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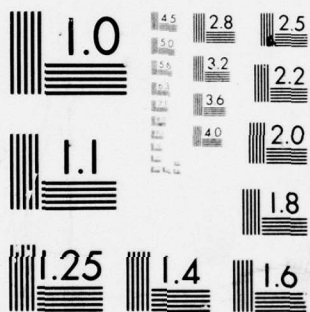
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Contract No. N00014-75-C-0686

Project No. NR 356-584

TECHNICAL REPORT NO. 7

"DIMENSIONAL CHANGES IN ULTRADRAWN POLYETHYLENE"

by

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June 1, 1977



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1. REPORT NUMBER Technical Report No. 7 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) Dimensional Changes in Ultradrawn Polyethylene		5. TYPE OF REPORT & PERIOD COVERED Interim <i>rept.</i>
6	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) 10 Numa J./Capiati and Roger S. Porter	15	8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0686 ✓
9. PERFORMING ORGANIZATION NAME AND ADDRESS Polymer Science and Engineering ✓ University of Massachusetts Amherst, Massachusetts 01003		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-584 (12-24 p.)
11. CONTROLLING OFFICE NAME AND ADDRESS ONR Branch Office 495 Summer Street Boston, Massachusetts 02210		12. REPORT DATE 11 June 1977
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 14 TR-7		13. NUMBER OF PAGES 19 (incl. tables and figures)
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) thermal expansion; high-density polyethylene; solid-state extrusion; ultra-orientation; chain extension; elastic modulus; strength; micro- fibers; series-parallel model		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Samples of ultradrawn high density polyethylene were studied by thermo-mechanica analysis. The purpose was to study the dimensional changes in polyethylene morphologies of extreme orientation. Dimensional changes were measured from -140°C to +70°C with a precision of better than 1%. A negative thermal expansion coefficient was observed along the length (c axis) of the fibers containing the polyethylene morphologies of extreme orientation. A change in negative coefficient		

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is observed between -35 and -45°C. The sign and magnitude of the expansion coefficient confirm, along with other evidence, the existence of extended chain structures in these morphologies. A series parallel model has been developed for the ultradrawn polyethylenes to describe the dimensional changes with temperature.

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DIMENSIONAL CHANGES IN ULTRADRAWN POLYETHYLENE

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ABSTRACT

Samples of ultradrawn high density polyethylene were studied by thermomechanical analysis. The purpose was to study the dimensional changes in polyethylene morphologies of extreme orientation. Dimensional changes were measured from -140°C to $+70^{\circ}\text{C}$ with a precision of better than 1%. A negative thermal expansion coefficient was observed along the length (c axis) of the fibers containing the polyethylene morphologies of extreme orientation. A change in negative coefficient is observed between -35 and -45°C . The sign and magnitude of the expansion coefficient confirm, along with other evidence, the existence of extended chain structures in these morphologies. A series parallel model has been developed for the ultradrawn polyethylenes to describe the dimensional changes with temperature.

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INTRODUCTION

Thermal expansion studies on polymer crystals have received considerable attention. Several authors have reported negative thermal expansion coefficients for the c-axis direction (chain direction) for the polyethylene orthorhombic unit cell (1-5). A reported value at ambient temperature (2), $-12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, is relatively small and of opposite sign compared with the coefficients in the other directions (basal plane); $\alpha_b = +3.8 \times 10^{-5}$ and $\alpha_a = +22 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$, resp. (4). Kobayashi and Keller (2) explained the negative coefficient by an increase in torsional vibration of the polyethylene planar zigzag with temperature. Equilibrium configurations in the crystal of shorter dimensions result at higher temperatures. Also, the chain contraction is facilitated, when temperature increases, by greater lateral chain separation due to the expansion in the a and b directions (2).

Negative thermal expansion coefficients, measured on macroscopic samples, have been published recently (1,7). Kim and DeBatist (1) observed a reversible and reproducible negative coefficient for cold-drawn polyethylene in the draw direction. The inversion, from positive to negative, occurs when polyethylene samples are drawn to ratios of over 4. Baughman and Turi (7) measured the c axis expansion coefficient of polydiacetylene single crystals. Solid-state polymerization and purification procedures provided single crystals with dimensions up to the order of 1 cm (8). This made possible the direct macroscopic measurement of dimensional changes with temperature (7).

Polyethylene fibers, obtained by solid-state extrusion in a capillary rheometer, contain certain proportions of extended chain crystals (9,10) and an extremely high orientation in the chain axis direction (11). The mechanical properties of these ultraoriented polyethylene fibers depend on pressure and temperature of extrusion (12). Briefly, a change in extrusion pressure corresponds to a change in undercooling and consequently different crystal shapes and dimensions result. Also, the temperature effect on fiber properties has been explained as a contribution to molecular mobility which decreases stress concentrations and improves the fibrillar packaging in the final fiber. Clearly, variations in preparation pressure and/or temperature produce marked changes in morphology and structural perfection. The fiber tensile modulus and its similarity to the perfect orthorhombic crystal modulus (13), $\sim 2.4 \times 10^{12}$ dynes/cm², indicate the high degree of structural perfection that has been attained in the polyethylene fibers. An evaluation of the corresponding thermoelastic properties also seems to be a proper approach for a better morphological understanding as well as a measure of perfection of samples prepared under different conditions.

EXPERIMENTAL

A thermomechanical analyzer, TMS-1, was used together with a differential scanning calorimeter, DSC-1B, both by Perkin Elmer Corporation, Norwalk, Connecticut.

The polymer used throughout was a high density polyethylene, DuPont Alathon 7050, $M_w = 58,500$, $M_n = 18,400$. The samples were prepared by the solid-state, crystal-crystal transformation process described in detail elsewhere (12). In brief, constant pressure and temperature were maintained throughout the crystallization from the melt in the extruder reservoir (Instron Rheometer). This was followed by a solid-state extrusion below the polyethylene melting point through a special capillary for the Rheometer (12).

Thermal expansion coefficients were measured on fibers prepared at temperatures between 130 and 135°C and pressures between 1270 and 2400 atm. Samples were run, in the TMS-1, between 70 and -140°C at a scanning rate of 10°C/min under nitrogen atmosphere. A "zero load condition" on the probe was used; that is the minimum load required for the probe to follow the sample dimensional changes was employed (2.5 g). The instrumental error is less than $\pm 1\%$ for the magnification of 10^4 used throughout these tests. Both the probe and holder are made of quartz and, from geometrical design, the test gap should be invariant in length over the measured temperature range.

Strands of the special polyethylene morphology with a diameter of 0.14 cm were sectioned to a length of about 1 cm using a high-speed drill with a steel blade. Special care was taken to achieve flatness and parallelism for the ends of the strands.

RESULTS AND DISCUSSION

The expansion coefficients for the orthorhombic crystals of polyethylene in directions parallel and perpendicular to the chain axis are of opposite sign and notably different in magnitude (1-6). As mentioned before, the reported value (2) for the c axis direction is $-12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and for the a and b directions (6) $+22 \times 10^{-5}$ and $+3.8 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$, resp. This is a consequence of different mechanisms controlling the length-temperature relation for the different directions. The positive coefficient, in the a and b directions, is due to the increase in separation distance between chains with temperature. In contrast, parallel to the c axis, the controlling mechanism is the change in torsional vibration states of the planar zigzag with shorter equilibrium lengths corresponding to higher temperatures (2,14). This notable anisotropy suggests that thermal expansion might be used to evaluate the structural perfection in ultraoriented polyethylene fibers.

The specific change in length parallel to the fiber axis, for a typical sample, is shown as a function of temperature in Figure 1. The temperature and pressure of preparation were 134°C and 2100 atm, resp. The slope in this plot is the thermal expansion coefficient. Two almost linear regions can be distinguished. One between 70 and -35°C with coefficient $\alpha_1 = -10.6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and another between -45 and -140°C with coefficient $\alpha_2 = -7.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. All the samples showed negative expansion coefficients and a variation in slope between -35 and -45°C . The slope break is sharpest for highest modulus samples as can be seen in Figure 2.

The change of the slope in Figure 1 may suggest a transition within the crystalline phase. Although not conclusive, the transition may be caused by a discontinuity in the rotational-vibration energy states at this transition temperature.

The negative thermal expansion coefficients, which are illustrated in Figure 1, show the presence and high axial orientation of extended chains in the fiber. Chain extension and orientation have been generally recognized as the main contributors to rigidity and mechanical strength in fibrillar materials (10, 12, 15-17).

Figure 2 shows a correlation between the expansion coefficients α_1 , higher temperature, and α_2 , lower temperature, and the tensile modulus (E). The modulus data were obtained from stress-strain curves (12). The values used in Figure 2 correspond to a strain rate of $6.67 \times 10^{-5} \text{ sec}^{-1}$. The straight lines are the best fit to the experimental values. The lines were obtained by least squares analysis.

The corresponding equations are:

$$-\alpha_1 = 6.07 \times 10^{-6} + 0.79 \times 10^{-17} E. \quad (1)$$

$$-\alpha_2 = 6.45 \times 10^{-6} + 0.13 \times 10^{-17} E. \quad (2)$$

The 95% confidence limits for the slopes are ± 0.01 and ± 0.19 for α_1 and α_2 , respectively.

The coefficient α_1 becomes more negative for higher moduli indicating a greater contribution of the extended chains to the equilibrium length. A correlation coefficient of 0.95 for Equation (1) indicates the strength of linearity between elastic modulus and thermal expansion above -45°C in the experimental range covered. At lower temperatures, on the other hand, the coefficient α_2 seems to be insensitive if not independent of modulus, since the small negative slope in Equation (2) can be positive within the confidence limits. Because the modulus depends strongly on the amount of extended chains, its relation to thermal expansion measures the contribution of extended chains to dimensional changes. The almost independency of α_2 on E_1 below the transition is consistent with a smaller extended chain contribution to expansion at such low temperatures or due to a similarity of crystalline and amorphous (glassy) regions at low temperature.

The thermoelastic behavior of these polyethylene fibers may be approached by considering them as composed of three different morphologies: (1) "Continuous crystals" (17), i.e. a crystalline arrangement in which molecular chains are perfectly aligned and extended, their chain ends being randomly distributed throughout the crystal; (2) folded chain crystals, including only the aligned chain regions between folds; and (3) amorphous phase composed of chain folds and unoriented material lying between consecutive chain-folded crystals. Figure 3 shows schematically the proposed model. The amorphous phase acts both in series with chain-folded crystals and in parallel with continuous crystals. This

arrangement is consistent with the transformation from spherulite to fibrillar structure (12, 15). In fact, microfibers are formed by clusters of longitudinally-aligned folded crystals and extended chains passing over several of these clusters. In addition, the concept of continuous crystals is reintroduced here (17). The fully-extended chains are thus continuously arranged throughout the fiber. If continuous crystal length becomes macroscopic and equal to the total length of the model, its thermal expansion coefficient will approach the coefficient for polyethylene single crystals in the c axis direction (2), $-12 \times 10^{-6} \text{C}^{-1}$. Equal thermoelastic properties (E and α) are assumed for chains in folded and continuous crystals. If the effect of the small chain ends concentration in the continuous crystal phase is neglected, both structures will be similar. They, obviously, differ in length. The thermal expansion for the amorphous phase is taken as $+2 \times 10^{-6} \text{C}^{-1}$ (2, 4, 5, 18).

The series-parallel model in Figure 3 may be considered to be subjected separately to an external tensile force and to a temperature difference high enough to generate the same total deformation. Under these conditions a relation between thermoelastic properties and the fraction of continuous crystals, A_e/A_T , in the fiber can be derived on the basis of the model. The direct conversion would require a knowledge of the stress-temperature coefficient.

The symbols used are: A , cross sectional area (cm^2); L , length (cm); F , force (dynes); ΔL , length increment (cm); ΔT , temperature increment ($^{\circ}\text{C}$); ϕ , volume fraction of crystals. The sub-indices being: T , total; e , continuous crystal phase; f , folded chain crystal phase; a , amorphous phase.

From Figure 3 it is clear that $L_T = L_e = L_a + L_f$. Also the cross sectional area of folded chain crystals is equal to that of the amorphous phase and $A_T = A_e + A_f$ and $A_f = A_a$.

The elastic modulus and thermal expansion coefficient are defined as:

$$E = \frac{F/A}{\Delta L/L} \left[\frac{\text{dynes}}{\text{cm}^2} \right] \quad \text{and} \quad \alpha = 1/L \cdot \Delta L/\Delta T [^{\circ}\text{C}^{-1}] \quad (3a)$$

A force balance under an external load, see Figure 3, gives

$$F_T = A_T E_T \frac{\Delta L_T}{L_T} = A_e E_e \frac{\Delta L_e}{L_e} + (A_T - A_e) E_{af} \frac{(\Delta L_e + \Delta L_f)}{(L_e + L_f)}$$

and therefore

$$A_T E_T \frac{\Delta L_T}{L_T} = A_e E_e \frac{\Delta L_e}{L_e} + \frac{(A_T - A_e) (\Delta L_a + \Delta L_f)}{\frac{L_f}{E_f} + \frac{L_a}{E_a}} \quad (3b)$$

Since from Figure 3

$$E_{af} = \frac{L_a + L_f}{\frac{L_f}{E_f} + \frac{L_a}{E_a}}$$

The deformation resulting from the action of an external force may then be replaced in Equation 3 by the corresponding deformations generated by a temperature difference:

$$\Delta L = \alpha L \Delta T$$

Therefore

$$A_T E_T \alpha_T = A_e E_e \alpha_e + \frac{(A_T - A_e) (\alpha_a L_a + \alpha_f L_f)}{\frac{L_f}{E_f} + \frac{L_a}{E_a}}$$

Then by factoring out A_T and A_e gives:

$$A_T \left[\alpha_T E_T - \frac{\alpha_a L_a + \alpha_f L_f}{\frac{L_f}{E_f} + \frac{L_a}{E_a}} \right] = A_e \left[E_e \alpha_e - \frac{\alpha_a L_a + \alpha_f L_f}{\frac{L_f}{E_f} + \frac{L_a}{E_a}} \right] \quad (3a)$$

From the model in Figure 3, it is clear that $L_a = L_T - L_f$. Therefore by making this substitution in Equation 3a and clearing L_f/L_T results in:

$$A_T \left[\alpha_T E_T - \frac{\alpha_a + \frac{L_f}{L_T} (\alpha_f - \alpha_a)}{\frac{1}{E_a} + \frac{L_f}{L_T} \left(\frac{1}{E_f} - \frac{1}{E_a} \right)} \right] = A_e \left[\alpha_e E_e - \frac{\alpha_a + \frac{L_f}{L_T} (\alpha_f - \alpha_a)}{\frac{1}{E_a} + \frac{L_f}{L_T} \left(\frac{1}{E_f} - \frac{1}{E_a} \right)} \right]$$

The fraction of continuous crystals is expressed:

$$\frac{A_e}{A_T} = \frac{\left[\frac{L_f}{L_T} \alpha_T E_T \left(\frac{1}{E_f} - \frac{1}{E_a} \right) + \alpha_a - \alpha_f \right] + \frac{\alpha_T E_T}{E_a} - \alpha_a}{\frac{L_f}{L_T} \left[\alpha_e E_e \left(\frac{1}{E_f} - \frac{1}{E_a} \right) + \alpha_a - \alpha_f \right] + \frac{\alpha_e E_e}{E_a} - \alpha_a} \quad (4)$$

The relation L_f/L_T represents the fractional length occupied by the folded chain crystals and can be stated as a function of the volume fraction of crystals (ϕ) and the fraction of continuous crystals present.

$$\frac{L_f}{L_T} = (\varphi A_T - A_e) / (A_T - A_e) \quad (5)$$

Substituting in Equation 4, using $E_e = E_f$ and $\alpha_e = \alpha_f$ and rearranging

$$\frac{A_e}{A_T} = \frac{\frac{E_T \alpha_T - E_e \alpha_e}{E_e} \varphi + \frac{E_T \alpha_T - E_a \alpha_a}{E_a} (1 - \varphi)}{\frac{E_T \alpha_T - E_e \alpha_e}{E_e} + \frac{E_e \alpha_e - E_a \alpha_a}{E_a} (1 - \varphi)} \quad (6)$$

Equation 6 relates the fraction of fully-extended and aligned chains forming the fiber structure to the thermomechanical properties. The product $E \cdot \alpha$ is the stress induced per unit of temperature increment, under constant length.

The fraction of extended chains calculated from Equation 6 agrees with the value obtained experimentally by nitric acid etching and posterior gel permeation chromatography (10). That is:

Assuming $E_e = 2.4 \times 10^{12}$ dynes/cm² (12), $\alpha_e = -12 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (2), $\alpha_a = 2 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ (2,4,5,18), $E_a = 10^9$ dynes/cm² and $\phi = 0.85$; the fraction A_e/A_T calculated for $E_T = 5 \times 10^{11}$ dynes/cm² and $\alpha_T = -10 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ results 0.18. The experimental value for samples with similar mechanical properties was 0.15 ± 0.03 (10).

The product $E_T\alpha_T$ may be obtained by measuring the force necessary to maintain the length constant when the sample is subjected to a temperature change. Hence, the continuous crystal content may be evaluated, on these ultraoriented fibers, by a single thermoelastic measurement in a relatively simple experiment. From such values the tensile modulus is also predictable with good precision.

CONCLUSIONS

(1) The negative thermal expansion coefficients, found experimentally along the length of ultraoriented polyethylene fibers, confirm the existence of extended chains in the structure.

(2) The expansion coefficient measured parallel to the fiber axis between -45 and $+70^\circ\text{C}$ correlates linearly with the tensile modulus in the experimental range covered. This suggests a strong contribution of extended chains to the fiber equilibrium length.

(3) A series-parallel arrangement, involving continuous and chain-folded crystals and an amorphous phase, may be considered to explain the thermoelastic behavior and predict the fraction of extended chains as a function of measurable properties. A calculated value of 18% is in good agreement with that obtained experimentally, $15 \pm 3\%$ on a sample with similar mechanical properties (9,10).

(4) A distinct transition in the c-axis expansion coefficient was found at near -45°C with values ranging here from -35 to -45°C . Previously on three, probably-less-perfect, polyethylene strands we observed this transition at -49 , -52 and -53°C (19). The comparable data of Kim and DeBatist indicate a break in their expansion curve at near -50°C (1). This transition might be attributed to the crystalline phase since it is also observed in a related single crystal. No change in the c-axis dimensions for polyethylene was observed, however, from x-ray studies on polyethylene single crystals in this temperature range (20).

ACKNOWLEDGMENTS

This study has been carried out by a fellowship from the Consejo Nacional de Investigaciones Cientificas y Tecnicas de la Republica Argentina granted to N.J.C. and by a grant from the Office of Naval Research.

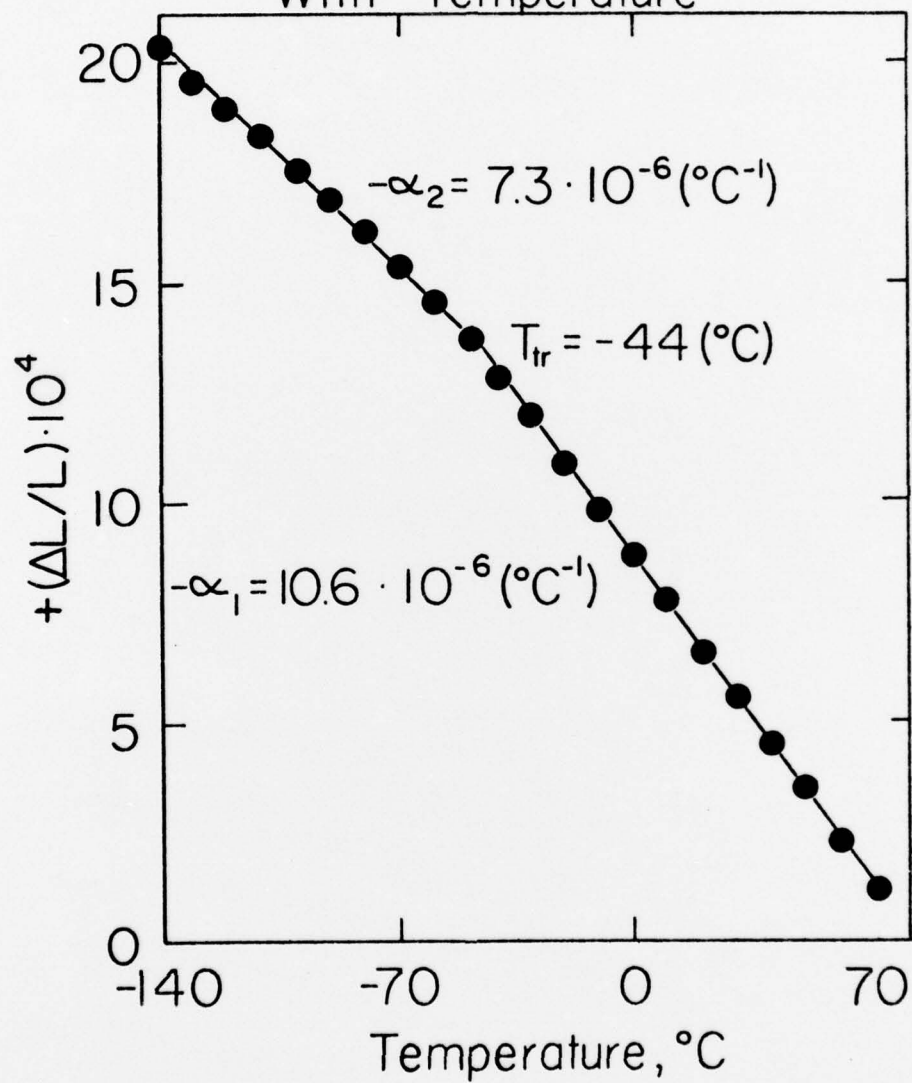
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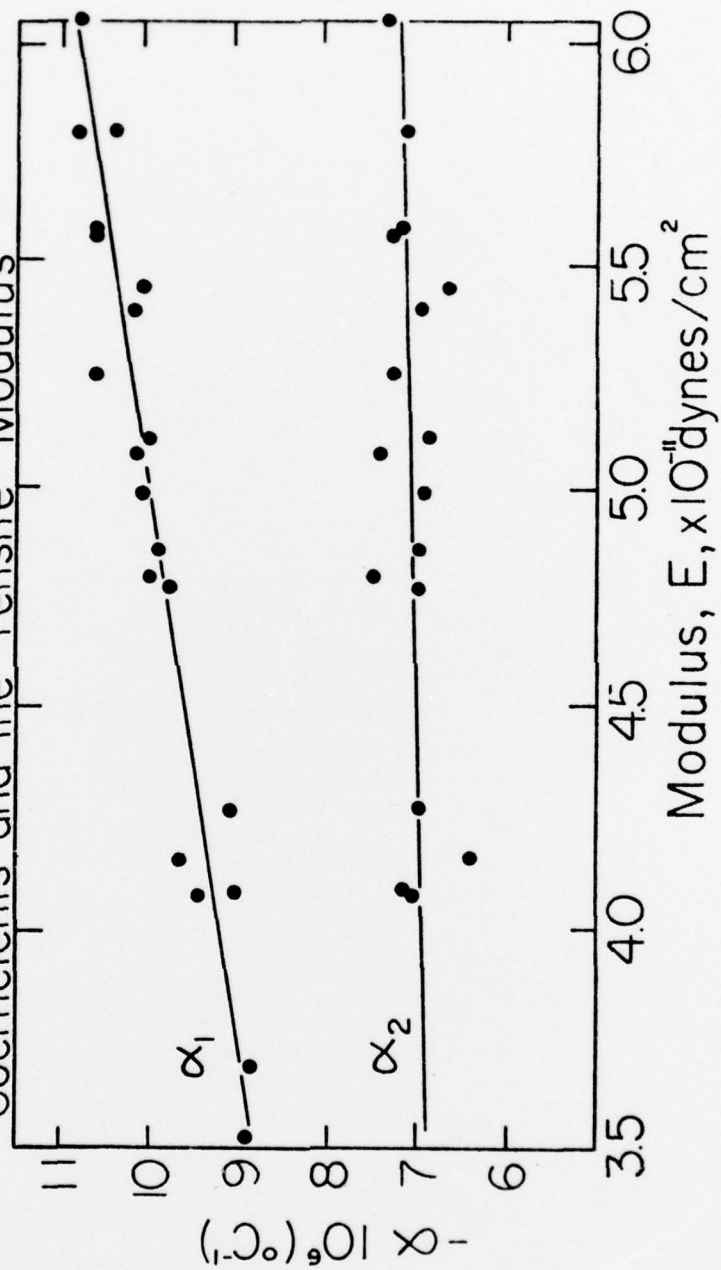
1. Specific change in length parallel to the fiber axis as a function of temperature.
2. Correlation between the thermal expansion coefficients α_1 and α_2 and the tensile modulus. α_1 for 70 to -35°C ; α_2 for -45 to -140°C .
3. Series-parallel model for the ultraoriented polyethylene fiber.

Ultraoriented Polyethylene
Specific Length Changes
With Temperature



Ultraoriented Polyethylene

Correlation Between the Thermal Expansion Coefficients and the Tensile Modulus



Series-Parallel Model
Depicting Changes in Length With
Stress and Temperature
for Ultraoriented Polyethylene Fibers

