an optical quantity (for example birefringence, IR absorption, light scattering or X-ray diffraction) measured simultaneously with stress and strain as a function of time (READ 1962, STEIN 1966, ONOGI and ASADA 1971). The advent of rapid-scanning FTIR systems has tremendously expanded the application of vibrational spectroscopy in the field of rheo-optics (SIESLER and HOLLAND-MORITZ 1980) and will certainly stimulate further progress in this research area.

EXPERIMENTAL

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

The electromechanical apparatus constructed for the simultaneous measurement of FTIR spectra and stress-strain diagrams during elongation, recovery and stress relaxation of polymer films is shown schematically in Fig. 1.

By exploiting the automated information processing capability of the dedicated computer in the FTIR system much of the routine analysis of spectra series as they are produced in rheo-optical measurements has been alleviated with the aid of specifically developed BASIC software (SCHLEMMER

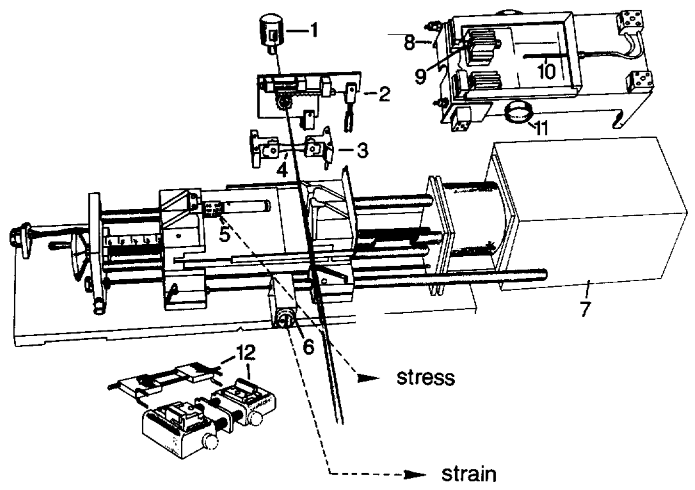

FIGURE 1 Film stretching machine: (1) FTIR detector, (2) pneumatic polarizer unit, (3) clamp, (4) polymer film sample, (5) stress transducer, (6) displacement transducer, (7) driving motor, (8) heating accessory, (9) cartridge heater, (10) temperature control, (11) KBr window, (12) specimen preparation and transfer device.

and SIESLER 1981). Thus, for the evaluation of the polarization measurements where a series of spectra are recorded alternately with light polarized parallel and perpendicular to the direction of elongation a program is applied which, based on the peak maximum or integrated intensity, automatically calculates the dichroic ratio or orientation function (in the case of well-defined transition moment directions) of specified absorption bands for each spectrum by appropriately correlating the successively measured intensity values. Upon data processing with this routine the individual values can subsequently be plotted as a function of strain.

The results have been obtained from a series of three polyester urethanes synthesized from diphenylmethane -4,4'-diisocyanate, a dihydroxy-terminated 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 soft segments of this type of polyurethane basically consist of the reaction products of the diisocyanate component and the macroglycol, whereas the hard segments contain largely aromatic and butane diol moieties linked together by urethane groups.

Films of the different polyester urethanes were prepared under identical conditions with a thickness of approximately 0.010 mm by casting from 2% w/v DMF solutions on surface-roughened glass plates and drying at 323 K in vacuum for 6 h. The film samples were then removed from the glass plates in hot water, boiled for 0.5 h and finally dried in vacuum at 323 K for 0.5 h. The densities of the different polyester urethanes as measured in a gradient column (carbontetrachloride/chlorobenzene) were 1.236 gcm^{-3} (a), 1.251 gcm^{-3} (b) and 1.257 gcm^{-3} (c), respectively.

In the mechanical treatment film specimens of 12 mm length and 10 mm width were elongated at a draw rate of 1.2% strain/s to 220% strain and then unloaded at the same rate to zero stress and 12-scan spectra were

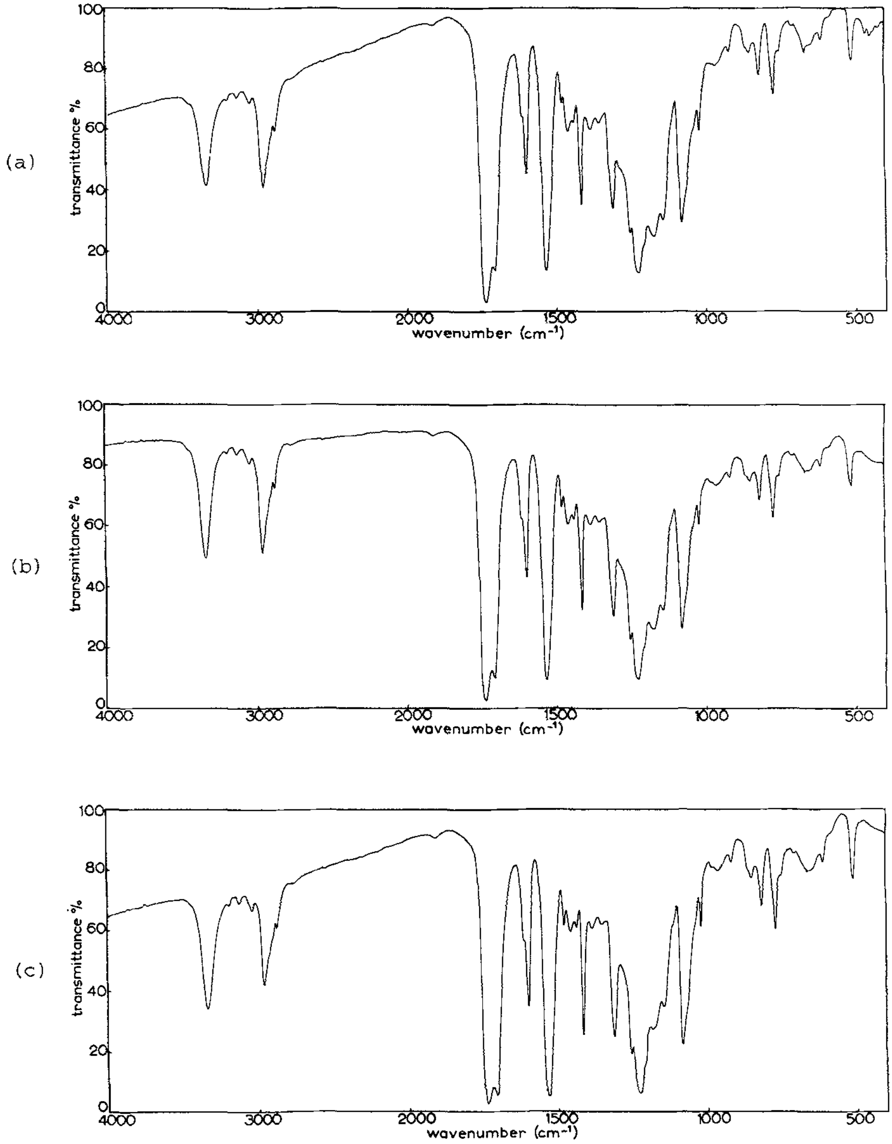

FIGURE 2 IR spectra of the investigated polyester urethane films based on different polyester:chain extender:diisocyanate molar ratios:
(a) 1.0:2.2:3.4, (b) 1.0:5.4:6.6, (c) 1.0:7.5:8.7.

taken in 14-seconds intervals at a resolution of 2 cm^{-1}.

From DSC measurements the hard segments were found to melt in dependence of the composition in the temperature range from 400 K to 490 K and the corresponding heats of melting increased with hard segment content from 4.8 Jg^{-1} (a) to 7.9 Jg^{-1} (b) and 13.7 Jg^{-1} (c).

In the wide-angle X-ray diagrams only for the polyester urethane (c) with the largest hard segment content the Bragg reflection at about 0.75 nm (BONART et al. 1974, BLACKWELL et al. 1981) could be detected apart from the intense amorphous halo at about 0.45 nm. Furthermore, no strain-induced crystallinity of the soft segments was observed in the 200% elongated samples.

RESULTS AND DISCUSSION

The IR spectra of the investigated polyester urethanes are shown in Fig. 2. On the basis of the established frequency correlations for the functional groups of polyurethanes (ISHIHARA et al. 1974) the extent of hard and soft segment orientation can be monitored by means of the polarization properties of the ν(NH) (3331 cm^{-1}) and $\nu(CH_2)$ (2959 cm^{-1}) absorption bands, respectively. The transition moment angles for both vibrations have been taken as 90^o although it is recognized that some deviation of this value may occur for the $\nu(CH_2)$ stretching vibration due to superposition with the corresponding wagging mode. Under these assumptions the orientation functions for the hard and soft segments (FRASER 1956) read:

$$f = -2 \cdot \frac{(R-1)}{(R+2)} \qquad (1)$$

where $R = A_{\parallel}/A_{\perp}$ is the experimentally determined dichroic ratio of the ν(NH) and $\nu(CH_2)$ absorption bands, respectively. Generally, for perfect parallel chain alignment f is 1, for perpendicular alignment f is -1/2 and for random orientation f becomes zero. In view of the hard segment crystal structure proposed by BLACKWELL et al. (1981), however, the maximum value to be expected for the ν(NH) orientation function of the hard segments is only about 0.65. Furthermore it should be kept in mind that the intensity contributions of the $\nu(CH_2)$ absorption bands of the chain extender and the diphenylmethane functionality increasingly contribute to the $\nu(CH_2)$ absorption intensity of the soft segments in the sequence polyester urethane (a) to (c). Nevertheless, the principal differences of hard and soft segment orientation can be readily derived from the spectroscopic data.

The close relation between the composition and the mechanical properties of these polymers is reflected in the stress-strain diagrams measured at 300 K (Fig. 3). Hence, for the specified experimental conditions a distinct increase of initial modulus (11, 45 and 120 MNm^{-2}), stress-hysteresis (ratio of area bounded by a strain cycle to the total area underneath the elongation curve: 60, 80 and 90%), and extension set (30, 65 and 100%) can be observed with increasing hard segment content for the polyester urethanes (a) to (c).

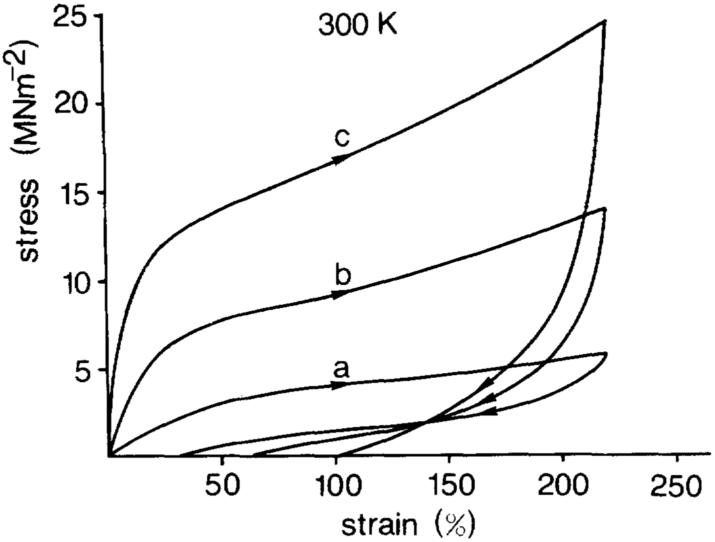

FIGURE 3 Stress-strain diagrams of the loading-unloading cycles of the investigated polyester urethane films with different hard and soft segment composition (see text) at 300 K.

The segmental structure of polyurethanes becomes apparent from Fig. 4 which shows the linear polymer primary chains made up of alternating hard and soft segments. However, in the solid polymer the primary chains do not really exist separately but rather the hard segments tend to associate with each other through hydrogen bonding and aromatic π-electron attraction. As a consequence, the hard segments form domains in the mobile soft segment matrix and a two-phase system results. The separate hard segment domains effectively crosslink the primary chains and produce a network which accounts for the elastic character of the polymer. These virtual crosslinks can be reversibly overcome by heat or solvation whereupon the polymer primary chains are more or less regenerated. Numerous studies are available on the segmental structure of polyurethanes particularly the hard segment domains (BONART et al. 1974, BLACKWELL et al. 1981, BORN et al. 1982) which might be expected to be crystalline but do not appear to be by conventional crystallinity tests. It seems that the strong mutual attraction of the hard segments restricts their ability to readily organize themselves into a crystalline lattice. In this respect primarily small-angle X-ray scattering (WILKES and YUSEK 1973) and electron microscopy (FRIDMAN and THOMAS 1980) have contributed to a better knowledge of the size, order and separation of these domains.

Recently, BONART and HOFFMANN (1982) have shown that the extent of orientation of the hard segment phase during elongation depends on the morphology of the hard segment domains and the interrelationship of two deformation mechanisms based on a morphological and a molecular level. As long as the chains of the soft segments are randomly coiled the matrix can be regarded as a continuum and the hard segment domains will be oriented by a continuum mechanical transfer of stress with their long axis dimension into the direction of stretch. Therefore, small, fibrillar hard segments in which the long axis dimension coincides with the polymer chain axes (see Fig. 4, F) will take up a positive orientation while lamellar domains with their long axis dimension perpendicular to the polymer chain axes (see Fig. 4, L) will be negatively oriented. This deformation mechanism dominates at low strains up to about 150% strain and the strain value of the maximum negative orientation depends on the stability of the lamellar morphology and the length of the soft segments. With increasing exten-

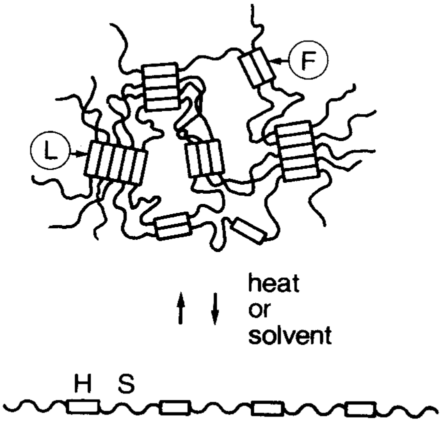

FIGURE 4 Schematic of phase separation in a polyurethane elastomer: H hard segments, S soft segments; F fibrillar hard segments, L lamellar hard segments.

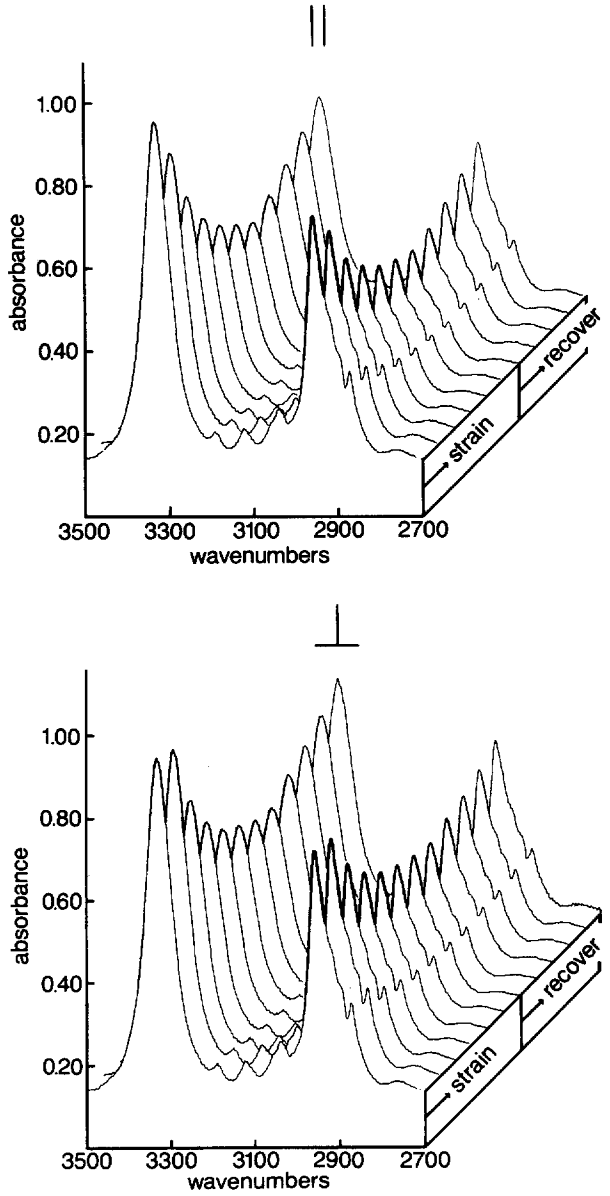

FIGURE 5 FTIR spectra of polyester urethane (c) in the ν(NH) and ν(CH_2) stretching vibration region recorded at 300 K during uniaxial elongation to 220% strain and subsequent recovery to zero stress with radiation polarized alternately parallel and perpendicular to the direction of stretch.

sion of the soft segments a molecular transfer of stress by individual chains becomes operative. For lamellar hard segment domains this mechanism leads to a disruption of the initially transversely oriented structural units with a subsequent positive orientation of the fragments into the direction of stretch. In the case of fibrillar hard segments continuum and molecular mechanical stress transfer both contribute to a positive alignment of the polymer chains.

To illustrate the dichroic effects the polarization spectra taken during a loading-unloading cycle of polyester urethane (c) at 300 K in the 3500 - 2700 cm^{-1} wavenumber region are shown in a threedimensional representation in Fig. 5. In Fig. 6 the corresponding orientation functions of the ν(NH) and $\nu(CH_2)$ absorption bands have been plotted for the investigated polyester urethanes versus strain. Despite the comparatively low values of these orientation functions (see above) distinct differences between the hard and soft segment orientation, respectively, can be derived both during elongation as well as recovery with increasing hard segment content. Generally, up to the maximum elongation of 220% strain the soft segments

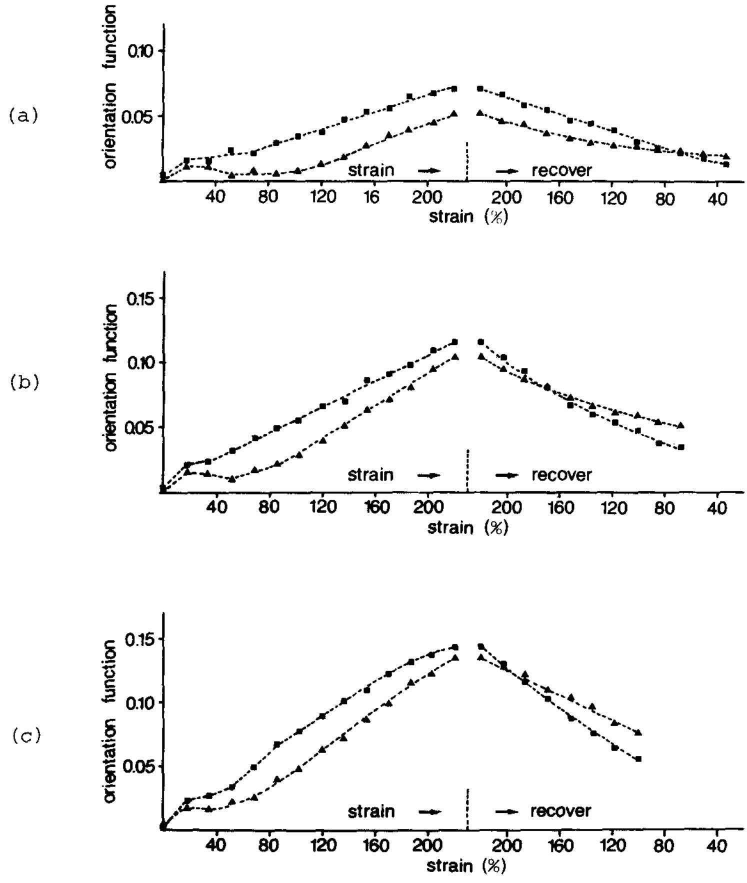

FIGURE 6 Orientation function-strain plot of the hard and soft segments of the polyester urethanes (a) - (c) as monitored by the ν(NH) (▲) and $\nu(CH_2)$ (■) absorption bands, respectively, at 300 K.

exhibit a better average alignment in the direction of stretch than the hard segments. Additionally, the soft segments directly respond to the application of stress with an almost linear increase in positive chain orientation as a function of strain. In contrast, an initial strain interval with orientation function values in the vicinity of zero is observed for the hard segments before the onset of significant positive orientation. This difference can be explained in terms of the abovementioned antagonism of lamellar hard segment alignment during elongation. In this region obviously the positive orientation of small fibrillar hard segments is compensated by the negative orientation of lamellar hard segment domains. The shift in the onset of significant positive orientation to higher strain values for increasing soft segment content (polyester urethane (c) to (a)) is an indication of the corresponding increase in soft segment length.

Upon recovery to zero stress the orientation is more effectively retained by the hard segments. This phenomenon may be attributed to the entropy-driven relaxation and flow of the soft chain segments during unloading. As the soft segments relax they exert a tension on the hard segments thereby imposing an additional barrier to their recovery. The larger amount of this residual orientation for increasing hard segment proportion is the consequence of a more extensive disruption of the hard segments during elongation and their reorganization during recovery.

Further experimental evidence of the aforementioned structural changes occurring during elongation and recovery in this class of polymers will be reported in subsequent papers on rheo-optical FTIR investigations of NH-deuterated specimens and studies at elevated temperature.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the experimental assistance of H. Devrient, H. P. Schlemmer and W. Schmitt and helpful discussions and the supply of the model polyester urethanes from Dr. H. Hespe. The author also thanks Bayer AG for the permission to publish the experimental data.

REFERENCES

B. E. READ: Polymer 3, 143 (1962).
R. S. STEIN: J. Polym. Sci. C15, 185 (1966).
S. ONOGI, and T. ASADA: Progr. Polym. Sci. Jap. 2, 261 (1971).
H. W. SIESLER, and K. HOLLAND-MORITZ: Infrared and Raman Spectroscopy of Polymers, Marcel Dekker, New York, 1980.
H. P. SCHLEMMER, and H. W. SIESLER: unpublished data, 1981.
R. J. BONART, L. MORBITZER, and E. H. MÜLLER: J. Macromol. Sci. Phys. B9, 447 (1974).
J. BLACKWELL, M. R. NAGARAJAN, and T. B. HOITINK: Polymer 22, 1534 (1981).
H. ISHIHARA, I. KIMURA, K. SAITO, and H. ONO: J. Macromol. Sci. Phys. B10, 591 (1974).
L. BORN, H. HESPE, J. CRONE, and K. H. WOLF: Colloid & Polym. Sci. 260, 819 (1982).
C. E. WILKES, and C. S. YUSEK: J. Macromol. Sci. Phys. B7, 157 (1973).
I. D. FRIDMAN, and E. L. THOMAS: Polymer 21, 388 (1980).
R. BONART, and K. HOFFMANN: Colloid & Polym. Sci. 260, 268 (1982).

Received January 7, accepted January 13, 1983 C