JOURNAL OF MATERIALS SCIENCE 18 (1983) 2969–2975

Surface controlled crystallization of poly(tetramethylene terephthalate)

H. GHAVAMIKIA, S. E. RICKERT
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

Epitaxial crystallization of poly(tetramethylene terephthalate) from dimethyl phthalate solution on alkali halide crystals has been studied using electron microscopy and electron diffraction techniques. Rod-like crystals oriented in the ⟨1 1 0⟩ directions of the substrate were found to form at short crystallization times. At longer times, however, lamella-like crystals, which were nucleated at the sides of the rod-like crystals, grew in directions dictated by the substrate. Besides the normal bidirectional orientations induced by the substrate, the polymer crystals showed twinning which was found to be due to the triclinic lattice structure of the polymer.

1. Introduction

This paper reports our initial attempt to study morphological changes which accompany stress-induced phase transitions in poly(tetramethylene terephthalate) (PTMT). PTMT has become a subject of interest over the last few years as it became evident that many of its useful properties are related to a stress-induced reversible phase change which can take place [1]. The structures of the two known phases (α: relaxed, β: under strain) have been studied in detail [2–5]; and although there are some discrepancies on the lattice parameters of the β-phase, there is almost a general agreement with respect to the lattice parameters of the α-phase, as is shown in Table 1.

Stambaugh *et al.* [6–8] re-examined the β-phase crystal structure of PTMT using X-ray and infrared techniques and confirmed values given by Mencik [3]. Therefore, in the present work (although it does not change any conclusion) the β-phase lattice parameters given by Mencik were used.

2. Experimental details

In order to carry our morphological studies of PTMT, it is necessary to have well defined single crystals of this polymer. However, due to the stiffness of the chain backbone, it is almost impossible to grow a large enough single crystal for direct mechanical testing.

Epitaxial crystallization of PTMT from a dilute solution on alkali halides seems to be an appropriate approach for production of a thin film of oriented single crystals. The epitaxial method is well known to produce crystalline films from hard-to-crystallize materials. A group of oriented crystals of PTMT would show the same behaviour as a larger single crystal would show to an applied strain. Further an unaxial strain can be applied in thin films merely by pulling the supporting film. The phase transition rate can be controlled by the draw direction.

Since epitaxial crystallization of PTMT has not been studied before, some preliminary experiments were run to identify an acceptable solvent. Nitrobenzene and dimethylphthalate were found to be suitable solvents and the latter was chosen for safety reasons. In the course of experimentation, three different polymer concentrations, i.e. 0.01, 0.05 and 0.3%, were used and we observed that the higher the concentration, the higher the nucleation density and the initial growth rate. This is in accordance with previous observations [9]. Experiments were carried out using KI, KBr, NaCl and KCl substrates at the same polymer concentration and temperature.

0022–2461/83 $03.00 + .12

TABLE I Unit cell data

Reference	*a* (nm)	*b* (nm)	*c* (nm)	α^0	β^0	γ^0	Volume (nm^3)
Menchik [2]	0.483	0.596	1.162	99.9	115.2	111.3	0.2600
Yokouchi *et al.* [3]	0.483	0.594	1.159	99.7	115.2	110.8	0.2604
Hall and Pass [4]	0.489	0.595	1.167	98.9	116.6	110.9	0.2628
Desborough and Hall [5]	0.487	0.599	1.167	99.8	116.2	110.9	0.2629

On the basis of the growth rate, the amount of growth after 30 min and the nucleation density, KCl was found to be the best substrate. Changing the substrate had no effect on the phase of PTMT produced. The crystallizations were carried out by cleavage of the salt at the crystallization temperature in the solution. This provided two fresh surfaces for adsorption at a well-controlled starting point.

Epitaxial crystallization of PTMT, therefore, was carried out using solutions of 0.05 wt % polymer in dimethylephthalate on KCl at different temperatures. The resulting films were Pt/C coated, removed from the surface by substrate dissolution in water and picked up on the water surface by copper EM grids. These grids were examined in the bright field and diffraction modes using a Jeol 100B transmission electron microscope. The result of these experiments follows.

3. Results and discussion

At the temperature range from 170° C to the melting point of PTMT, i.e. 228° C, sporadic nucleation and deposition of the polymer on the substrate takes place (Fig. 1). Results show that although the deposited material is to some extent oriented in both of the ⟨1 1 0⟩ directions of the substrate, diffraction patterns could not be obtained. This is probably due to the thinness and poor crystallinity in these samples. This behaviour has also been observed from other polymers like polyethylene [10] when the high molecular weight fraction is preferentially adsorbed.

At a temperature range from about 150 to 170° C, rod-like crystals were observed to grow in the ⟨1 1 0⟩ directions of the salt. The lower the temperature, the thicker these crystals grew in a given time period. Fig. 2a shows crystals grown on KCl at 155° C for 30 sec and Fig. 2b

Figure 1 Electron micrograph of high molecular weight PTMT epitaxially crystallized on KCl for 5 min at 190° C. Arrow points in the substrate ⟨1 1 0⟩ direction.

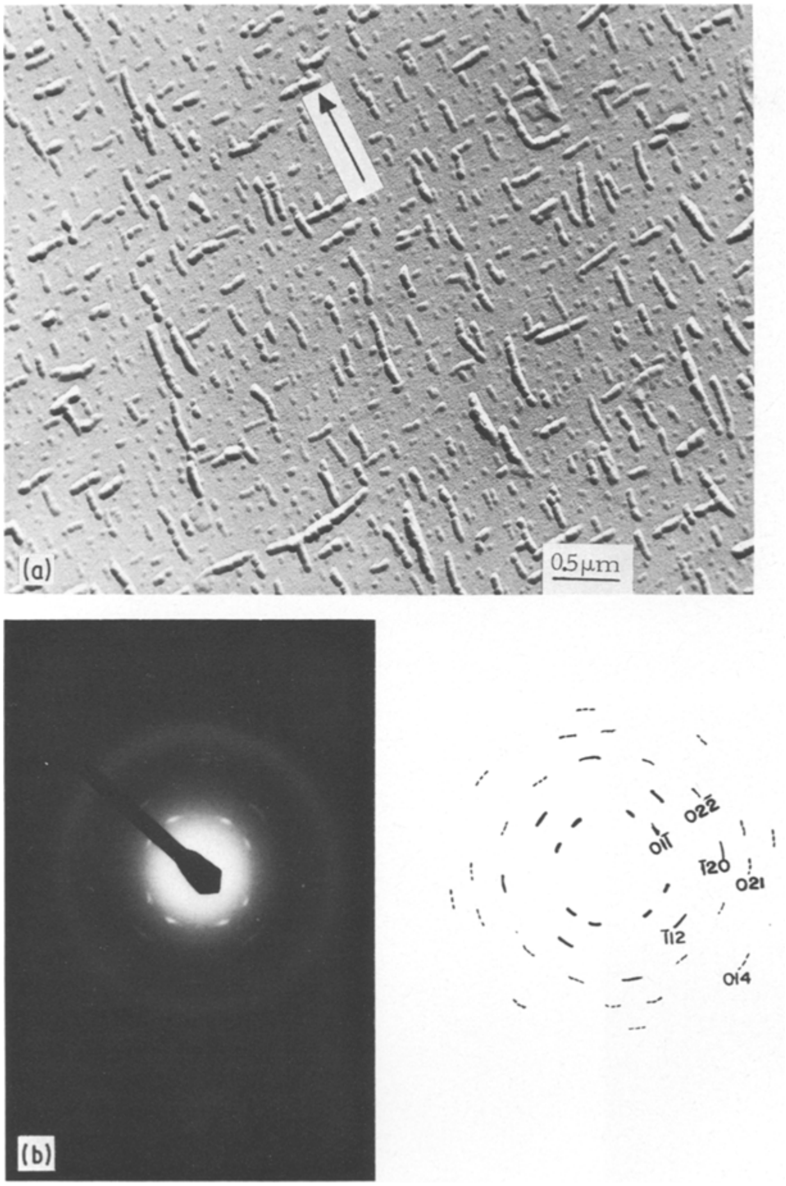

Figure 2 (a) Electron micrograph of PTMT epitaxially crystallized on KCl for 30 sec at 155° C. Arrow points in the substrate ⟨1 1 0⟩ direction. (b) Electron diffraction pattern and indexing scheme obtained from PTMT rod-like crystals shown in Fig. 2a.

is the diffraction pattern of the same area. It is evident that the chain axis of the molecules is parallel to the (1 0 0) plane of the substrate and aligned in two directions 90° apart, i.e. the ⟨1 1 0⟩ and ⟨1 $\bar{1}$ 0⟩ directions.

At longer times, the rod-like crystals grow as thick as 50 nm without any change in width but, most important, the molecules start crystallizing with their chain axes perpendicular to the surface, giving rise to lamella-like crystals (Fig. 3a). Fold surface epitaxy (FSE) seems to be a more descriptive term for this type of growth in contrast with fold plane epitaxy (FPE) which describes rod-like crystals (Fig. 4). These terms refer to the top plane of each crystal. FSE has the fold tips in this plane, whereas FPE has the chains in this plane. Dense nucleation and growth at 150° C led to rows of highly oriented FSE lamellae (Fig. 5).

Close examination of the diffraction patterns show the FSE nucleation takes place such that the *b*-axes of the two types of crystals fall in the same direction.

The nucleation and growth of the FSE crystals on the substrate, has been observed in other systems [11, 12] but so far has been misinterpreted as a "collapsed" or "toppled over" part of overgrown rod-like crystals. What is common

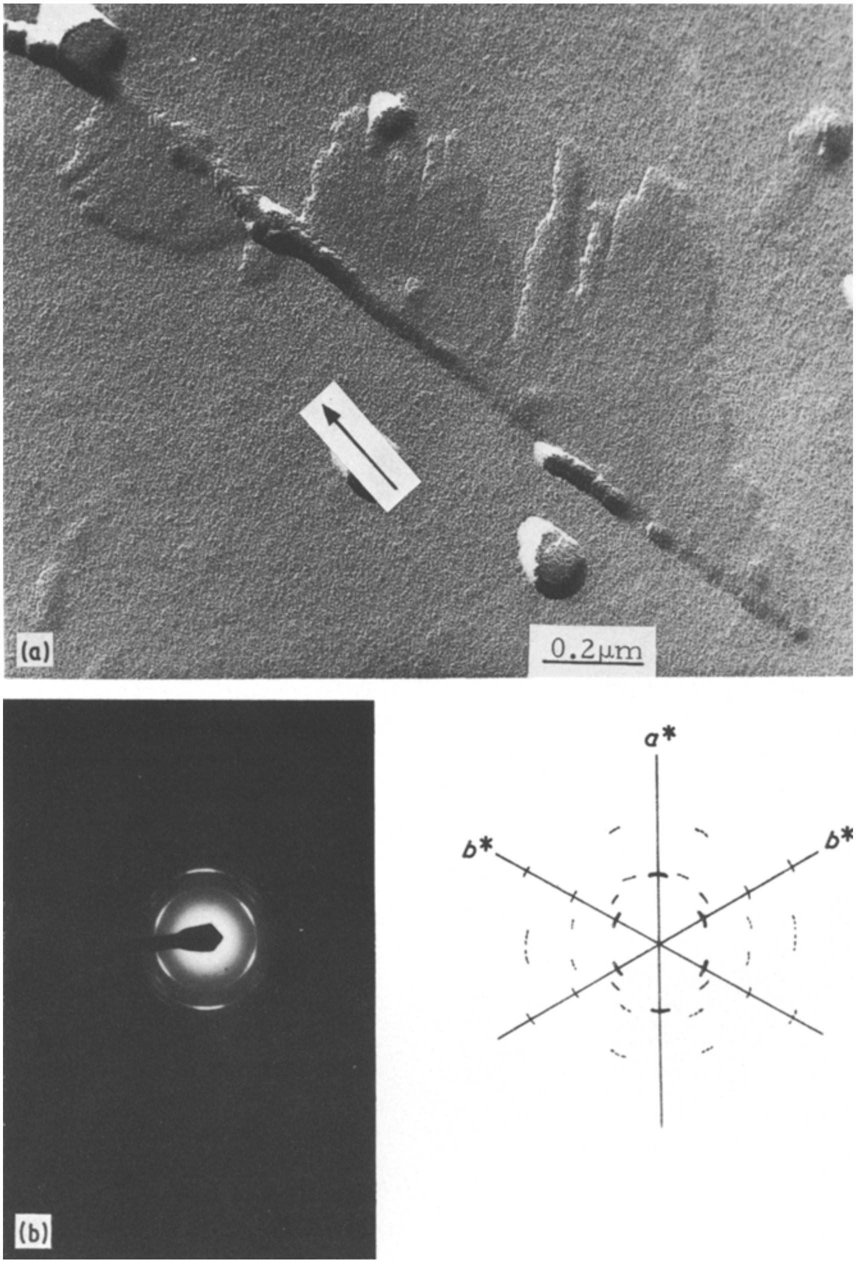

Figure 3 (a) Electron micrograph of PTMT epitaxially crystallized on KCl for 5 min at 155° C. Arrow points in the substrate ⟨1 1 0⟩ direction. (b) Electron diffraction pattern and indexing scheme obtained from PTMT lamella-like crystals shown in Fig. 3a.

among those situations is that for one reason or another, rod-like crystals do not cover much of the surface of the salt and polymer molecules find it easier to nucleate and grow at the sides of the overgrown rod-like crystals with their chain axes perpendicular to the surface rather than merely grow on top of the few existing sites.

As to the morphology of the rod-like crystals, they accept a feather-like pattern with a central line along the FPE rod. Closer observations show that each rod-like crystal is composed of smaller entities (Fig. 6). Diffraction patterns show that besides orientation in the ⟨1 1 0⟩ and ⟨1 $\bar{1}$ 0⟩ directions, there is a twinning which occurs along the (0 1 0) plane. This twinning happens because the crystals which are growing with their *c*-axes in the ⟨1 1 0⟩ direction have two equally possible

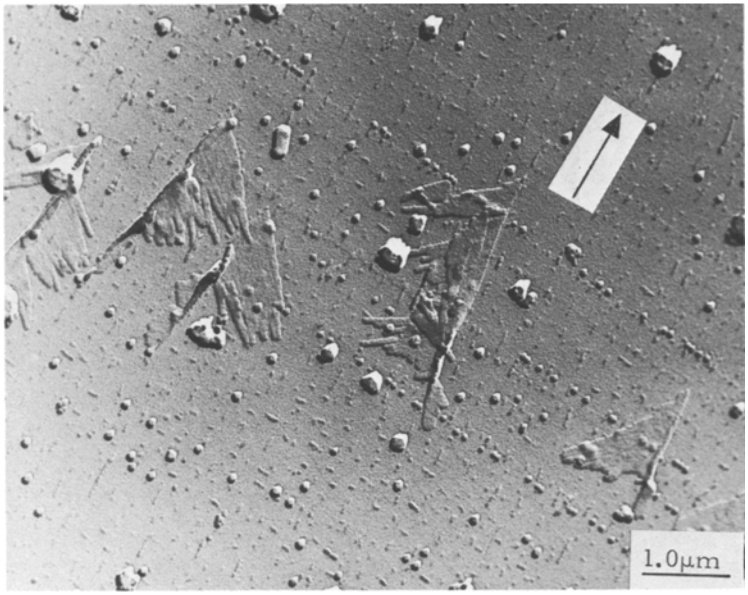

Figure 4 Electron micrograph of PTMT rod-like crystals and lamella-like crystals, epitaxially grown on KCl for 5 min at 155° C. Arrow points in the substrate ⟨1 1 0⟩ direction.

directions for the *b*-axis. This double orientation of the molecules might be the reason for the observed discontinuity in the morphology of the rod-like crystals (Fig. 6).

FSE crystals, because of how they nucleate, accept the orientations associated with the FPE crystals plus a double orientation with respect to the (1 0 0) plane. This happens again for the same reason, i.e. in a crystal with a given *b*-axis there are two equally possible directions for the *a*-axis. Fig. 3b shows a diffraction pattern from a part of a crystal which focuses on this effect. One can also observe a pattern of double orientation with its plane of twinning at ($7\bar{3}0$) (see Fig. 7). This is due to the fact that the *b*-axis of FSE crystals is the same as that of FPE crystals. As was mentioned before, there are two directions for the *b*-axis of FPE crystals with an angle 20° apart. This gives rise to a double orientation when FSE crystals grow on the side of rod-like crystals.

Although the crystal growth of PTMT seems very complicated and inconvenient for further study, one has to bear in mind that it is always possible to find regions, due to surface defects in the substrate, where some orientations are preferentially favoured. Therefore the number

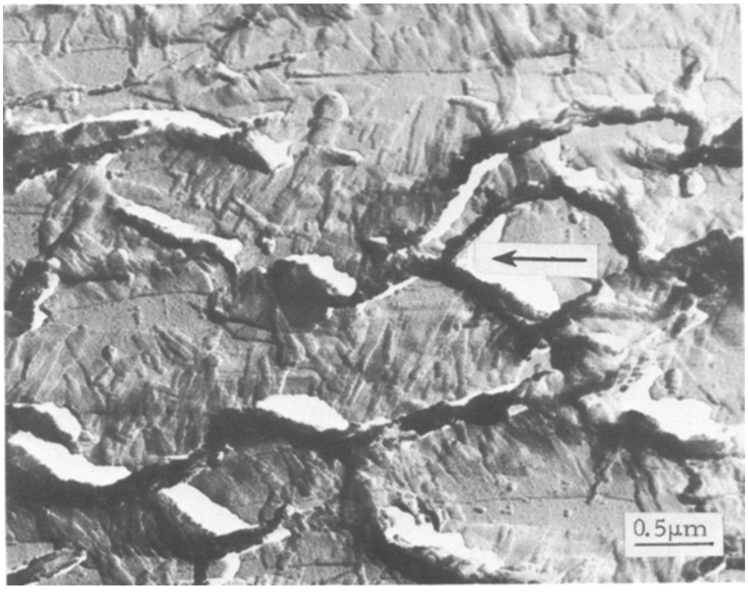

Figure 5 Electron micrograph of PTMT lamella-like crystals densely grown on KCl at 150° C for 5 min. Arrow points in the substrate ⟨1 1 0⟩ direction.

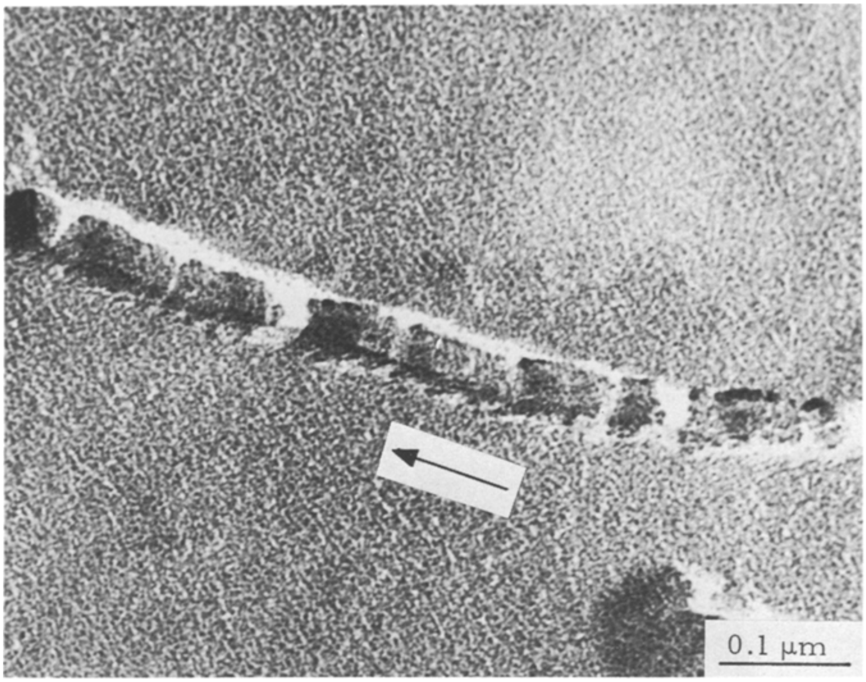

Figure 6 Electron micrograph of a PTMT rod-like crystal grown on KCl for 30 sec at 155° C. Discontinuity in the morphology of the crystal is in evidence. Arrow points in the substrate ⟨1 1 0⟩ direction.

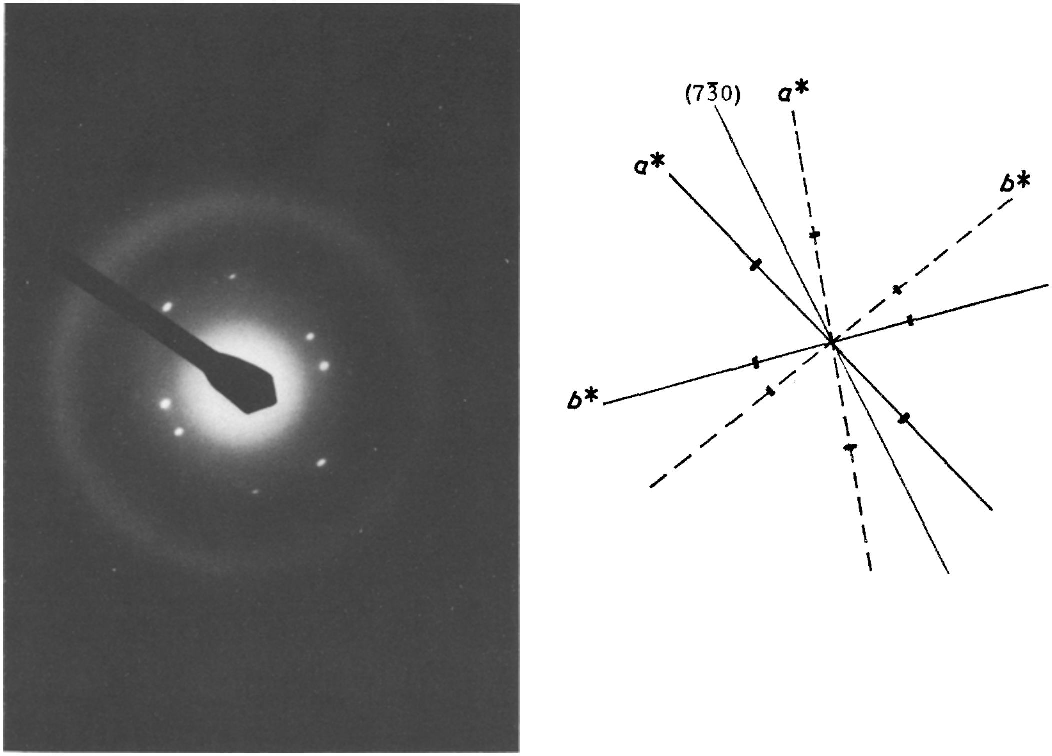

Figure 7 Electron diffraction pattern and indexing scheme obtained from PTMT lamella-like crystals showing double orientation with its plane of twinning at (7$\bar{3}$0).

of variables is decreased in these cases. This preliminary examination of PTMT crystallization has given insight into the mechanism of the epitaxial crystallization of polymers with a triclinic structure as well as paving the way for further studies of morphology of this type of crystal under strain.

4. Conclusions

Poly(tetramethylene terephthalate) (PTMT) has been crystallized as both rod-like and lamellae crystals on the (100) freshly cleaved surfaces of a variety of monovalent alkali-halides. The nature of the interaction was an epitaxial one. Both the fold planes and fold surfaces of PTMT were observed to orient along certain preferred substrate directions.

Thus, the presence of a single crystal surface was sufficient to allow the growth of distinct crystal morphologies of PTMT which are easily isolated for individual observation in an electron microscope. Such a technique should prove useful in allowing a detailed study of morphology changes accompanying deformation of PTMT. This study is being currently pursued.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Science Foundation Polymer Program under Grant No. DMR81-19425. In addition, we are most grateful to Dr J. B. Lando for his advice and stimulating discussions on the results of this work.

References

1. C. A. BOYE and J. R. EVERTON, *Bull. Amer. Phys. Soc.* 19 (1974) 352.
2. Z. MENCIK, *J. Polym. Sci. Polym. Phys. Ed.* 13 (1975) 2173.
3. M. YOKOUCHI, K. SAKAKIBARA, Y. CHATANI, M. TADOKORO, T. TANAKA and K. YODA, *Macromolecules* 9 (1976) 366.
4. I. H. HALL and M. G. PASS, *Polymers* 17 (1976) 807.
5. I. J. DESBOROUGH and I. H. HALL, *ibid.* 18 (1977) 825.
6. B. STAMBAUGH, J. L. KOENIG and J. B. LANDO, *J. Polym. Sci. Polym. Lett. Ed.* 15 (1977) 299.
7. *Idem, J. Polym. Sci. Polym. Phys. Ed.* 17 (1979) 1063.
8. *Idem, ibid.* 17 (1979) 1053.
9. S. WELLINGHOFF, F. RYBNIKAR and E. BAER, *J. Macromol. Sci. Phys.* **B10** (1974) 1.
10. G. ELIOPOULOS, MS Thesis, Case Western Reserve University (1978).
11. S. E. RICKERT and E. BAER, *J. Appl. Phys.* 47 (1976) 4304.
12. J. A. KOUTSKY, A. G. WALTON and E. BAER, *J. Polym. Sci.* A-2 4 (1966) 611.

Received 12 October 1982
and accepted 18 February 1983