Segmental Orientation Studies of Block Polymers. I. Hydrogen-Bonded Polyurethanes

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ABSTRACT: Differential infrared dichroism was used to study the orientation behavior of a series of elastomeric polyurethane block copolymers. The orientation of hard and soft segments was studied under uniaxial extension, as a function of time and temperature, and in cyclical deformation experiments. The mode of hard segment orientation was found to be a function primarily of hard segment length. Three distinct mechanisms were found, depending on a large scale whether or not the hard domains are interlocking and on the molecular level whether the aromatic urethane segments were amorphous or partially crystalline in internal order. Soft segment orientation is little affected by changes in polymer composition. Advantages of the differential method over conventional dichroism studies are discussed and illustrated.

The question of structure-property relationships in block polymer systems has received considerable attention in recent years, owing in part to the unusual morphologies and mechanical properties exhibited by these materials. An important class of block polymers is the segmented polyurethanes which are composed of incompatible segments having glass transition temperatures above and below the use temperature. The segments above their glass temperature are designated the soft segments; those below T_g, the hard segments. The soft segments are generally polyethers or polyesters, 1000–5000 in molecular weight, while the hard segments are formed from the extension of an aromatic diisocyanate with a low molecular weight diol.

The existence of microphase separation, caused by clustering of at least some of the hard and soft segments into separate domains, has been well established. The mechanical properties of these materials reflect their heterophase nature and are characterized by an enhanced rubbery modulus and a rubber-like stress–strain response.[1] Recently it has been established that the hard segment domains may contain short- and/or long-range segmental ordering, depending on the block length and thermal history.[2] The soft segments are generally noncrystalline, except at the higher molecular weights.[3]

The orientation behavior of urethane and urethane–urea block polymers under uniaxial extension has been studied by X-ray diffraction and infrared dichroism. Orientation studies of Bonart and coworkers[4,5] were concerned with the morphology and orientation response of polyurethanes and urea–urethanes with polyether or polyester soft segments. The soft segments were found to orient into the direction of stretch, with strain-induced crystallization beginning at about 150% elongation. Polyether (poly(tetrahydrofuran)) soft segments showed true crystallization, while only paracrystallization was observed in mixed polyester soft segments.[4]

Hard segment behavior was somewhat more complex. Using a weak X-ray interference at 12 Å which was identified with a particular short-range order brought about by a specific arrangement of hydrogen bonds, Bonart followed hard segment orientation as a function of strain. The aromatic urethane segments were found to orient perpendicular to the direction of stretch at elongations below about 200%. Further stretching moves the X-ray reflection to the meridian, indicating that the hard segments are then orienting into the direction of stretch. A model of hard segment domains in a soft segment matrix was proposed to account for this behavior. The soft segments are envisioned as being stretched initially to different extents depending on their position within the material, giving rise to local torques which twist the hard segments preferentially transverse to the direction of the applied load. Further elongation causes the hard segments to slip past one another, breaking up the original structure. The hard segments then become increasingly oriented into the direction of stretch.

Further studies with polymers of longer segment length[5] showed the existence of both crystallized and "paracrystallized" hard segments. While suitable thermal treatment may induce true crystallization in a "paracrystalline" sample, this process does not involve a simple reordering within the original domain structure. Rather, small-angle X-ray scattering indicates[5] that a change in form and spatial arrangement of the domains accompanies the crystallization process. Bonart also distinguishes between the behavior of crystalline and paracrystalline hard segments in the orientation process. Paracrystalline segments behave as previously described, showing two distinct mechanisms. The crystalline segments apparently do not contribute to this process, however, and they are described as reacting more as an inert filler. This conclusion regarding the crystallized hard segments is based on the fact that the corresponding X-ray reflection orients preferentially orthogonal to the stretch direction, even at high elongations.

A similar set of experiments on a different series of urea–urethanes has been reported by Kimura *et al.*,[6] who used both infrared dichroism and X-ray techniques. The dichroic behavior of the absorption band due to the C=O group showed hard segment orientation initially transverse to the stretch direction, crossing over to parallel with increasing elongation. The amount of transverse orientation decreased with decreasing soft segment length or increasing temperature, so that a polymer with a soft segment of mol wt 500 shows only parallel hard segment orientation at room temperature. Soft segments were found to orient into the direction of stretch at all times.

An X-ray reflection at a spacing of 4.4 Å with an orientation behavior similar to that observed for the C=O vibration in infrared dichroism was found[6] and assigned to the lattice dimension in the direction of hydrogen bonding. The model developed to explain the observations is similar to Bonart's. The direction of hydrogen bonding is

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(1) G. M. Estes, S. L. Cooper, and A. V. Tobolsky, *J. Macromol. Sci., Rev. Macromol. Chem.*, 4, 167 (1970).

(2) R. W. Seymour and S. L. Cooper, *Macromolecules*, 6, 48 (1973).

(3) D. S. Huh and S. L. Cooper, *Polym. Eng. Sci.*, 11, 369 (1971).

(4) R. Bonart, *J. Macromol. Sci., Phys.*, 2, 115 (1968).

(5) R. Bonart, L. Morbitzer, and G. Hentze, *J. Macromol. Sci., Phys.*, 3, (2), 337 (1969).

(6) I. Kimura, H. Ishihara, H. Ono, N. Yoshihara, and H. Kawai, *XXIII IUPAC Prepr.*, 525 (1971).

thought to orient into the stretch direction at low elongations (giving rise to transverse orientation of the hard segments themselves). Further elongation disrupts the hard segment crystallites, allowing the segments to orient into the stretch direction.

Infrared dichroism of oriented polyether and polyester urethanes with a soft segment molecular weight of 1000 has been studied by Estes.[7] He found no evidence for transverse orientation, with both segments orienting similarly into the direction of stretch. The absence of hard segment transverse orientation may be due to the shorter hard segment length compared to the polymers studied by Bonart and Kimura. On removal of the load the soft segments relaxed almost completely within 5 min, whereas the hard segments retained a significant degree of orientation. The residual orientation in the hard segment coupled with plastic deformation of the domains was suggested as the cause of the stress softening observed in these systems.

Estes found that the molecular orientation at a given strain level passes through a maximum as a function of temperature. This was attributed to an initial increase in ordering due to a softening of the domains, followed by their disruption with further temperature increase. The temperature at which this maximum occurs appears to be near the hard segment T_g. Kimura[6] also found that segment orientability increased going from 20 to 80°, but insufficient tests were run to define whether a maximum appeared.

The materials studied by these various groups of workers differ significantly in such important variables as chemical constitution and segment length, making comprehensive conclusions about the morphology and orientation behavior difficult. In general, however, the hard blocks may be envisioned as separating more or less completely into segregated regions, or domains, with varying degrees of internal order. The short lengths of the alternating hard and soft segments restrict the growth of these regions in the direction of the chain axis, so that formation of a lamellar structure having a long dimension perpendicular to the local chain axis is favored. The orientation behavior of the hard segments is apparently dependent on the type of ordering within the hard domains, though the exact role and origin of the influence of domain morphology and ordering is unclear.

The purpose of the work reported here is to provide a systematic study of orientation as a function of composition and segment length using the technique of infrared dichroism.

Experimental Section

A. Materials. The materials used in this study were a series of polyether and polyester urethane block polymers prepared by the B. F. Goodrich Chemical Co. The polyether segment was poly(tetrahydrofuran) and the polyester, poly(butylene adipate). The hard block was formed from the extension of *p,p'*-diphenylmethane diisocyanate (MDI) with 1,4-butanediol.

Composition and block lengths have been varied in two ways. First, a series of materials with diisocyanate contents varying between 24 and 38 wt % have been prepared. In this series, the soft block length is held constant while the average hard block length is increased by increasing the MDI and butanediol content. The second set of materials has a constant overall composition of 38 wt % MDI but varies both hard and soft block lengths. This is done by using higher molecular weight soft segments. Polyester soft segments of mol wt 1000, 2000, and 5000 have been used; polyether molecular weight was either 1000 or 2000. A more complete chemical characterization of the materials studied has been published previously.[3,7] These materials are referenced in this paper by the soft segment type, ES (polyester) or ET (polyether), weight per cent diisocyanate and soft segment molecular weight in thousands by a code such as ES-38-1.

Samples were prepared for dichroic measurements by casting from a 0.75% solution onto a clean mercury surface. Solvents were tetrahydrofuran (for materials with 1000 molecular weight soft segments) or pyridine (all materials with higher molecular weight soft segments). Solvent was successfully removed by vacuum drying the samples.

B. Differential Infrared Dichroism. The use of infrared dichroism involves orienting a sample and measuring the absorbance of selected bands with radiation polarized parallel and perpendicular to the orientation direction. If the transition moment vector of a particular vibration has been preferentially aligned, the two absorbances ($A_\parallel$ and $A_\perp$) will not be equal and the dichroic ratio, $D = A_\parallel/A_\perp$, may be calculated. The dichroic ratio can be related to an orientation function, f, through eq 1. D_0 is

$$f = [(D_0 + 2)/(D_0 - 1)][(D - 1)/(D + 2)] \tag{1}$$

the dichroic ratio for perfect alignment and is equal to 2 cot^2 α, where α is the angle between the transition moment vector for the vibration and the local chain axis. The function f as defined in eq 1 may be related to an average angle of disorientation θ, by

$$f = [3\overline{\cos^2\theta} - 1]/2 \tag{2}$$

The maximum value of the function f is unity, corresponding to perfect axial orientation into the stretch direction. $f = 0$ in the absence of orientation and $f = -(1/2)$ for perfect orientation transverse to the stretch direction. Implicit in the use of this orientation function is the assumption that the uniaxial model is sufficient to represent the state of orientation.

The most common and straightforward technique used in measuring dichroic effects is to record two spectra of the oriented polymer, one with the beam polarized parallel to the stretch direction and one perpendicular. The ratio of the absorbances obtained for a given band from these two experiments defines the dichroic ratio from which the orientation function of eq 2 can be calculated. A schematic of the experimental set up used to measure dichroism in this way is shown in Figure 1A. A conventional double-beam spectrophotometer is employed, with a single polarizer in the common beam. In practice the polarizer is set at 45° to the slit direction to minimize machine polarization effects. Two spectra are run with the sample at ±45°.

An alternative double-beam double polarizer arrangement has been described by Gotoh[8] and is shown schematically in Figure 1B. Two polarizers (at ±45° to the slits) are used, so that the chopped common beam going to the monochromator contains both $A_\parallel$ and $A_\perp$ information. The quantity recorded is the dichroic difference, $A_\perp - A_\parallel$. Thus the output for an unoriented sample will be a straight line, while orientation of any vibration will result in an upward or downward peak depending on the relactive magnitudes of $A_\parallel$ and $A_\perp$.

The dichroic difference is related to f, the orientation function through eq 3. A_0 is the absorbance of the peak in the unstretched specimen and d/d_0 the stretched to unstretched thickness ratio. In practice, this was calculated from the length ratio assuming constant volume deformation.

$$f = [(D_0 + 2)/(D_0 - 1)][(A_\parallel - A_\perp)/3A_0(d/d_0)] \tag{3}$$

The differential method for measuring dichroism is much more accurate than the conventional method. A quantitative comparison of the two techniques has recently been published by Read.[9]

In the present work a Perkin-Elmer Model 180 infrared spectrophotometer has been used. The sample was placed at an intermediate focus in the source beam before splitting at an angle of 45° to the slits. Wire grid polarizers were placed in the sample and reference beams at a setting of 45°. This results in a crossed polarizer configuration because of an unequal number of beam reflections between the source and polarizer location in the two beams. The 45° setting was chosen to minimize machine polarization effects. In this configuration, the recorded output is the dichroic difference $A_\perp - A_\parallel$.

Data were recorded in linear absorbance using programmed

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[7] G. M. Estes, R. W. Seymour, and S. L. Cooper, *Macromolecules*, **4**, 452 (1971).

[8] R. Gotoh, T. Takenaka, and N. Hayama, *Kolloid-Z. Z. Polym.*, **205**, 18 (1965).

[9] B. E. Read, D. A. Hughes, D. C. Barnes, and F. W. M. Drury, *Polymer*, **13**, 485 (1972).

slits and automatic gain control. The slit program was set for 1 mm at 3550 cm^{-1}. Most data were recorded using 5× ordinate expansion and a time constant setting of three. Sample stretching was accomplished in a jig designed to elongate the specimen from both ends simultaneously. Strain was measured using bench marks.

Orientation of the soft segment has been followed using the asymmetric CH_2 stretch vibration. This group resides primarily in the soft segment.[7] Hard block orientation has been characterized by the NH group, located entirely in the hard segment. In addition, orientation of the carbonyl group of the urethane linkage has been studied in polyether urethanes. This band is clearly split into free and hydrogen-bonded components.[10]

Orientation function-strain curves were generated by sequentially straining a single sample. Sufficient time was allowed between application of the strain and measurement of the spectrum for the orientation to reach a constant value. The time required varied with diisocyanate content and block length, the maximum being about 30 min for a 50% strain increment in the lowest diisocyanate content materials. Orientation as a function of time at fixed elongation was obtained with a special stretching device which allowed rapid straining to a predetermined level. Time dependence of the orientation was measured by setting the monochromator at the peak frequency of the absorption band of interest and recording as a function of time.

Heating of the samples was accomplished in an environmental chamber having a temperature control of ±0.5°. Temperature was measured with a thermocouple at the sample surface.

Baselines for unoriented samples were drawn according to the recommendations of Estes.[11] A single base line through the NH and CH regions was generally used for the differential spectra. In calculating orientation functions, transition moment directions of 90° were assumed for the NH and CH vibrations and 79° for the carbonyl.

Results and Discussion

Three basic types of experiments have been performed. The first is simple uniaxial extension, where a sample is strained to successively higher elongations and the orientation function measured at given strain intervals. The result is a plot of orientation function *vs.* elongation. These experiments have been performed on materials of all compositions, including some at elevated temperatures.

The second set of experiments measures the orientation as a function of time at fixed elongation. These have been performed on selected materials at ambient temperatures.

Third, some work has been performed using cyclical strain histories. This gives the orientation function-elongation plot for samples under specified prestrain conditions. Such data allows investigation of the phenomenon of orientational hysteresis.

A. Orientation-Elongation Studies. The lowest diisocyanate content material studied was ET-24-1, in which the hard blocks average only slightly greater than one MDI unit in length.[3] This material is mechanically quite soft and exhibited the orientation function-elongation curves for the NH, CH_2, and free and bonded carbonyl groups shown in Figure 2. Orientation in the hard block may be slightly higher than that in the soft, though it is extremely low in both. This results from the fact that most of the molecular alignment induced by the deformation process is able to relax during the time scale of the test. The lower level of mechanical properties and orientability of ET-24-1 may be ascribed to the inability of this material to form an interlocking domain structure. A more detailed description of this situation may be found elsewhere.[12]

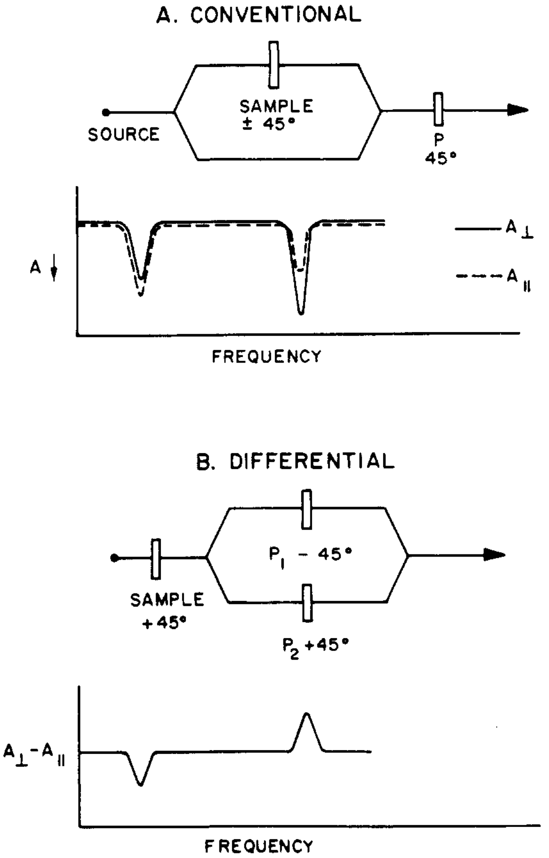

Figure 1. Dichroism measurements: (A) conventional, (B) differential.

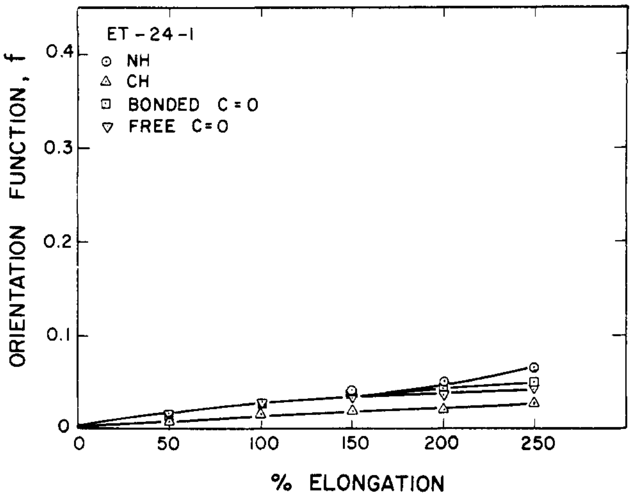

Figure 2. Orientation function-elongation curves for ET-24-1.

A significant change in orientation behavior is seen on raising the MDI content to 28%. Orientation function-elongation curves for ET-28-1 are shown in Figure 3. Overall there is a much higher degree of orientation and a much greater distinction between the behavior of the NH and CH_2 groups. This suggests an important change in morphology occurs on going from 24 to 28% MDI.

While some orientation of the flexible soft segment relaxes, resulting in a comparatively low value of the C—H orientation function, much more orientation is held in the hard blocks (bonded C=O and NH curves).

An interesting difference is also seen in comparing the free and bonded carbonyl groups. The bonded C=O are associated with other hard segments and thus are representative of the behavior of the segments within the domains. Free carbonyl, on the other hand, could exist in either of two situations. It may be located at a domain in-

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(10) R. W. Seymour, G. M. Estes, and S. L. Cooper, *Macromolecules*, 3, 579 (1970).

(11) G. M. Estes, Ph.D. Dissertation, Department of Chemical Engineering, University of Wisconsin, 1970.

(12) R. W. Seymour, Ph.D. Dissertation, Department of Chemical Engineering, University of Wisconsin, 1973.

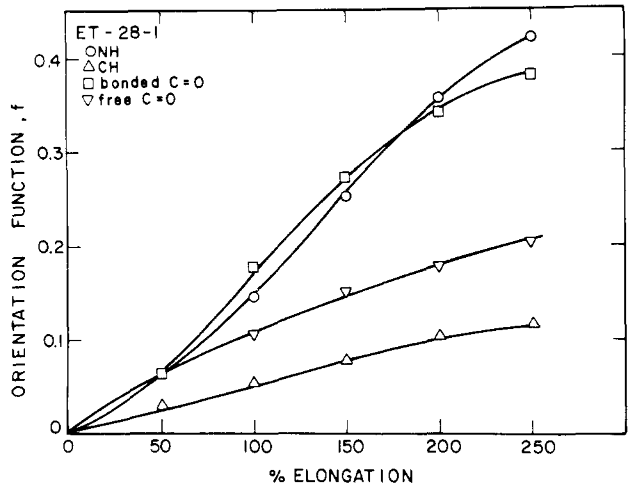

Figure 3. Orientation function-elongation curves for ET-28-1.

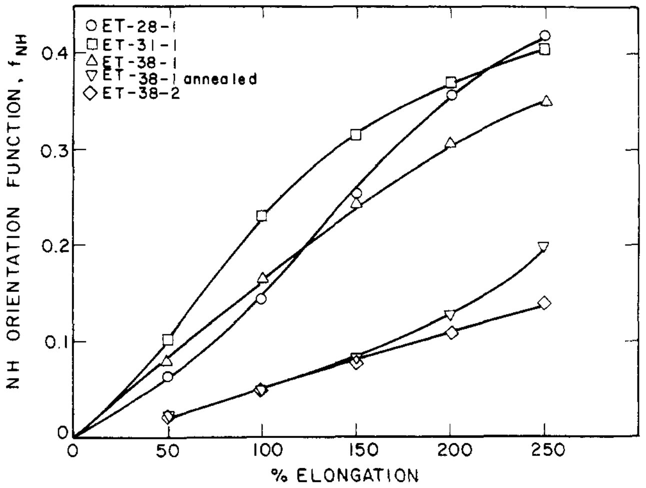

Figure 4. NH orientation functions for the ET series.

terface, where its degree of orientation would be expected to be at most comparable to that of the hard segments within the domain. Alternatively, a free C=O group can arise when the hard segment to which it is attached is dispersed in a soft segment region. Under these conditions, it should orient more like the CH_2 group. A combination of these effects could produce the observed orientation level intermediate between those for the bonded C=O and CH_2 groups.

The hard segment orientation behavior shown in Figure 3 is characteristic of materials with compositions between ET-28-1 and ET-38-1, there being only minor differences among them. This behavior is summarized in Figure 4, where the NH orientation function curves for ET-28-1, ET-31-1, and ET-38-1 all lie within the same band. The DSC curves for these materials show that only short range hard segment order is present.[2]

Introducing microcrystallinity into the hard block distinctly changes the orientation behavior. DSC[2] and X-ray diffraction[3] show that the materials whose NH orientation functions fall into the lower band on Figure 4 contain microcrystalline hard segments. ET-38-2 is normally crystalline and crystallinity may be introduced into ET-38-1 by prolonged annealing at 150°.[2,13]

No f values are shown at very low strains (below 100% in ET-38-2 and 50% in annealed ET-38-1) as the differential dichroic spectra show that two types of orientation are present at these strain levels. Some representative raw data for ET-38-2 are shown in Figure 5. The dichroic difference $A_\perp - A_\parallel$ at low strain levels is shown for the NH and C=O stretching regions in this figure. Owing to the transition moment directions, upward deviation from the base line corresponds to positive values of the orientation function, *i.e.*, orientation of the segments into the stretch direction. It can be seen that the NH and bonded C=O peaks contain both positively and negatively orienting components, while the free C=O shows only an upward peak. The splitting decreases with increasing strain, until at 100% elongation only positive orientation is observed. The CH_2 region orients positively at all elongations, as did all groups in materials with noncrystalline hard segments. Also shown in Figure 5 are the values of the dichroic ratio D which were measured with the conventional single polarizer technique. The value of $D = 1$ at 25% elongation indicates that the conventional measurement would lead to the conclusion that there is no orientation. In actuality there are both positively and negatively orienting structures whose differing optical anisotropies are not detected by the conventional dichroism measurement.

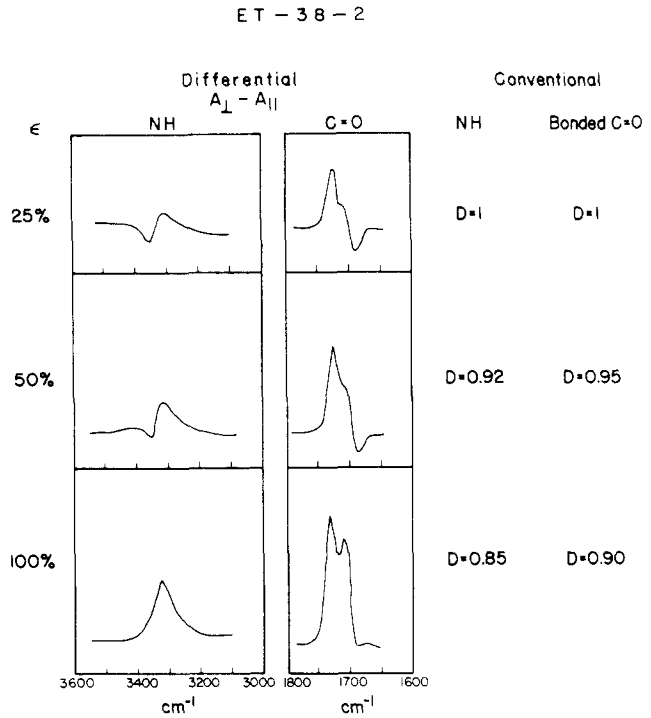

Figure 5. Low strain dichroism of ET-38-2.

The peak splitting observed in the NH and bonded C=O regions is observed only in samples with partially crystalline hard segments. By analogy with the data already discussed, the noncrystallized hard segments may be expected to orient positively, implying that it is the crystallized hard segments which are orienting negatively. Such a result may be explained on the basis of the generally accepted morphological models[4-7] which envision lamellar domains whose thickness is determined by the hard segment length. The long direction of the domain is perpendicular to the hard segment backbone. The observed transverse orientation of the hard segment backbone direction thus implies that, at low elongations, the long axis of the crystalline domain is turning into the stretch direction.

Orientation functions for the NH and bonded carbonyl regions have been calculated only when purely positive orientation is observed. f values that would be calculated for the split peaks are of doubtful value, as it is not clear

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(13) R. W. Seymour and S. L. Cooper, *J. Polym. Sci., Part B*, 9, 689 (1971).

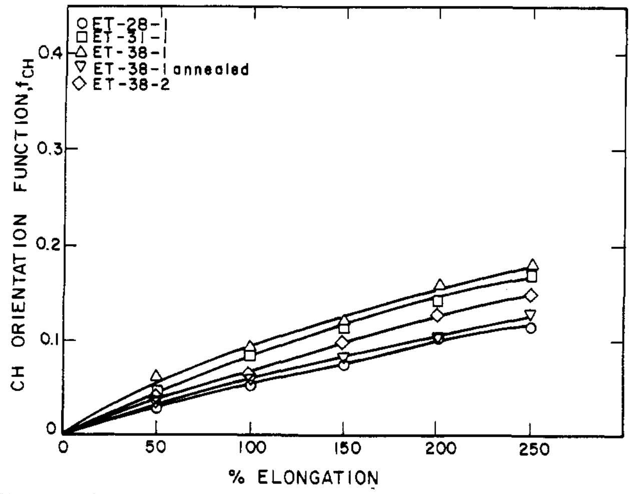

Figure 6. CH orientation functions for the ET series.

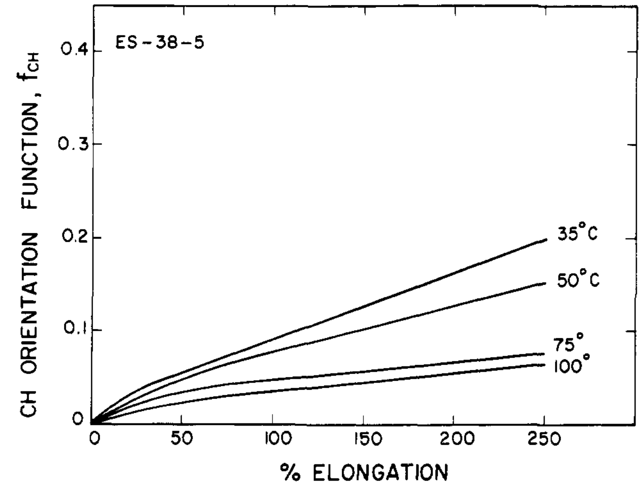

Figure 7. CH orientation functions *vs.* elongation at elevated temperatures for ES-38-5.

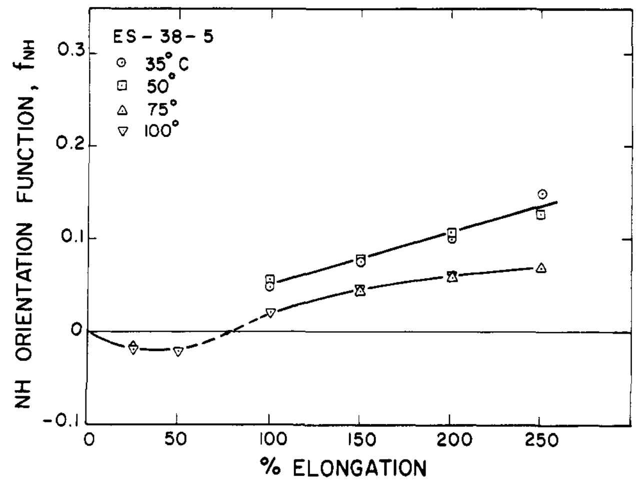

Figure 8. NH orientation functions *vs.* elongation at elevated temperatures for ES-38-5.

that the peak absorbance is a true measure of the maximum. It may be noted that the NH and bonded carbonyl orientation functions are significantly lower than those observed in the samples discussed previously.

As can be seen in Figure 5 by 100% elongation no negative peak can be detected. This does not mean that the crystalline domains have been totally disrupted. If the crystalline regions were totally disrupted and oriented, one would expect the hard segment f values to be equivalent to those of the noncrystalline polyurethanes. Since this does not occur, it is probable that the crystalline domains are not completely disrupted until higher strain levels than were used in this investigation.

The ir dichroism results indicate that the crystalline hard segments do not orient in the same manner as the noncrystalline hard segments. Rather, the orientation of the crystalline regions occurs in two steps. Initially the long axis of the crystalline domain orients into the stretch direction, resulting in a transverse segment orientation. The crystalline regions gradually break up with increasing strain and the segments then begin to orient into the stretch direction. The initial transverse orientation, which may be partially retained even at higher elongations, serves to lower the overall value of the orientation function.

Figure 6 summarizes the CH orientation functions for the ET series. From this figure it may be concluded that the soft segment orientation is relatively insensitive to polymer composition. Hard segment orientation functions, on the other hand, fall into two bands, depending on whether the hard segments have crystallized (Figure 4).

B. Temperature Studies. Estes found that the NH orientation function at 200% strain passed through a maximum as a function of temperature for ET-38-1 and ES-38-1.[7] The temperature of the maximum was about 90°. The CH orientation function showed either a peak or a greater rate of decrease above 90°.

The effect of segment length, and thus block crystallinity, on the temperature dependence of the orientation function has been studied by examining ES-38-2 and ES-38-5 at elevated temperatures. The results for ES-38-2, a material of low crystallinity, are similar to those reported by Estes for ES-38-1. The soft segment orientation decreases and the NH orientation passes through a maximum as the temperature is raised. The temperature of the maximum lies between 75 and 100°, as reported for ES-38-1. This maximum in orientability occurs near the glass transition temperature of the hard segments.[2] Near T_g the segments are more easily deformed by the strain and orient more completely into the stretch direction. As the temperature is raised above T_g the amorphous portions of the hard segments can relax after orientation assuming a more random configuration. The level of orientation thus decreases with increasing temperature above T_g. It is also interesting to note that purely positive NH orientation is obtained at the elevated temperatures, whereas a negative-positive split (similar to that shown for ET-38-2) was observed at ambient conditions and low elongations. It appears that at elevated temperatures the small hard segment crystallites in this material are easily disrupted by the force exerted by the positively orienting soft segments.

ES-38-5, a material of relatively high crystallinity, behaves quite differently (Figures 7 and 8). The CH orientation decreases markedly around 50° (Figure 7). This corresponds to the melting point of the soft segments noted in this material with DSC.[3] The overall level of the soft segment orientation function is lower at the elevated temperatures than that observed in ES-38-2 (not shown) which may be due to the fact that the negatively orienting crystalline hard segments of ES-38-5 are pulling the melted soft segments transverse to the stretch direction.

Figure 8 shows that there is also a distinct change in hard segment (NH group) orientation between 50 and 75°. Data at 50° are very similar to those at ambient conditions, showing the characteristic combined positive-negative orientation at low elongation. At 75 and 100°, however, a single negatively orienting peak is seen at 25 and 50% elongation, which becomes purely positive by 150%.

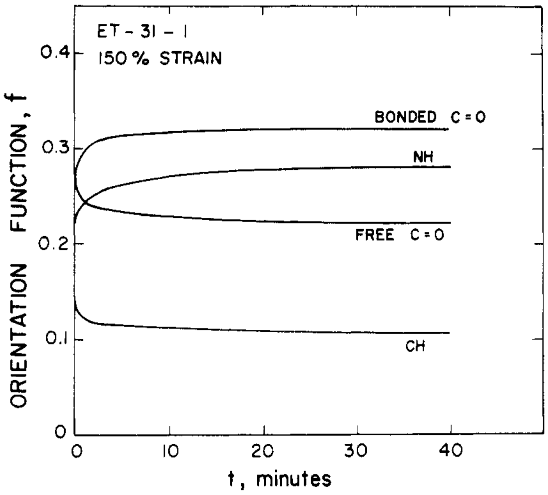

Figure 9. Orientation functions *vs.* time at 150% strain for ET-31-1.

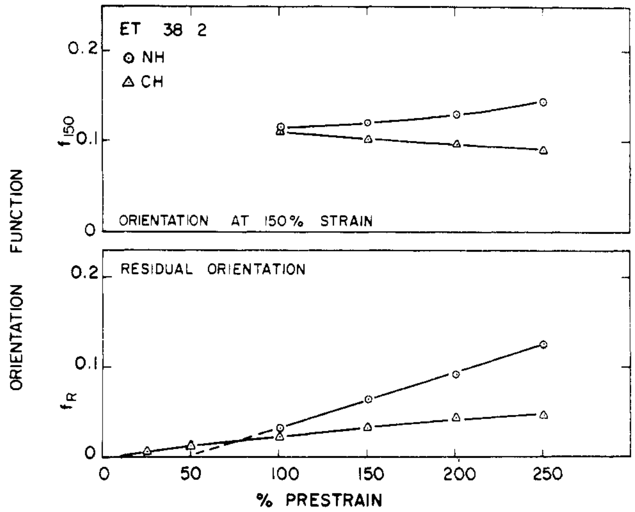

Figure 10. Orientational hysteresis in ET-38-2.

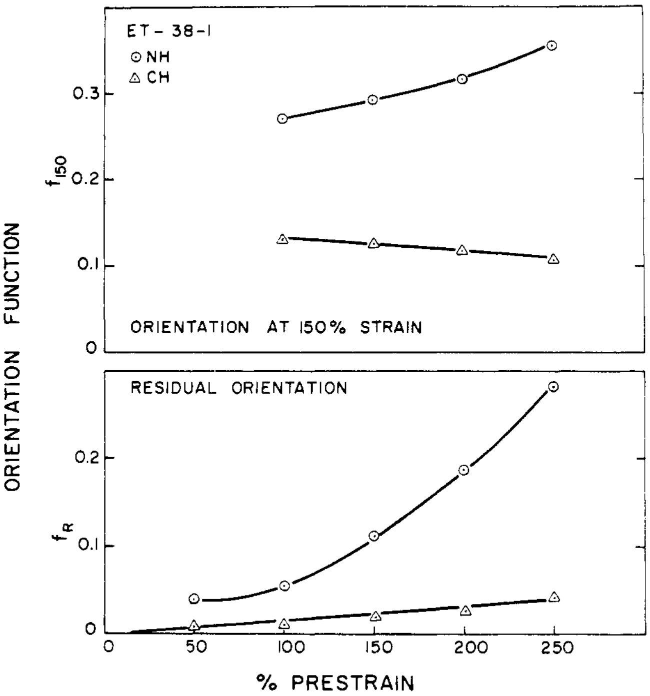

Figure 11. Orientational hysteresis in ET-38-1.

Between 50 and 150% the NH orientation splits into positive and negative components. More complete transverse orientation of the hard segments is thus observed at elevated temperatures. Above 75° and at low elongations the noncrystalline portions of the hard domains relax toward a random configuration since they are near or above their T_g. This leaves the more crystallizable segments as the main source of hard segment dichroism which at low strains is negative. At these temperatures the crystalline regions break up and begin to orient positively at strains above 100%.

C. Orientation-Time Studies. The viscoelastic nature of these materials is demonstrated in the time dependence of the orientation after imposing a step strain increment. Figure 9 shows the time variation of the four orientation functions for ET-31-1 after step straining to 150%. The behavior of ET-28-1 and ET-38-1 are similar. In all samples the NH and bonded carbonyl groups increase in orientation with time while the CH and free carbonyl decrease. This is consistent with the viscoelastic states of the two segments. The soft segment, being flexible, undergoes rapid initial orientation followed by an entropy-driven relaxation and flow of the chain segments. As the soft segments relax they exert a tension on the hard segments which causes them to orient into the stretch direction.

The magnitude of the CH orientation change with time is generally less than that of the NH or bonded carbonyl groups and is unaffected by hard block length. The free carbonyl responds in the same direction as the CH group indicating that the location of free carbonyl is such that its behavior is strongly affected by the soft segments. This is in accordance with the results of the dichroism-elongation experiments.

D. Hysteresis Studies. Orientational hysteresis in ET-38-1 and ET-38-2 has been investigated by subjecting a sample to a cyclic strain history. A virgin sample is stretched to 25%, allowed to come to stress equilibrium, and dichroic measurements made. The load is removed and the sample relaxed for 5 min, then stretched to 25%, 50%, relaxed, etc., through 250%. Dichroic measurements are made at each strain level generating f values at different prestrains. Residual orientation function data are obtained from the measurements made at zero load. These data are summarized in Figures 10 and 11.

Residual measurements on partially crystalline ET-38-2 show zero (~25% prestrain) and positive (>50% prestrain) orientation functions. The splitting of the peak into positive and negative components observed in the orientation-elongation studies is absent, indicating that the orientation of the crystalline regions is reversible at low strains. Noncrystalline ET-38-1 shows positive residual orientation function values at all strain levels. In both materials the residual NH orientation is higher than the CH, but the effect is much more marked in the noncrystalline ET-38-1. A portion of this difference, however, must be ascribed to the overall lower level of NH orientation in ET-38-2 compared to ET-38-1. Relative to the magnitude of orientation in virgin samples, the two materials behave similarly. Such residual hard segment orientation has been suggested by Estes[7] as a factor in the mechanical hysteresis or stress softening commonly observed in these and other block polymer systems.[14]

Also shown in Figures 10 and 11 are the orientation functions at 150% strain as a function of prestrain. In both samples the NH orientation increases with prestrain and

(14) S. L. Cooper, D. S. Huh, and W. J. Morris, *Ind. Eng. Chem. Prod. Res. Develop.*, 7, 248 (1968).

the CH decreases. Both of these effects may be attributed to a disruption of the domains on repeated deformation which allows greater relaxation of the flexible segments and greater orientation of the aromatic urethane segments. It should be noted, though, that while there is an effect of strain history on the orientation level, it is not great. A future publication will explore this observation in relation to intermolecular bonding.

Conclusions

It has been pointed out that there is a drastic change in orientation behavior in going from ET-24-1 to ET-28-1. Very little orientation is held in either segment in ET-24-1. In ET-28-1, ET-31-1 and ET-38-1, relatively high degrees of orientation are maintained, particularly in the hard segments. It is suggested that this is connected with the development of interlocking hard segment domains in ET-28-1 which do not exist in ET-24-1. In ET-24-1, the independent hard domains allow extensive relaxation of the orientation in both segments. In ET-28-1, relaxation of orientation is severely restricted by the interconnecting morphology of the hard segments. The flexible soft segments can relax to a greater degree, but they too are restrained by covalent bonding to the hard segments.

The first change in orientation behavior with composition thus occurs at the point where the morphology changes from independent hard domains to an interlocked structure. Once the interlocked subcrystalline hard regions are formed, only minor changes in orientation behavior due to the changing volume fraction of hard segment occur. The basic mechanism for these materials is an increasing orientation of both segments into the stretch direction (positive orientation) at all elongations. A similar conclusion based upon low-angle X-ray studies on comparable noncrystalline segmented polyurethanes was made by Wilkes.[15]

A fundamental change in orientation mechanism is observed when crystallinity (as determined by the existence of an intense high temperature DSC endotherm[12] is introduced into the hard blocks. While the noncrystalline segments present still orient as before, the crystalline regions show a transverse (negative) orientation of the segments at low elongations. This may be visualized as an orientation into the stretch direction of the crystalline regions themselves, pulling the chains transverse to the stretch direction. Low strain level hysteresis experiments show that this is a nearly reversible process. As the elongation is increased, however, the original crystallites are broken up and the segments orient positively. Orientation of the crystalline hard segments thus occurs in two steps. First the positive orientation of the crystalline region itself, followed by disruption of the region and increasing positive orientation of the segments. Crystalline and noncrystalline hard segment orientations are affected differently by temperature. Noncrystalline hard segment orientation shows a maximum value at about 90° for 38% MDI polyurethanes, all orientation being positive. For crystalline hard segments, lower orientation levels were observed and more negative orientation at low elongation was found at temperatures above 50°C. A two-step orientation mechanism still obtains, however, as the orientation becomes purely positive at about 100% elongation.

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Thermal Expansion of Amorphous Polymers at Atmospheric Pressure. I. Experimental

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ABSTRACT: The design and calibration of a simple volume dilatometer are described. It overlaps and extends to about 250° the range of our cryogenic dilatometer and thus is suitable for expansivity studies of some polymeric high-temperature glasses, the corresponding liquids, and rubbery polymers. Measurements of specific volume are accurate within $\pm 1.3 \times 10^{-4}$ cm^3/g. The results for three methacrylate polymers are given, namely, cyclohexyl, cyclopentyl, and a highly isotactic methyl. The thermal expansivities and derived free-volume quantities are compared with each other and with previous results for homologous series of poly(alkyl methacrylates) and poly(vinyl ethers). The typical effects in systems with linear side chains, which are reflected in reduced values of the characteristic product $\Delta\alpha T_g$, are not encountered in the present systems. They retain "normal" values, not withstanding the enhanced mobility of the rings.

In the past several years we have undertaken studies of the pressure–volume–temperature (PVT) surface of amorphous polymers in the liquid and glassy domains.[1] At atmospheric pressure the range between room temperature and about 10°K has been investigated for a variety of polymeric structures, primarily as a low-frequency tool in mechanical relaxation spectroscopy and in connection with certain free-volume ideas. At elevated pressure ($P \leq$ 2 kbar) the PVT surface has been determined in the range between about 10 and 200°.

It has been possible to compare experimental results in the equilibrium liquid ($T > T_g$) successfully with the statistical theory[2-5] and, continuing on this basis, to explore

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