Dynamic mechanical studies of oriented *p*-oxybenzoate (POB)–poly(ethylene terephthalate) (PET) copolyester films

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(*Received 20 February 1989; accepted 6 April 1989*)

The effects of orientation on the dynamic mechanical properties of *p*-oxybenzoate/poly(ethylene terephthalate) (POB/PET (60/40)) copolyesters were studied using films prepared by extrusion drawing and by uniaxially drawing sections of compression moulded sheets. The extrusion drawn sample ED-1 showed a higher degree of orientation than uniaxially drawn samples U-2S and U-8S. The loss tangent curves for these oriented samples are characterized by a β-relaxation at 62°C and a high temperature (α') relaxation. The position of the α'-relaxation peak is dependent on the degree of orientation. Samples U-8S ($f_H = 0.05$), U-2S ($f_H = 0.06$) and ED-1 ($f_H = 0.21$), have their α' relaxation peak at 135, 140 and 156°C, respectively. The dynamic storage modulus (E') below 50°C increases with the degree of orientation. The highly oriented sample ED-1 maintains its high storage modulus (4 GPa) over a larger temperature range (25–125°C).

(Keywords: liquid crystalline copolyester; dynamic mechanical properties; poly(*p*-oxybenzoate)–poly(ethylene terephthalate); orientation; small angle light scattering)

INTRODUCTION

Three structural factors are known to profoundly affect the dynamic mechanical properties of most conventional semicrystalline polymers including polyesters and polyamides. These factors are chemical structure, crystallinity, and molecular orientation[1,2]. The presence of aromatic groups, or double- and triple-bonded chemical moieties in a polymer molecule represent chemical entities which can restrict segmental motion and raise glass transition temperatures. In the case of crystallinity, the distribution of crystallites and the size of crystalline regions both affect segmental motion by altering the size and continuity of amorphous regions in which the mobile segments reside[1]. Molecular orientation, the third factor, mainly influences segmental motion by restricting the free volume available to each of the mobile segments[1].

In our preliminary communication[3], the influence of chemical structure on the dynamic mechanical properties of a series of liquid crystalline copolyesters, poly(*p*-oxybenzoate-*co*-ethylene terephthalate) (POB/PET), was examined. The effect of the chemical structure in these polyesters manifested itself in two ways: the phase segregation of rigid POB-rich and flexible PET-rich phases; and the relative distribution of the two phases. The rigid POB-rich phase consists of microblock sequences of *p*-oxybenzoate and terephthalic acid units in a 4:1 or greater ratio[3,4].

Segmental motion in the different copolyester compositions was dramatically affected by the size, distribution and proximity of rigid POB microblocks in each phase.

The study reported here focuses on the effect of uniaxial molecular orientation on segmental motion and dynamic relaxation spectra of a fixed copolyester composition, POB/PET (60/40). Both dynamic mechanical properties and small angle light scattering (SALS) studies are reported in order to form a correlation between molecular orientation, supramolecular structure (i.e., domains or ordered regions) and amorphous segmental mobility.

EXPERIMENTAL

Sample preparation

The material used in the present study was a POB/PET copolyester (Tennessee Eastman, Inc.) with molar composition of 60/40. The films of this copolymer were prepared by two different processes. Samples U-2 and U-8 were first compression moulded, and then uniaxially stretched using a T.M.Long Extensional Tester. The actual stretching process involved a 5 min preheat followed by stretching at a rate greater than 40% min^{-1} and with the transverse direction unconstrained. Sample ED-1 was prepared by a special die extrusion drawn process. In this process a hot POB/PET (60/40) melt (at 270°C) is forced through a ribbon die set at 220°C and then drawn uniaxially upon take-up of the film. *Table 1* summarizes the process conditions for the films investigated.

Orientation and moment ratio measurements

The orientation developed during the processing of the samples was studied with SALS. Isointensity contour plots of the SALS patterns were obtained by using an apparatus designed by Effler *et al.*[5].

The degree of orientation of each film was determined from SALS patterns using Herman's orientation function (f_H). Herman's orientation factors (f) were determined using the technique outlined in reference 6, with the value presented being the average f of two independent SALS patterns of the same specimen. A slight modification was

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0032-3861/89/122188-05$03.00

Table 1 Films studied

Film	Process	Process temperature (°C)	Extension ratio	Moment ratio	Orientation function
U-2	Compression moulded	285	1.00	1.07	0.05
U-2S	Uniaxially stretched	110	1.72	0.98	0.02
U-8	Compression moulded	285	1.00	1.07	0.05
U-8S	Uniaxially stretched	90	2.06	0.97	0.04
ED-1	Extrusion drawn	270		1.55[a]	0.16
				3.70[b]	0.21
				1.84[c]	0.15

[a] Machine direction at 0° to the polarizer
[b] Machine direction at 45° to the polarizer
[c] Machine direction at 90° to the polarizer

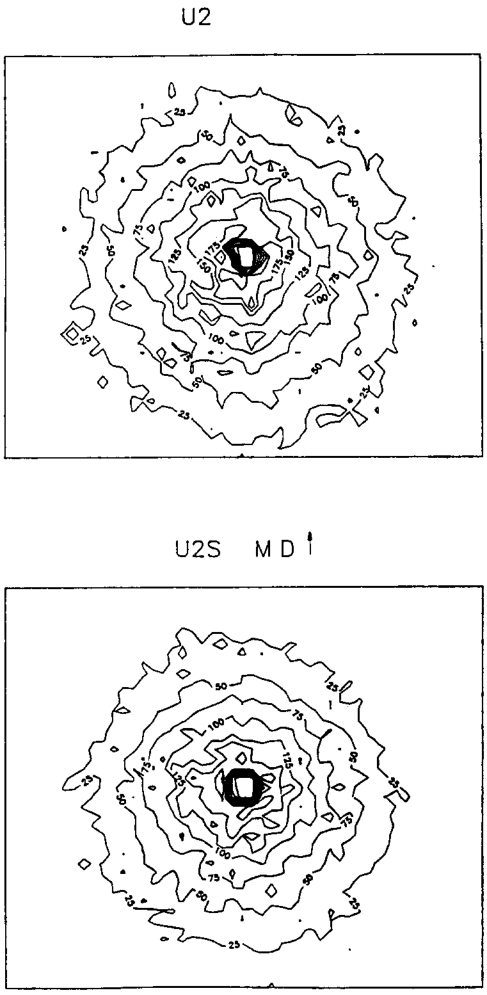

Figure 1 Small angle light scattering H_v patterns for samples U-2 (unstretched) and U-2S (stretched)

made to account for the appearance of anisotropic SALS patterns, where the streaklike pattern is aligned perpendicular to the orientation direction of the material. The reference direction (ϕ_{ref}) of the pattern was chosen to be 90° to the machine direction (MD). The $\langle \cos^2 \phi \rangle$ values were determined at $\mathbf{q} = 0.50\,\mu\text{m}^{-1}$, where $\mathbf{q}$ is the scattering vector. This value of $\mathbf{q}$ was chosen since it was common to all the patterns investigated, and close enough to the centre of the pattern to ensure that a large distribution of intensity values would be sampled. In determining the $\langle \cos^2 \phi \rangle$ values an average of 208 data points per SALS pattern was used, with 144 data points in one pattern being the minimum, and 264 data points in another being the maximum. The moment ratio (MR), presented in *Table 1*, were also determined from SALS patterns. These MR values represent the ratio of $\langle r^2 \rangle^{1/2}$ parallel and perpendicular to MD where r is the distance between scattering elements. A value greater than one indicates that the scattering particles are anisotropically shaped and oriented relative to MD. Since MR is a function of both shape and orientation it is not possible to separate the two. However, MR should reflect an orientation in the material due to an applied external force.

Dynamic mechanical measurements

The dynamic mechanical properties of the films were determined using an Autovibron (IMASS, Inc., USA). The storage modulus (E'), loss modulus (E'') and tan δ were measured at 110, 11, and 1.1 Hz at a heating rate of 1°C min^{-1}. The temperature range was −100 to 200°C.

RESULTS AND DISCUSSION

SALS measurements

The SALS H_v patterns for the uniaxially stretched samples U-2S and U-8S are given in *Figures 1* and *2*. These patterns are circularly symmetric and similar to their corresponding unstretched samples U-2 and U-8 which are also given in *Figures 1* and *2*. The calculated values for the moment ratio for samples U-2S and U-8S are approximately the same as the unstretched samples U-2 and U-8 (*Table 1*). Although samples U-2S and U-8S have been uniaxially stretched, the H_v patterns show no evidence to support the development of a preferred chain orientation within the films. Similarly, f (*Table 1*) has a value close to zero, which indicates the absence of preferred orientation. The lack of the development of orientation at an extension ratio of 2.0 for these copolyesters is not surprising since earlier studies by Shih *et al.*[7] found that a solvent treatment and extension ratio of 2.7 were required to obtain orientation in similar POB/PET samples.

The H_v patterns of sample ED-1 for measurements made with the polarizer at 0, 45 and 90° with respect to MD are given in *Figure 3*. These patterns are clearly asymmetric and therefore indicate the existence of preferential orientation of the polymer chains within these extrusion drawn films. The calculated values for f_H and MR given in *Table 1* indicate a certain degree of molecular orientation existing within the films. The development of orientation in sample ED-1 can be directly attributed to hot drawing.

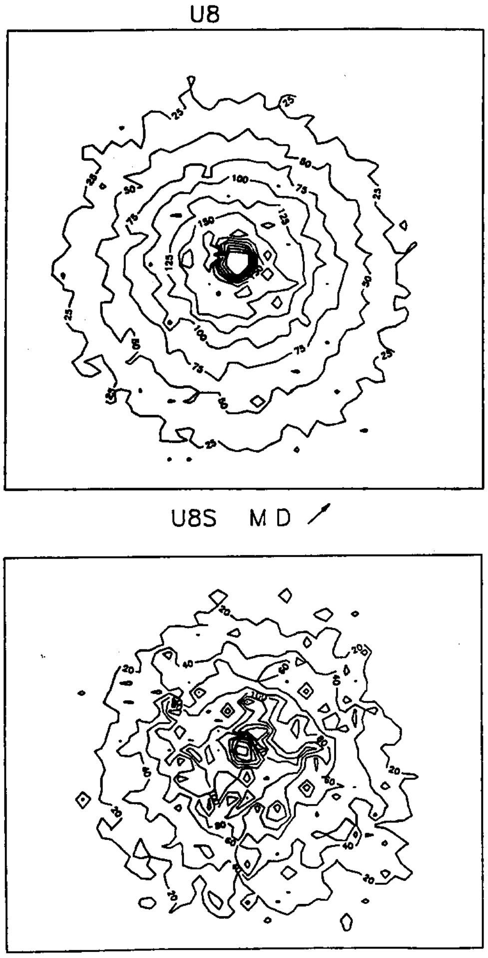

Figure 2 Small angle light scattering H_v patterns for samples U-8 (unstretched) and U-8S (stretched)

Dynamic mechanical measurements

The tan δ curves for all samples are given in *Figure 4*. The unstretched samples U-2 and U-8, as previously reported[3,8,9] exhibit four relaxation (γ, β, α and α') processes above room temperature and one additional relaxation process below room temperature. The γ-relaxation peak at 45°C, was assigned to local motions of PET segments found in the POB-rich phase. The β-relaxation peak at approximately 62°C was attributed to the motion of PET segments found in the PET-rich phase which have interactions with the POB comonomer units. An α-relaxation peak at approximately 88°C was attributed to main chain motions of PET segments located within the PET-rich phase in an environment which is similar to the homopolymer. This α relaxation at 88°C appears to be related to the glass transition temperature (T_g) of the PET-rich phase observed to occur between 80°C and 90°C in some differential scanning calorimetry (d.s.c.) studies[10,11]. The position of this T_g can vary between 60°C and 90°C, depending on the previous thermal history of the sample and the heating or cooling rates used in the d.s.c.[10–13]. The very broad α'-relaxation peak observed at 130°C was not previously assigned, but is very similar to high temperature relaxation processes observed in stretched PET. The nature and origin of this high temperature relaxation will be discussed later in this work.

The tan δ curves for oriented POB/PET copolyester films investigated (samples U-2S, U-8S and ED-1) are characterized by a β-relaxation process, a reduction in the intensity of the α-relaxation peak and the presence of a high temperature α'-relaxation process. In the case of the uniaxially oriented sample U-8S, the α- and β-relaxation peaks coalesce to form a broad peak

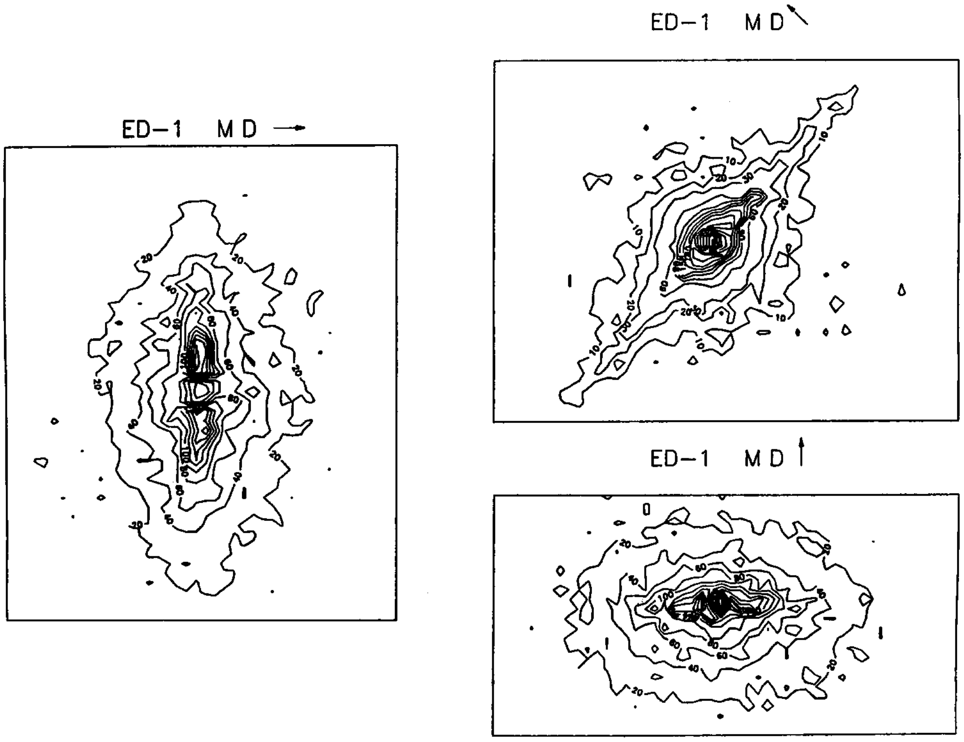

Figure 3 Small angle light scattering H_v patterns for sample ED-1 at 0, 45 and 90° with respect to the machine direction (MD)

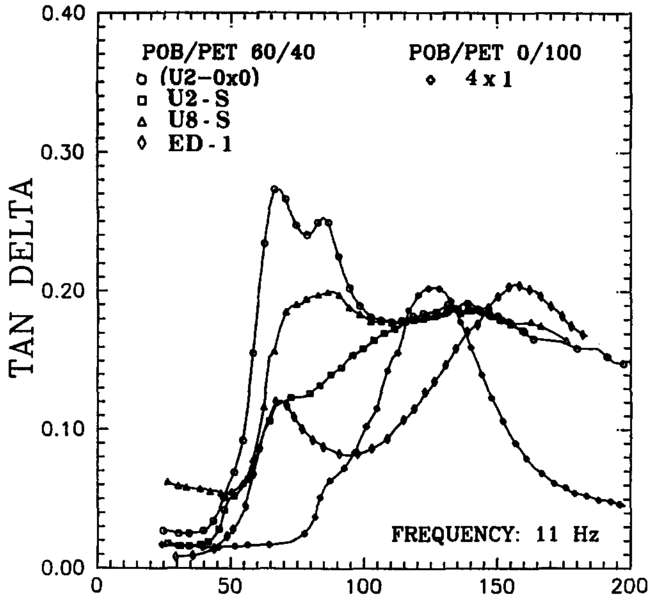

Figure 4 Tan δ–temperature curves for stretched samples of POB/PET (60/40) copolymers and PET

centred at 77°C. The position of the α'-relaxation peak in sample U-8S remains unchanged with respect to the unstretched sample U-8. The coalescing of these peaks is not thoroughly understood but preliminary indications attribute it to the development of slight restrictions to rotational motions of the ethylene groups.

The tan δ curve for sample U-2S is characterized by the presence of a β- and a very distinct α'-relaxation process. When compared with sample U-8S, we observe that the position and shape of the β-relaxation peak remains constant, the α relaxation has disappeared and the α' relaxation at 135°C is better defined. Davies and Ward[14] in their dynamic mechanical studies with drawn PET films observed a relaxation peak between 145°C and 150°C. Itoyama[15] observed a similar relaxation peak at 140°C in studies on cold drawn PET films. These high temperature peaks were associated with the relaxation of oriented chain segments[14]. The position of these relaxation peaks undergoes a gradual shift to higher temperatures with increasing extension ratio. The POB/PET (60/40) copolyesters are multiphase systems consisting of at least one PET-rich and one POB-rich phase[3]. The PET-rich phase contains morphological regions which are similar to amorphous PET and therefore, one would expect segments within these regions to become oriented and to observe the emergence of a high temperature relaxation peak above a critical extension ratio. Thus, the better defined α' peak observed in sample U-2S can be confidently assigned to relaxation of PET segments, which have been oriented upon the drawing of the films. The simultaneous disappearance of the α-relaxation peak can be attributed to the drastic reduction or elimination of the unoriented amorphous regions.

The development of orientation in sample U-2S is not evident from the SALS H_v patterns. However, scanning electron micrographs of these samples[5] showed parallel bands running normal to the stretching direction of the films. The existence of these bands, which are assumed to result from the slippage of parallel planar domains, provide evidence to support slight morphological changes in sample U-2S. In addition, sample U-2S was stretched at approximately 22°C above the temperature (88°C) at which the PET segments in the PET-rich phase achieve main chain motion. This means that only the flexible ethylene glycol residues of the PET could be oriented. Similar orientation should neither be expected or observed in sample U-8S because the stretching was performed at just 2°C above the temperature at which chain mobility begins. Apparently the orientation of a small number of these units does not affect the SALS H_v patterns.

The tan δ curve for sample ED-1 given in *Figure 4* exhibits a β- and a very distinct α'-relaxation peak at approximately 65 and 158°C, respectively. The α'-relaxation process observed in sample ED-1 occurs at a substantially higher temperature than previously observed for either the oriented PET or the uniaxially drawn sample U-2S. Based on oriented PET studies[9,14], the shift of the α'-relaxation process to higher temperatures must be the result of a higher degree of orientation within the sample ED-1 films. The development of a higher degree of orientation in these samples ED-1 is supported by the SALS studies. The H_v patterns (*Figure 3*) obtained at different angles with respect to MD are all asymmetric and their corresponding MR greater than the values obtained for samples, U-2S and U-8S (*Table 1*). The f_H values for sample ED-1 are all larger than for samples U-2S and U-8S.

The higher level of orientation in the ED-1 sample is a consequence of the unique extrusion–draw process employed at Virginia Polytechnic Institute and State University to prepare the film. In this process, the POB/PET (60/40) melt is heated at 270°C, a temperature 10–20°C above the POB-rich phase melting endotherm occurring between 250°C and 260°C[10–13,16]. The melt is extruded through a cooler die, set at 220°C or some 30°C above the PET-rich phase melting endotherm near 190°C[10,12,16]. The ribbon extrudate exiting from the die is uniaxially drawn to produce an oriented film. This extrusion–drawing process of T. Wilson and D. G. Baird represents an extension of the work reported earlier by

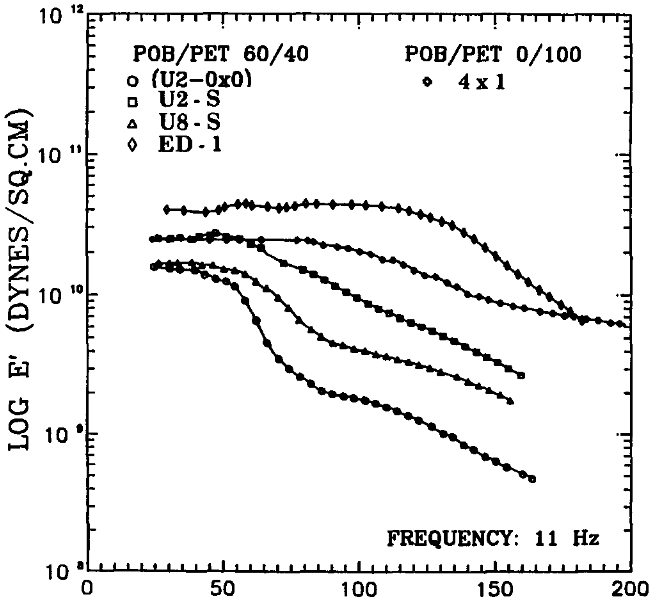

Figure 5 Storage moduli (E') curves for stretched samples of POB/PET (60/40) copolymers and PET

Done and Baird[17]. This earlier study reported dynamic rheological measurements of the POB/PET (60/40) melts and compared ribbons extruded from melts at the same temperature as the die, 220°C, with these extruded from higher temperature melts (260°C) and a cooler die (220°C). The dynamic rheological measurements[17] of viscosity, η, and shear modulus, G', suggested the presence of a 'supercooled nematic state' for the POB/PET (60/40) melt between 190°C and 260°C. Based on this 'supercooled nematic state', Done and Baird[17] concluded that the melt could be readily deformed at temperatures above 190°C and conceived the 'hot melt (260°C)–cool die (220°C)' extrusion process. Scanning electron micrographs[17] of the ribbons indicated the hot melt–cool die process increased the level of surface orientation when compared with the 220°C melt–220°C die process. In contrast however, wide angle X-ray diffraction studies[17] of the same samples indicated the level of overall or bulk orientation was lower for the 260°C melt–220°C die process ribbons.

The E' values of the oriented samples are given in *Figure 5*. The unoriented sample U-2 has the lowest value and the overall curve exhibits characteristics of a system with a certain degree of phase separation[18]. The qualitative knowledge obtained from the shape of the storage modulus curve agrees with morphological studies on POB/PET (60/40) copolyester which proposes a multiphase system consisting of at least one PET-rich and one POB-rich phase[4]. Samples U-8S and U-2S show progressive increases in E over the entire temperature range and apparent differences in the degree of phase separation. For sample U-8S, the temperature range over which E' decreases is similar to that observed for the unoriented sample U-2, but the modulus after the transition is higher. After an initial increase in the E' curve for sample U-2S, it shows a steady decrease over a very wide range. Qualitatively the E' curve for sample U-2S corresponds to a polymeric multiphase system with very little phase separation. The E' curves for samples U-8S and U-2S suggest some morphological differences amongst them. These differences can be related to the fact that sample U-2S was stretched at a temperature that permitted development of a small degree of orientation. The extrusion drawn film, sample ED-1, has the highest overall E' and exhibits a curve which is characteristic of a single phase system. The E' of sample ED-1 remains at approximately 4 GPa up to 125°C, then decreases to 0.6 GPa at 185°C. An oriented sample of PET (*Figure 5*) exhibits a similar behaviour. The E' value remains constant at approximately 1.5 GPa up to 85°C and then gradually decreases to 0.6 GPa at 200°C. The ability of sample ED-1 to maintain a high modulus over such a wide temperature range is due to the orientation imposed on the PET segments by the drawing process. The larger decrease in E' of sample ED-1 above 125°C as compared with sample PET (4 × 1), can be attributed to the phase-separated morphology of the POB/PET copolymer which prohibits complete alignment of the chains.

A review of the E' curves for samples U-2S and ED-1 shows an increase in the modulus at approximately 45 and 52°C, respectively. These increases suggest that a certain amount of molecular rearrangement takes place during the heating cycle. This rearrangement, although not yet understood, appears to be associated with the POB segment since it is absent in the oriented PET (*Figure 3*). Also the temperature at which the rearrangement begins shows a dependence on the initial degree of orientation, for samples U-2S and ED-1 the reorganization starts at 45 and 52°C, respectively.

CONCLUSIONS

Dynamic mechanical analysis of oriented POB/PET (60/40) copolyesters reveals the existence of α'- and β-relaxation processes. The β-relaxation process is independent of degree of orientation and occurs at approximately 62°C for all samples studied. The α'-relaxation process occurs at high temperatures and its position is dependent on the degree of orientation of the PET units. The highest temperature for α'-relaxation process was 158°C obtained for sample ED-1 with f_H of 0.21.

The E' values of the oriented POB/PET (60/40) copolymers show a dependence of the degree of orientation. Sample ED-1 with the largest degree of orientation ($f_H = 0.21$) has a low temperature storage modulus of 4 GPa, a much higher value than the 1.5 GPa observed for either samples PET (stretched 4 × 1) or U-2S (stretched 2 × 1). The temperature range over which E' remains constant is also influenced by orientation.

ACKNOWLEDGEMENT

The sample ED-1 was kindly provided by Professor D. Baird and T. Wilson of Virginia Polytechnic Institute and State University.

REFERENCES

1 Dumbleton, J. H. and Murayama, T. *Kolloid-Z. Z. Polym.* 1967, **20**, 41

2 McCrum, N. G., Read, B. F. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Ch. 13, John Wiley and Sons, New York, 1967

3 Benson, R. S. and Lewis, D. N. *Polym. Commun.* 1987, **28**, 289

4 Nicely, V. A., Dougherty, J. T. and Renfro, L. W. *Macromolecules* 1987, **20**, 573

5 Effler, L. J., Lewis, D. N. and Fellers, J. F. in 'Polymer Association Structures Liquid Crystals and Microstructures' (Ed. by M. El-Nokaly), ACS Symposium Series, Washington, 1989; Effler, L. J. *MS Thesis*, University of Tennessee, 1987

6 Alexander, L. A. 'X-Ray Diffraction Methods in Polymer Science', Robert E. Drieger Publishing Co., New York, 1979

7 Shih, H. H., Hornberger, L. E., Siemens, R. L. and Zachariades, A. E. *J. Appl. Polym. Sci.* 1986, **32**, 4897

8 Takase, Y., Mitchell, G. R. and Odojima, A. *Polym. Commun.* 1986, **27**, 76

9 Gedde, U. W., Buerger, D. and Boyd, R. H. *Macromolecules* 1987, **20**, 988

10 Wissbrun, K. F. *Br. Polym. J.* 1980, **12**, 163

11 Meesiri, W., Menczel, J., Gaur, U. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 719

12 Viney, C. and Windle, A. H. *J. Mater. Sci.* 1982, **17**, 2661

13 Menczel, J. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1433

14 Davies, G. R. and Ward, I. M. *J. Polym. Sci. A2* 1972, **10**, 1153

15 Itoyama, K. *J. Polym. Sci. C* 1987, **25**, 331

16 Lewis, D. N. *PhD Dissertation*, University of Tennessee, 1986

17 Done, D. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 816

18 Bonart, R., Morbitzer, L. and Renke, H. *Kolloid-Z. Z. Polym.* 1970, **240**, 807