Infrared Studies of Segmented Polyurethane Elastomers. II. Infrared Dichroism

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ABSTRACT: Strain dichroism experiments on thin films of polyurethane elastomers are reported. Studies of the effect of temperature and strain history on molecular orientation in different segments of the block-polymer chain provide a basis for the interpretation of mechanical property data. A two-phase model is proposed to represent the polyurethane morphology. The model envisions two nearly pure domains—one containing the urethane blocks and the other the prepolymer segments—which are semicontinuous and interpenetrating. A characteristic domain dimension is 50 Å, which agrees closely with the known block molecular weights. Higher modulus domains containing the aromatic urethane blocks act to reinforce the rubbery prepolymer phase, and since the two phases are interpenetrating, both are deformed by the applied stress. When the load is removed, the soft domains relax to a nearly isotropic state, while the rigid phase remains plastically deformed. The nonrecoverable deformation of the reinforcing phase gives rise to the phenomenon of stress softening.

A block polymer may be defined as a macromolecule which consists of alternating polymer segments or blocks along the polymer backbone. If X and Y represent the constituent polymer segments, then the block polymer can be represented schematically by the formula $(XY)_k$, where k indicates that the block structure may repeat k times in the polymer. Given this general definition, block polymers may be divided into two general categories.

First, there are the block polymers which contain only a small number of blocks, with each block having a relatively high molecular weight. Characteristic of this first type are the styrene–butadiene–styrene terblock polymers (SBS) in which a central polybutadiene block of molecular weight around 50,000 is flanked by two terminal polystyrene blocks of molecular weight 15,000. Much of the recent research on block polymers has been concerned with the properties and morphology of this first type of block polymer.

The second type of block polymer includes those block polymers which are composed of a large number of relatively low-molecular-weight blocks. Commonly, the component blocks have molecular weights in the range 1000–5000, with the block structure repeating a sufficient number of times to produce overall molecular weights between 30,000 and 100,000. Representative of this latter group of block polymers are the segmented polyurethane elastomers with which the present study is concerned.

The mechanical properties of both types of block polymers have been well documented in a recent review.[1] Characteristic of both are high initial moduli, high extensibility, and high resilience. Also common to block copolymers is the phenomenon of stress softening,[2,3] whereby the stress and modulus of the elastomer are substantially lowered by the cyclic application of strain. It is generally agreed that these properties are the product of a domain structure which results from the segregation of unlike blocks into separate domains. Electron microscopic studies have shown that such a domain structure exists on a microscopic scale and that the size and shape of the domains are dependent upon composition and block molecular weights.[1]

Recently, a great amount of effort has been expended in an endeavor to understand the structure–property relationships which are observed for block polymers. The fact that the mechanical properties of these elastomers are strongly dependent upon the details of the domain structure increases the complexity of the overall problem since the morphology is in turn very sensitive to the method of sample preparation. The exact role of the hard domains in providing reinforcement and particularly in producing stress softening has remained unexplained.

In order to understand the morphological changes which occur during straining, it is necessary to have information describing how each of the phases of the block polymer deforms. Several investigators have used strain-birefringence techniques to study segmented polyurethane elastomers,[4–6] terblock polymers based on polystyrene–diene rubber,[7–10] and other block-polymer systems.[1,11] Although it has not been proven rigorously correct, it has been generally assumed that the total birefringence in a heterophase system is equal to the sum of component contributions from the different phases plus an environmental birefringence (including "form" birefringence) which arises from local electric-field anisotropies throughout the domain structure. The latter component is not well defined, and although recent studies[9,10] have suggested it to be important, most investigators[7,8,11] have assumed it to be negligible.

As compared to birefringence methods, infrared dichroism is a more powerful technique since it allows the orientation of specific polymer chain segments to be monitored.[12–14] Quantitative analysis of appropriate infrared absorption

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(7) J. F. Henderson, K. H. Grundy, and E. Fischer, *J. Polym. Sci., Part C*, No. 16, 3121 (1968).

(8) E. Fischer and J. F. Henderson, *Rubber Chem. Technol.*, 40, 1373 (1967).

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(12) G. M. Estes, Ph.D. Dissertation, University of Wisconsin, 1971.

(13) R. Zbinden, "The Infrared Spectroscopy of High Polymers," Academic Press, New York, N. Y., 1964.

(14) R. D. B. Fraser, *J. Chem. Phys.*, 21, 1511 (1953); 28, 1113 (1958).

bands allows the orientation of polymer segments in the different domains to be determined.

A preliminary comparison of the total birefringence response[4,5] and the molecular orientation in the separate phases of polyurethane elastomers[12] has indicated that orientational birefringence alone cannot account for the observed birefringence response. Owing to the small domain sizes and the high levels of orientation which are achieved during extension, the environmental birefringence contribution can be expected to make a significant contribution to the overall birefringence response, and appears to be considerably more important in polyurethane elastomers and perhaps other block polymer systems than has been previously thought.

It is the purpose of this investigation to study morphological changes which occur in polyether and polyester urethanes by measuring the infrared dichroism of samples in uniaxial extension. The stress–strain-birefringence response[4,5] and hydrogen bonding[15] of similar materials have been described previously.

Experimental Section

A. Materials. The materials used in this study were a polyether urethane and a polyester urethane, both described in part I of this series.[15] The polyurethanes were block polymers composed of alternating blocks of soft (polyether or polyester prepolymer) and hard (urethane based) segments. The soft-segment prepolymers ($\sim\!\sim$) were poly(tetramethylene oxide) in the polyether-based urethane and poly(tetramethylene adipate) in the polyester-based urethane. The molecular weight of the prepolymers was 1000. The hard segments were based on a *p,p'*-diphenylmethane diisocyanate (U) chain extended with 1,4-butanediol (G). The composition data in Table I show that both copolymers contained nominally 38 wt % diisocyanate. Throughout this report, the materials will be designated ET-38 and ES-38, with the prefix indicating the type of material (ET for polyether urethane and ES for polyester urethane) and the suffix indicating the weight per cent diphenylmethane diisocyanate.

The backbone structure of these polyurethane elastomers can be written schematically by the formula

$$\mathrm{H}\left[\sim\!\sim-(\mathrm{UG})_x-\mathrm{U}\right]_m\sim\!\sim-\mathrm{H}$$

where it is assumed that both ends of the molecule are terminated by prepolymer segments. Two parameters (m and x) characterize the polyurethane backbone. The first, m, is indicative of the overall polymer molecular weight and is a representative degree of polymerization for the repeating block structure. The second, x, is an indication of the average size of the hard blocks. Larger values of x reflect higher diisocyanate concentrations at a fixed prepolymer molecular weight. By knowing the number-average molecular weight and the weight-fraction MDI in the polymer (given in Table I), one can compute the two structural parameters for each polymer. The values of m and x for ET-38 and ES-38 are given in Table I. On the average, approximately three MDI and two chain-extender segments separate the prepolymer segments. With regard to the interpretation of physical properties and morphological characteristics, it is important to remember that x as calculated is representative solely of the average hard block length. It is expected that the molecular weight of the hard blocks is distributed so that the calculated value of x is a number-average value. The number-average molecular weight of the hard blocks is then about 930, while the number-average molecular weight of the soft blocks is 1000.

A structural difference between ET-38 and ES-38 occurs in the number-average molecular weights of the elastomers (87,300 for ET-38 and 32,400 for ES-38). These molecular weight differences as characterized by the values of m are, however, not of primary importance in determining physical properties due to the low molecular weight of the repeating block structure (about 2000). Even in the lower molecular weight ES-38, the block structure is repeated about 16 times, whereas in hydrocarbon block copolymers such as those based on polystyrene and polybutadiene, only two or three blocks are necessary to produce mechanical properties characteristic of block polymers with longer block sequences.

TABLE I
POLYURETHANE CHARACTERIZATION

	ET-38	ES-38
MDI weight fraction[a]	0.386	0.377
Molecular weight[a]		
Number average, M_n	87,300	32,400
Weight average, M_w	252,000	236,000
M_w/M_n	2.88	7.28
Parameter m	44.8	16.4
Parameter x	1.99	1.96

[a] Data from B. F. Goodrich Chemical Co.; molecular weight obtained by gel permeation chromatography.

B. Infrared Dichroism.[13] The dichroic ratio D for a particular absorption band is defined by

$$D = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ represent the peak absorbancies of infrared radiation polarized parallel and perpendicular to the stretching direction (uniaxial tension). Using a base-line technique, the peak absorbance A at the frequency of maximum absorption ν_0 is given by

$$A = \log\left[I_0(\nu_0)/I(\nu_0)\right] \tag{2}$$

where I_0 is the base-line intensity and I is the intensity of the transmitted radiation. The dichroic ratio is unity for an isotropic sample and, depending upon the nature of the vibrational mode, may become either greater or less than unity with increasing molecular orientation. Further comments on the exact base lines used and an analysis of variance of the infrared dichroism experiment can be found in Appendix C.3 of ref 12.

The dichroic ratio may be used to determine an orientation function[14] for the absorbing group through

$$f = [(D_0 + 2)/(D_0 - 1)][(D - 1)/(D + 2)] \tag{3}$$

where D_0 is the dichroic ratio for perfect alignment. It is related to the transition moment direction α by the expression

$$D_0 = 2\cot^2\alpha \tag{4}$$

The applicability of infrared dichroism to the study of polyurethane elastomers is determined by the availability of at least one well-characterized absorption band in each type of domain. It has been postulated that the soft domains are comprised of prepolymer (polyether or polyester) segments, while the hard domains contain urethane segments. The N–H stretching vibration which is located in the urethane linkage has been employed to characterize the orientation of the higher modulus or hard domains. It appears at 3320 cm^{-1} in both ET-38 and ES-38. The asymmetric C–H stretching absorption occurs at 2935 cm^{-1} in ET-38 and at 2960 cm^{-1} in ES-38 and has been used to describe the orientation of prepolymer segments which comprise the rubbery or soft domains. Although the methylene linkage also is present in the chain-extending diol in the hard domains, the fraction of the methylene linkages in the soft segments is sufficiently greater (84% in ET-38 and 78% in ES-38) that the C–H asymmetric stretch can be confidently employed for soft segment characterization.

The use of eq 3 in calculation of orientation functions requires an assignment of the transition moment direction for each vibration used, in this case the urethane NH vibration and the CH asymmetric stretch.

The NH vibration has been discussed by Fraser,[14] who concluded that the transition moment lies essentially in the NH bond direction. $\alpha = 90°$ may then be taken as a reasonable value.

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

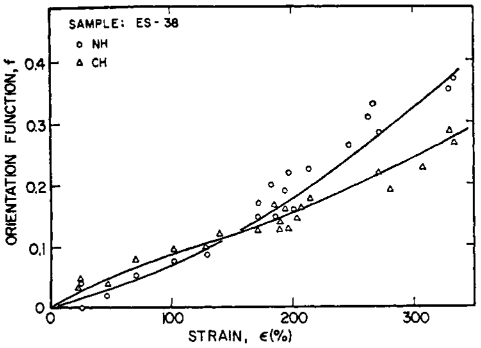

Figure 1. Orientation function *vs.* strain for ES-38 at 28° (type I experiment).

Various calculations of the transition moment direction for the CH_2 stretching vibrations have been reviewed by Zbinden.[13] While $\alpha = 90°$ would be expected for a pure stretching motion, other vibrations which occur simultaneously (most particularly the CH_2 wag) will displace the transition moment from this direction. A value of $\alpha = 90°$ will be used in the calculation of orientation functions, though it is recognized that some deviation may occur. In this connection it should be noted that substantial variations in α (greater than 10°) are required before the orientation function is changed significantly.

Two experiments have been performed. In the first type (type I) the polymer films were stretched to a nominal strain level and the polarized ir spectra were scanned. Then the samples were relaxed at zero load for 5 min, after which the spectra were again obtained. Each sample yielded only one data point on an orientation function–strain curve. The second type of experiment (type II) involved extending one sample by step increments to 360% strain and scanning the polarized ir spectra at each step. In this case one sample yielded the entire orientation function–strain curve. Type II experiments have the advantage that only one sample is used, thereby eliminating the variability between samples as a source of experimental error. The type II experiments were performed in duplicate.

Details of sample preparation, techniques used for infrared measurements, and complete infrared spectra for ET-38 and ES-38 have been published elsewhere.[15] Because the strain-dichroism behavior of ET-38 and ES-38 are qualitatively identical, only the results for ES-38 will be presented, but with the understanding that all conclusions are equally applicable to ET-38.

Results

Figure 1 displays the orientation functions for both the hard and soft segments in ES-38 during the initial extension in type I experiments. The ambiguity in transition moment direction for the CH_2 vibration discussed above would serve to raise the CH orientation slightly. The orientation of both segments is of similar magnitude, but the CH orientation at low strain levels is greater than the NH orientation, with the two functions crossing at about 150% strain.

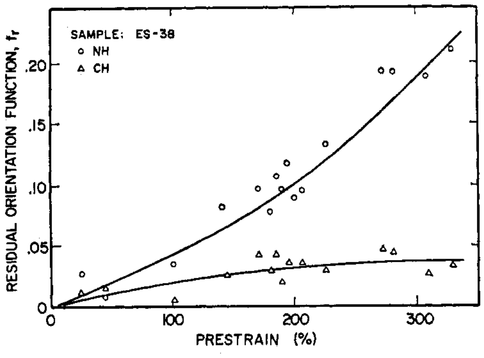

Figure 2. Residual orientation function *vs.* prestrain for ES-38 at 28° (type I experiment).

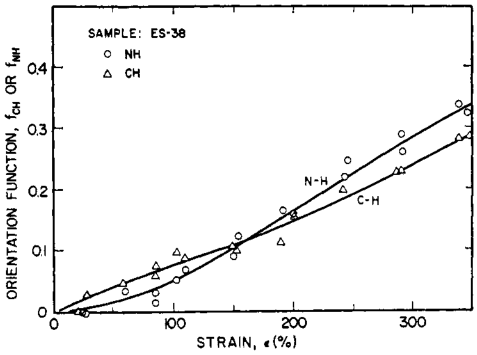

Figure 3. Orientation function *vs.* strain for ES-38 at 28° (type II experiment).

The residual orientation measured in the type I experiments following a 5-min relaxation period is represented by the residual orientation functions plotted in Figure 2. The abscissa is the strain level to which the samples were extended prior to relaxation, hence it is labeled as prestrain. Although both soft and hard segments orient to nearly the same degree upon initial straining, when relaxed the hard segments (NH orientation) exhibit substantially larger orientation functions than the soft segments. Both ET-38 and ES-38 show this behavior. Since the elastomers creep considerably (65–70% following straining to 300%), it might be thought that the residual orientation is due to the residual strain. This could be true in part, but cannot explain the entire residual hard segment orientation, for at 70% initial strain the orientation function for NH alignment is only about 0.07. Moreover, if creep were entirely responsible, then the residual orientation functions for the two phases should be approximately equal, but lower than those in Figure 1. It appears that the differences in the residual orientation functions are due to different retractive stresses acting on the separate domains.

For comparison of type I and type II experiments, Figure 3 shows the orientation function–strain behavior for ES-38 in the latter experiment. Despite the different time scales of the two types of experiments, the curves in Figure 3 compare favorably with those for the type I experiments. As may be seen by comparison of Figures 1 and 3, the use of a single sample decreases the scatter in the data to a level which is reasonable for quantitative infrared measurements.[12]

To further investigate the connection between strain history and residual orientation, films of ES-38 were subjected to type II experiments after prestraining to 200% elongation. The results of these experiments are shown in Figure 4, along with comparable data for nonprestrained samples.

For ES-38 the orientation of the soft segments is relatively insensitive to prestrain, while the orientation of the hard segments is very dependent upon strain history. At strain levels lower than that of the prestrain (200%), the hard segments are oriented to a noticeably higher degree than is observed for nonprestrained samples. However, at extensions above the prestrain level, the NH orientation functions are essentially independent of prestrain. The high residual orientation of the hard domains is related to the stress softening observed in the repeated stress–strain experiments of segmented polyurethanes which has been reported previously.[3,4]

The type II experiments have also been used to investigate the effect of temperature on the strain-dichroism results for ES-38. Data at selected temperatures up to 120° are shown

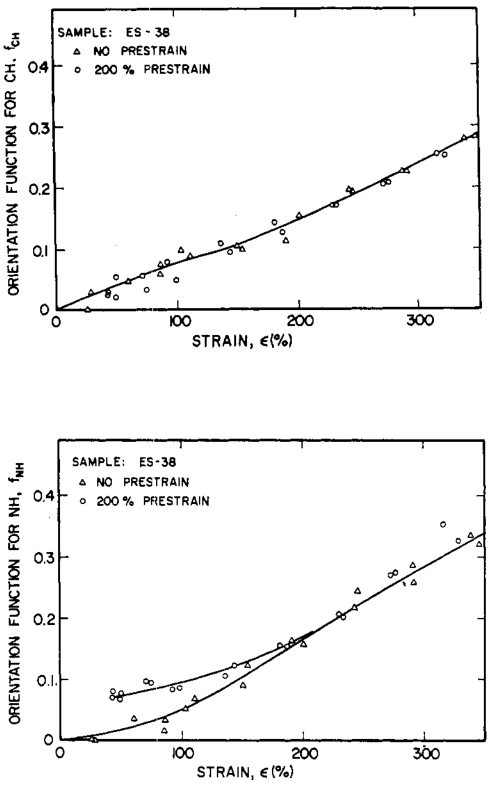

Figure 4. Orientation functions for ES-38 as a function of prestrain (type II experiment).

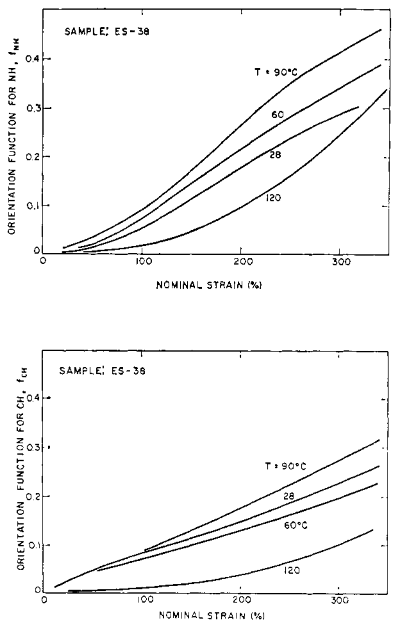

Figure 5. Orientation function–strain curves for ES-38 at various temperatures (type II experiment).

in Figure 5. Both the NH and CH orientation functions at a given strain level go through a maximum with respect to temperature. The orientation functions increase gradually with increasing temperature up to about 90°, above which they decrease rapidly with temperature. This behavior is demonstrated in Figure 6, which shows the temperature dependence of orientation functions measured at 200% extension.

The maximum in orientation at 90° is consistent with preliminary results which indicate that the integrated absorbance of the overlapping free and bonded NH peaks decreases with increasing temperature above 100°.[16] Since the free-NH absorption has a substantially lower average extinction coefficient,[17] it is postulated that this decrease is due to an increasing concentration of free-NH groups. Hence the thermal transition apparent in the dichroism data appears related to the disruption of some hydrogen bonds in the hard domains. It is interesting that the temperature behavior of the (birefringence) strain-optical coefficient as reported previously[4,5] does not indicate this thermal event at 90°. The strain-optical coefficient decreases monotonically throughout this temperature range.

Discussion

A. Evidence of Heterophase Microstructure. By monitoring the N–H and C–H infrared stretching absorptions, it has been shown that the orientation of different backbone segments depends strongly upon strain history. Upon initial straining both segments orient similarly, but after relaxation chains containing the NH group remain oriented to a substantially higher degree than those containing the CH functional group. If the sample is again strained, at strain levels lower than those previously applied, the NH-containing chains are more highly oriented than during initial extension. The orientation of backbones containing CH groups is unaffected by the prestrain. The distinct difference between the orientation functions for the two types of chains provides further evidence that the different block polymer segments reside in different domains, which react somewhat independently to the application and removal of stress.

Recently, Koutsky, Hien, and Cooper[18] obtained transmission electron micrographs of both ES-38 and ET-38 which showed a definite domain structure. The shape of both the urethane-based domains and the prepolymer domains varied from almost spherical to long, winding ribbons, with a characteristic smaller domain dimension of about 50 Å. Each type of domain appeared to comprise about 50% of the polymer.

This latter observation is consistent with the fact that ET-38 and ES-38 are both nearly 50/50 block polymers by weight. Moreover, the smaller 50-Å dimension measured from the micrograph is consistent with the approximate block lengths based on average block molecular weights. This comparison is summarized in Table II.

The high degree of molecular orientation which remains in

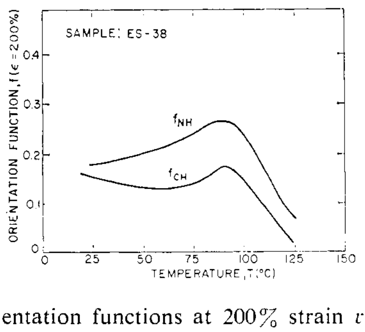

Figure 6. Orientation functions at 200% strain *vs.* temperature for ES-38 (type II experiment).

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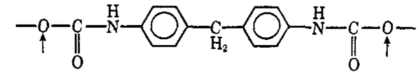
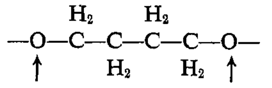
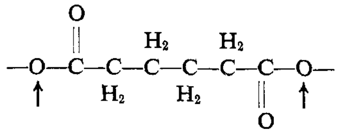
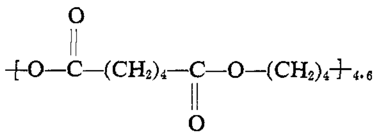
(16) S. L. Cooper, R. W. Seymour, and G. M. Estes, manuscript in preparation.

(17) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 70.

(18) J. A. Koutsky, N. V. Hien, and S. L. Cooper, *J. Polym. Sci., Part B*, **8**, 383 (1970).

Table II
Estimated Block Lengths

Chemical structure[a]	Designation	Segment Length, Å[b] Contour	Rms
	MDI, U	14.18	
 $\underset{\uparrow}{-O}-\overset{H_2}{C}-\underset{H_2}{C}-\overset{H_2}{C}-\underset{H_2}{C}-\underset{\uparrow}{O-}$	G, ether repeat unit	6.25	
 $\underset{\uparrow}{-O}-\overset{\overset{O}{\|}}{C}-\underset{H_2}{C}-\overset{H_2}{C}-\underset{H_2}{C}-\overset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{\uparrow}{O-}$	Ester repeat unit	8.47	
UGUGU	Average hard block	55.0	
$-[O-(CH_2)_4]_{14}-$	Polyether soft segment	82.0	23.2
 $-[O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-O-(CH_2)_4]_{4.6}-$	Polyester soft segment	68.0	22.4

[a] All segments assumed to be in the planar, zigzag conformation. [b] Length measured between arrows on chemical structure; bond length data from R. Bonart, *J. Macromol. Sci., Phys.*, **2**, 115 (1968), and R. Bonart, L. Morbitzer, and G. Hentze, *ibid.*, **3**, 337 (1969).

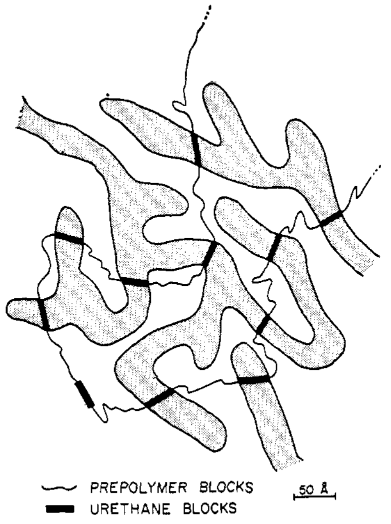


Figure 7. Schematic representation of domain structure.

the hard domains following initial straining can arise if the domains contain a preferential ordering of chains. Long-range order (such as crystallinity) is not present in these regions because wide-angle X-ray studies of ET-38 and ES-38 stretched up to 300% showed no evidence of crystallinity.[19] However, short-range order between neighboring chain segments is possible, especially when the high degree of hydrogen bonding involving the urethane carbonyl and the urethane active hydrogen is considered.[15] In such an ordered regime, the hard segments are predominantly in an extended conformation. In order to form nearly pure domains, the UGUGU urethane sequence must traverse an entire domain, which from space-filling considerations could not have a smaller limiting dimension larger than the fully extended length of this sequence, *i.e.*, about 55.0 Å. This picture of ordering in the hard domains would predict the smaller domain dimension to be slightly less than 55 Å, which is in agreement with the experimental electron micrograph estimate.

The soft domains, on the other hand, consist of rubbery blocks which in the unstrained elastomer are more randomly arranged. The fully extended end-to-end lengths for these chains (68 Å in ES-38 and 82 Å in ET-38) provide an upper limit on the width of the soft domain, though it is unlikely that many chains are found in this conformation. At the other end of the scale, the Gaussian root-mean-square (rms) end-to-end distances given in Table II provide a minimum domain dimension. If one accepts 6 backbone atoms in the polyester and 5 in the polyether as reasonable length statistical segments, then the polyester prepolymers contain only about 9 equivalent segments and the polyether segments 14. With this low number of segments, the prepolymers cannot achieve Gaussian chain character, but rather must exhibit average end-to-end distances greater than those predicted from Gaussian statistics. They can be expected to have mean lengths in the range from the Gaussian rms values (about 22 Å) on the low end to the contour lengths (70–80 Å) on the high end. Falling into this range are the dimensions estimated by electron microscopy.

B. Proposed Two-Phase Model. A domain model consistent with these mechanical, optical, electron microscopic, and X-ray data envisions a dispersion of irregularly shaped soft and hard domains, with neither type of domain being more dispersed in, nor enveloped by, the other. Both phases are continuous and interpenetrating. A schematic illustration of what a two-dimensional cross section of the domain structure for an unstrained polymer might look like is shown in Figure 7, where the shaded regions represent hard domains and the white regions represent soft domains. Also shown is one representative polymer molecule, which winds its way through many domains. In most instances, the soft and hard blocks are joined at domain interfaces. However, since phase separation is probably not complete, some of the urethane blocks are also dispersed in the rubbery matrix.

In the unstrained state, the prepolymer blocks are randomly arranged, so the rubbery domains are isotropic.

(19) D. S. Huh, unpublished observations.

The urethane blocks are lined up approximately perpendicular to the long edge of the hard domains, thereby making the hard domains individually anisotropic. However, the hard domains are randomly arranged so that the bulk sample appears mechanically and optically isotropic.

Because the soft and hard phases are interpenetrating, large deformation of one is impossible without a similar, simultaneous deformation of the other. While the lower modulus of the rubbery domains allows these regions to absorb much of the strain at very low extensions, as the strain level is increased the most highly extended soft segments become taut, so that further straining tends to also affect the hard domains. The residual infrared dichroism data indicate that the hard domains are oriented so that the aromatic urethane chain backbones which make up these domains are aligned into the direction of strain. This means that the hard domains must be moved into a position where their longer dimensions are predominantly oriented perpendicular to the stretching direction, *i.e.*, a configuration where the hard domains appear to align perpendicular to the applied stress. To achieve the high degree of hard block orientation indicated by the dichroism data, it is necessary that the irregularly shaped hard domain undergo plastic deformation, with the extent of deformation being uniquely determined by the initial strain level. By deformation of both domains, polymer chains in both phases become oriented simultaneously up to high levels of strain. At sufficiently high strains, the hard domains may in fact be broken into smaller units. Both of these mechanisms are expected to contribute to stress hysteresis.

If, after a highly oriented state is achieved, the load is removed, the sample's bulk recovery is accompanied by the return of the mobile soft segments to an almost isotropic state. However, there is no equivalent restoring force to disorient and re-form the hard domains into their original isotropic state, so that the hard domains retain a large degree of the induced deformation and the accompanying orientation.

The temperature dependence of the orientation function curves shown in Figures 5 and 6 may be understood as the result of two thermally activated processes occurring simultaneously. The first is an ordering process due to softening of the domains which allows greater orientation under the applied strain. This causes an increase in the orientation function. The second process is disruptive, as the forces responsible for domain cohesion decrease with increasing temperature. This effect may be identified with the break-up of hydrogen bonding. It becomes dominant above 90°, where the orientation function begins to drop with temperature.

Conclusions

The orientation of different segments of the polyurethane backbone structure has been studied using the technique of infrared dichroism. The chain segments containing the N–H functional group are thought to reside in hard, reinforcing, aromatic urethane domains, while methylene linkages exist primarily in the lower modulus polyether- or polyester-rich domains. It has been possible to accurately monitor the orientation of both the hydrocarbon and urethane linkages.

The hydrocarbon segments are readily oriented by an applied stress, and return to an unoriented state when the stress is removed. The urethane domains align much to the same extent as the soft domains, but tend to remain in a partially oriented conformation after removal of the applied stress. The set of the urethane domains provides a molecular interpretation for the observed phenomenon of stress hysteresis.

To represent the heterophase morphology of segmented polyurethanes, a domain model has been proposed which envisions mutually interpenetrating soft and hard phases. The domain structure provides mechanical reinforcement, since the semicontinuous hard phase functions both as a multifunctional physical cross link and a reinforcing filler.

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