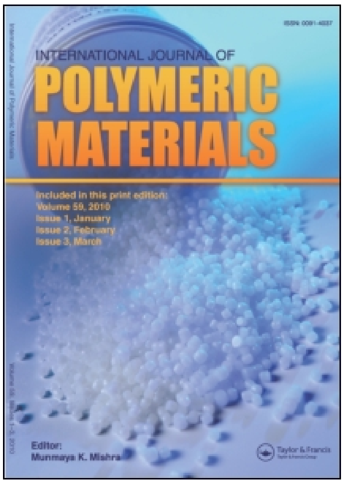

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The Structure of High Molecular Weight Linear Polyethylene Injection Moulded at High Pressures

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High density polyethylene with a low melt flow index (0.1 g/10 min) was injection moulded at pressures ranging from 100 to 500 MPa. The tensile modulus and strength in the flow direction increased substantially with the injection pressure. Three regions are characteristic of the specimens produced; a thin layer near the surface, a transition layer beneath the skin, and a core. DSC, wide angle X-ray scattering (WAXS), scanning and transmission electron microscopy were used to study the structure of the different layers. It was concluded that the skin was slightly oriented containing primarily chain-folded lamellae; the transition layer had a fibre texture and was oriented in the flow direction; the orientation of the core was similar to that of the transition layer but contained extended chain-morphologies similar to those found by Porter *et al.* in capillary extruded specimens. The composite structure gives rise to the improvement of mechanical properties and the increase in modulus is due to the core material. A monoclinic phase in the core was found by X-ray diffraction.

INTRODUCTION

During recent years there has been considerable interest devoted to the development of certain high-modulus materials, mainly from polyethylene,[1–6] using solidification under high pressure. The increase in strength of polyethylene is interpreted as a formation of an extended chain component in the crystal structure. The majority of methods for producing these materials are laboratory techniques, difficult to apply in processing. Commercially, it would be important if such techniques could be applied in practice. We have developed a method achieving similar results with a conventional injection moulding process.[7] The aim of this communication is to describe the structure of the material obtained in this way. Structure elements of the extended chain type can be found in our material, which, according to the laboratory experiments mentioned above, give rise to the high strength and modulus.

EXPERIMENTAL

Material and injection moulding

High density polyethylene (DMDS-2215, Unifos Kemi AB), with a density of 0.953 g/cm^3 and a very low melt flow index (high molecular weight) 0.1 g/10 min (MFI 190/2) was injection moulded using a modified conventional injection moulding machine (Engel 500/250 AS). The injection pressure was varied between 100 and 500 MPa, the cylinder temperature was 250–280°C and the mould temperature 30°C. Details of the moulding procedure have been described earlier.[7,8]

The injection moulded specimens were small tensile test bars with a gauge length of 25 mm, width 5 mm and thickness of 1.5 mm, see also ref. 8. The flow direction of the molten polymer was along the gauge length.

Scanning electron microscopy

Scanning electron micrographs from gold coated fracture surfaces were obtained using a JSM/U3, JEOL.

Differential scanning calorimeter experiments

DSC-endotherms of thin slices (30 μm) of the specimens, cut with a microtome, were determined with a Perkin Elmer, DSC 2-instrument. The slices were cut at different depths from the surface of the samples. The accuracy of these measurements was ± 2°C, and the heating rate 10 K/min.

Wide angle X-ray scattering (WAXS)

Wide angle X-ray photographs were taken at room temperature using nickel-filtered copper K_a radiation and a pin-hole camera. Thin slices (30 μm) of the specimens were mounted with their planes and flow directions perpendicular to the incident X-ray beam.

Transmission electron microscopy

Transmission electron micrographs were obtained from ultra-microtomed slices and from samples etched with fuming nitric acid using a Philips 300 electron microscope operated at 100 kV in defocusing mode.

Crystallinity measurements

The crystallinity of the specimens were evaluated from density measurements using the following values of the amorphous (ρ_a) and crystalline (ρ_c) component, $\rho_a = 0.851$ g/cm^3 and $\rho_c = 1.000$ g/cm^3, respectively. The density measurements were performed with a density column containing a mixture of isopropanol and water.

RESULTS

Figure 1 shows an optical micrograph of the fracture surface of a polyethylene sample, injection moulded with an injection pressure of 500 MPa. The sample had been cooled with liquid nitrogen prior to testing. A core region in the centre of the sample can clearly be distinguished, comprising about one third of the volume of the specimen. The core was only found in specimens moulded at pressures exceeding 300 MPa. The thickness of the core increased with the injection pressures.

Scanning electron micrographs from fracture surfaces of samples moulded at 100 and 500 MPa are given in Figure 2. The micrographs are taken from the

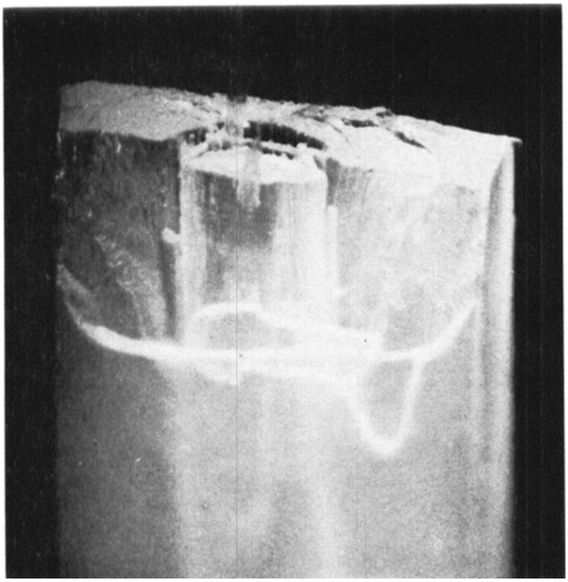

FIGURE 1 Optical micrograph of a fracture surface from a sample moulded at 500 MPa. Original magnification 10×.

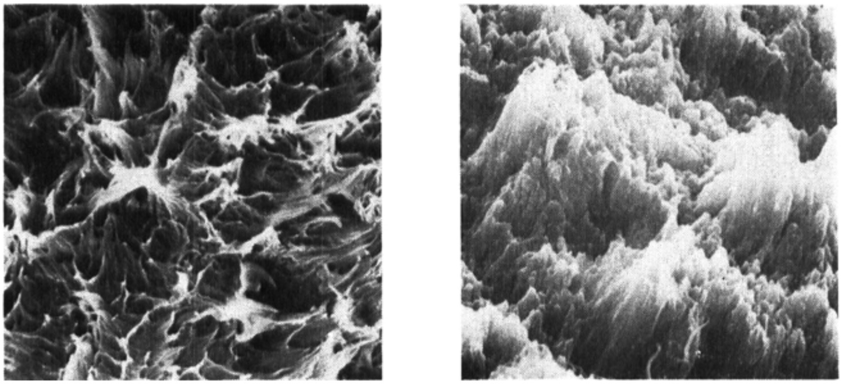

FIGURE 2 Scanning electron micrographs from the core region of fracture surfaces. Samples moulded at 100 MPa (left) and 500 MPa (right), respectively. Original magnification 1000×.

core region. The fracture surface of the 500 MPa sample has a fibrous appearance, contrary to samples produced at lower pressures.

A full account of the mechanical properties of the samples and their dependence on the injection pressure has been reported earlier.[7] In Figure 3 only the stress–strain properties of the bulk material and the core for specimens moulded at 500 MPa are shown. For the bulk material the elastic modulus (*E*) was 3.4 GPa and the tensile strength (σ_B) 130 MPa, while for the core the corresponding values were 5.0 GPa and 180 MPa, respectively. Obviously, the material behaves as a composite with a very strong core. In Figure 3 the

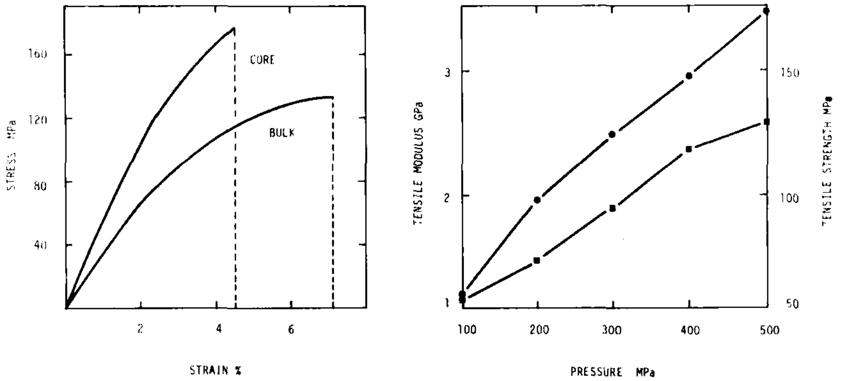

FIGURE 3 Stress–strain curves (nominal values) for the bulk sample and the core material; both curves relate to the flow direction (left figure). Injection pressure 500 MPa. The right figure displays the pressure dependence of the tensile modulus, *E*, (●) and the tensile strength at break, σ_B (■).

pressure dependence of E and σ_B for the bulk samples is also given. Both E and σ_B increased significantly with the injection pressure while the elongation at rupture decreased.

DSC-endotherms from thin slices taken from the skin and core region of samples moulded at 490 MPa are displayed in Figure 4. In both cases two melting peaks are observed, one at 128°C and the other at 137°C. The intensity of the second melting peak is much stronger for the slices taken from the core region. For samples moulded at pressures at 200 MPa and below only small irregularities in the DSC-endotherms are noted in the temperature region above 130°C.

In Figure 5 wide angle X-ray diffraction patterns are given for the three regions discussed above. The injection pressures are 100 and 500 MPa. From the results of the X-ray scattering and the optical microscopy it was concluded that the specimens could be divided into three regions; a thin surface layer (skin), a transition layer (shear zone) beneath it, and a core. At all pressure levels the molecules in the transition and core regions are oriented in the flow direction with about the same degree of orientation. The injection pressure does not influence the degree of orientation to any larger extent. The diffraction pattern of the surface layer shows a somewhat slighter preferred orientation of the molecular chains in the flow direction.[9] For the 500 MPa sample diffraction from a monoclinic structure appeared; being more intense in the core region

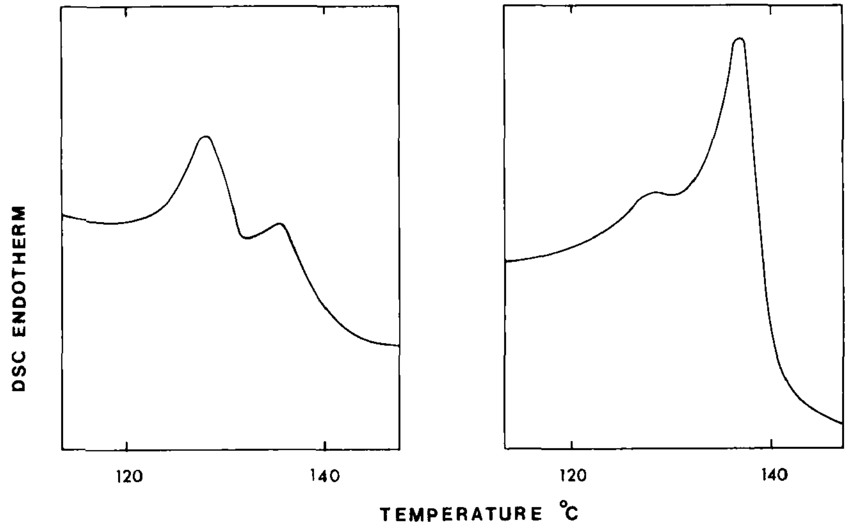

FIGURE 4 DSC endotherms (arbitrary units) for the skin (left) and core material (right). Injection pressure 490 MPa and heating rate 10 K/min.

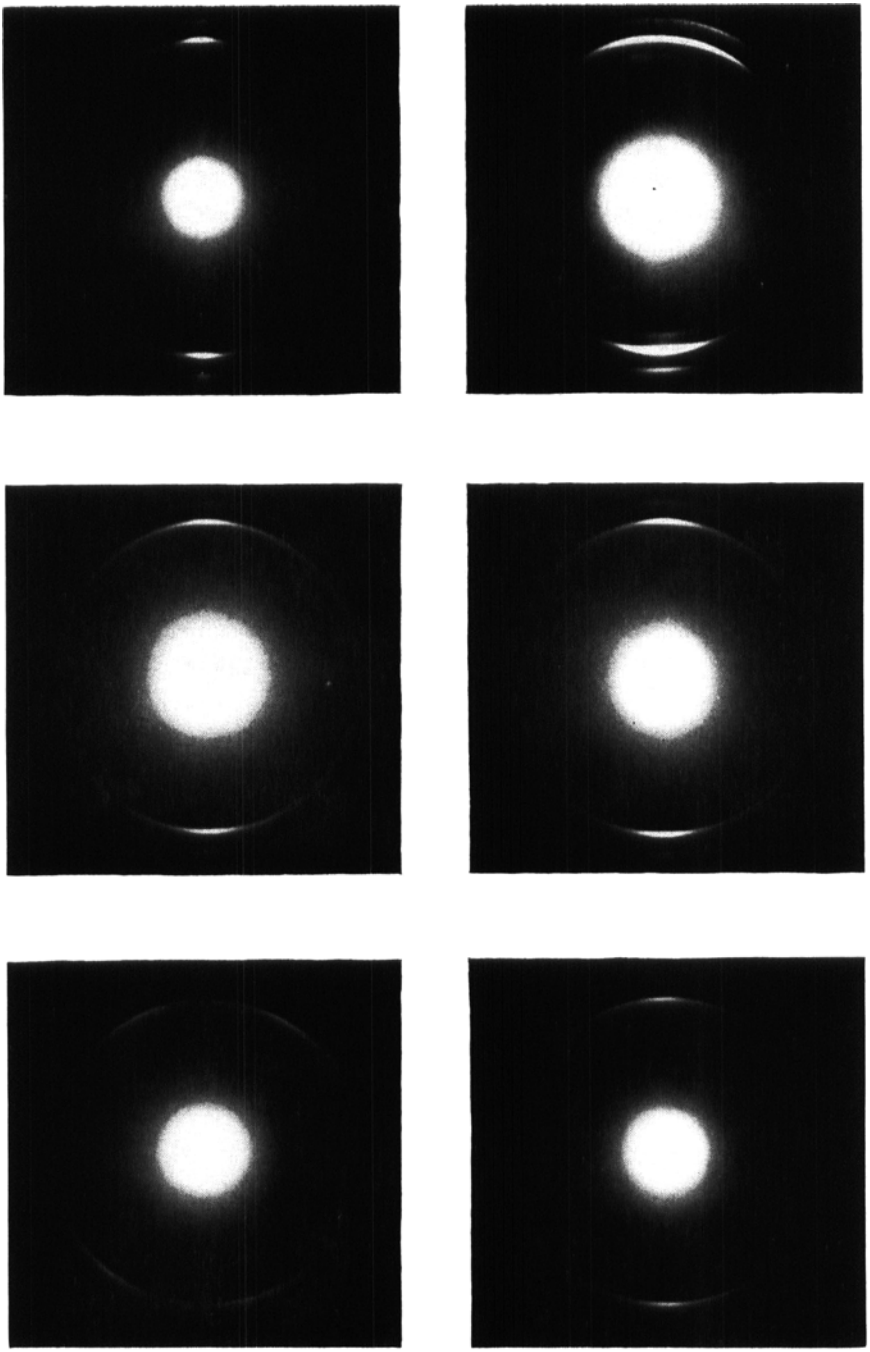

FIGURE 5 WAXS patterns for the skin (left), transition layer (middle) and core (right) for samples moulded at 100 (upper row) and 500 MPa (lower row), respectively.

than in the outer parts. A monoclinic structure has been reported earlier for capillary extruded polyethylene.[10]

Transmission electron micrographs of the transition layer of samples moulded at 500 MPa show stacked lamellae perpendicular to the molecule direction typical for oriented and annealed materials (Figure 6). In Figure 7 a micrograph of the fibrous core region (the same pressure as above) is given. The sample had been treated with fuming nitric acid at 80°C for 24 h to etch away amorphous material. Figure 7 shows that the remaining parts of the fibres in Figure 2 consists of agglomerates of material held together by fibrils.

In micrographs taken from samples crystallized at lower pressures (100 MPa) only crystalline lamellae had been observed. By comparing electron diffraction patterns and crystal thickness, it has been proved that the agglomerates consist partly of extended chains with the fibrils interconnecting them.

It has earlier[7] been found that the crystallinity of the samples increases about 10% (from 66 to 75%) when the pressure level is raised from 100 to 500 MPa. The core material had a crystallinity of 90% at 500 MPa. The crystallinity of the skin and the transition layer does not change with pressure much from that of the bulk specimen moulded at 100 MPa.

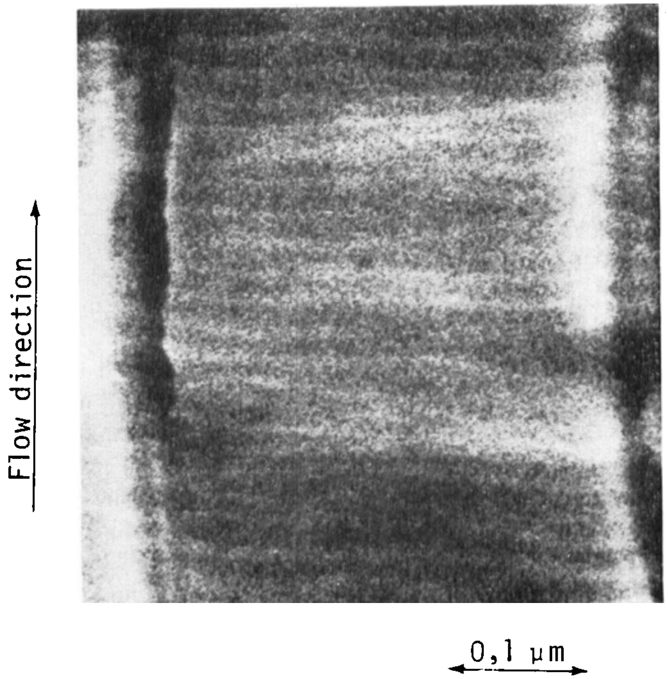

FIGURE 6 Transmission electron micrograph from the transition region showing a typical fibre structure. Injection pressure 500 MPa.

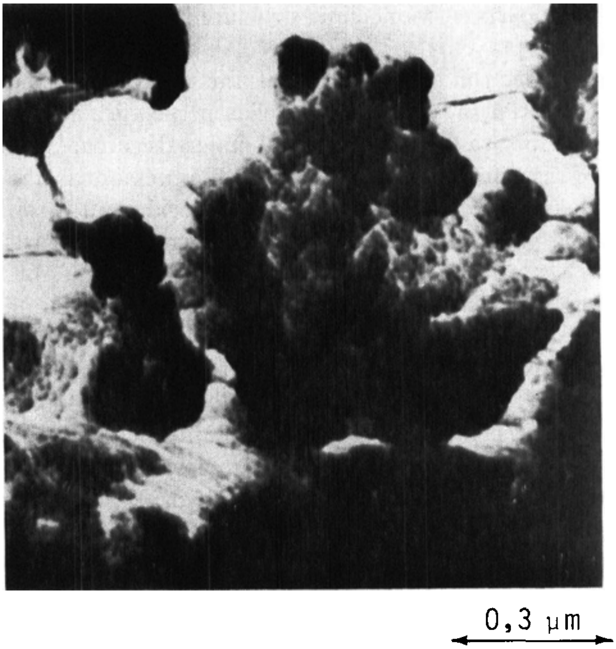

FIGURE 7 Transmission electron micrograph from the core region of a sample moulded with an injection pressure of 500 MPa. The sample had been treated with fuming nitric acid for 24 h at 80°C.

DISCUSSION

A three-layer structure was found to be characteristic for the injection moulded specimens described in this communication. In this case, the skin is only slightly oriented and behaves in a ductile way, compared to the core. All experiments performed, i.e. DSC, X-ray, scanning electron microscope, etc., show that the crystal structure of this layer is mainly of normal type, i.e. chain-folded lamellae. This seems to apply for all pressure levels investigated. Since the core gives the sample its high modulus and strength this layer is the most interesting in this work. Several structures in the crystalline component are known to increase the modulus and strength of polyethylene, e.g. extended chain crystals,[1] shish-kebabs[2] and the type of structure found by Porter *et al.*[3] in extruded samples.

Other reasons for the high strength of the injection moulded specimens could be orientation and/or the appearance of the monoclinic structure in the crystalline component. However, since the orientation does not change significantly when the injection pressure is raised from 100 to 500 MPa, while the modulus and strength increases markedly, this cannot be the primary reason. The monoclinic structure, present in samples moulded with higher injection pressures (500 MPa), is known to be a result of compressive strains[11] and has also been observed by Porter *et al.*[10] in capillary extruded samples and by Maeda and Kanetsuna in specimens crystallized at high pressures.[12] Annealing retransforms this structure into the ordinary orthorombic unit cell as seen in Figure 8, which is a wide angle X-ray diffraction pattern from the core of an annealed sample (100°C, 30 min). The diffraction ring corresponding to the monoclinic unit cell has vanished, cf. Figure 5. Since the mechanical properties do not deteriorate with this treatment, the monoclinic phase cannot be responsible for the high modulus.

Since neither the orientation nor the monoclinic structure can be the primary reason for the increase in modulus and strength, only the known high strength structures remain as an explanation. "Pure" extended chain crystals only, as described first by Wunderlich[1] do not explain the mechanical behaviour of the core. However, it seems likely that the extended chains form an important part of the high modulus structure. In fact, electron diffraction patterns from single crystals with a thickness of several thousand Å were observed in the core

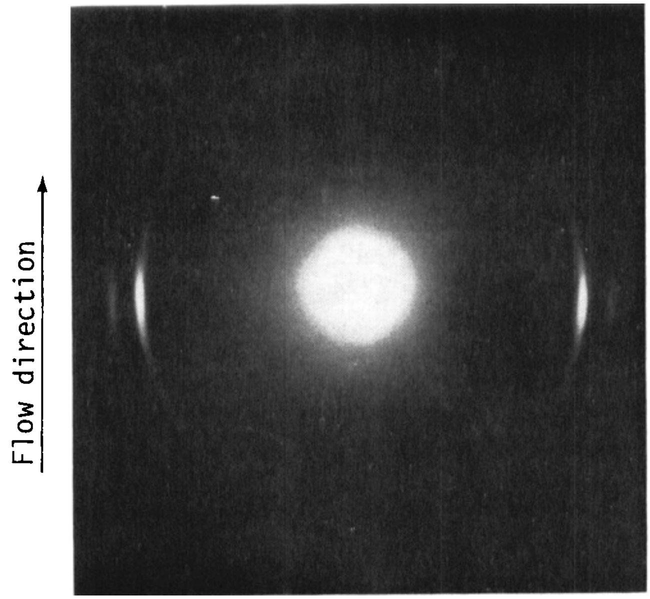

FIGURE 8 WAXS pattern for the core region of samples injection moulded at 500 MPa. This material had been annealed at 100°C for 30 min. The diffraction ring corresponding to the monoclinic structure has disappeared, cf. Figure 5.

material. Shish-kebab arrangements interconnecting extended chain crystals or lamellae crystals with a high amount of tightened tie molecules are in accordance with the observations mentioned above. The mechanical behaviour of the injection moulded specimens indicate that their structure is closely related to that of capillary extruded samples produced by Porter and co-workers.[3,10,13] The extrusion produces a material which also contains a central oriented core, which is believed to contain more or less perfect extended chain crystals. It can be mentioned that the capillary extruded samples had in the early stages of their development a modulus of the same order as for the injection moulded specimens.[3]

The very high crystallinity of the core in the moulded samples constitutes further support for the suggestion that extended chain crystallites form a substantial part of the core material.

In this work only one polyethylene grade with a high molecular weight has been used. Experiments with a lower molecular weight material showed that, under the processing conditions used, no improvement of the mechanical properties could be achieved using high injection pressures. In agreement with this result, no second melting peak and no core material of the same kind as in the high molecular weight material was observed. The reason for this molecular weight dependence could be due to the fact that extended chains are more easily formed using higher molecular weight grades.[14]

CONCLUSION

Using a common processing method, we have produced a material containing extended chains and possible also related structures. The nature of these structures results in a material with a high modulus and strength compared with normal injection moulding grades of polyethylene.

Acknowledgement

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References

1. B. Wunderlich and T. Arakawa, *J. Pol. Sci.* **A-2,** 3697 (1964).
2. A. Pennings and A. Kiel, *Kolloid Z.Z. Polymere* **205,** 160 (1965).
3. J. H. Southern and R. S. Porter, *J. Appl. Pol. Sci.* **14,** 2305 (1970).
4. D. W. Rees and D. C. Bassett, *Nature* **219,** 368 (1968).
5. G. Capaccio and I. M. Ward, *Polymer* **15,** 233 (1974).

6. K. Imada, T. Yamamoto, K. Shigematsu, and M. Takayanagi, *J. Mater. Sci.* **6,** 537 (1971).
7. K. Djurner, J. Kubát, and M. Rigdahl, *Polymer*, in press.
8. K. Djurner and J. Kubát, *Kunststoffe* **66,** 511 (1976).
9. A. Peterlin and G. Meriuel, *Makromol. Chemie* **142,** 227 (1971).
10. C. R. Desper, J. H. Southern, R. D. Ulbrich, and R. S. Porter, *J. Appl. Phys.* **41,** 4284 (1970).
11. T. Seto, T. Hara, and K. Tanaka, *Jap. J. Appl. Phys.* **7,** 31 (1968).
12. Y. Maeda and H. Kanetsuna, *J. Pol. Sci., Phys. Ed.* **14,** 2057 (1976).
13. R. G. Crystal and J. H. Southern, *J. Pol. Sci.* **A-2, 9,** 1641 (1971).
14. D. C. Bassett, B. A. Khalifa, and B. Turner, *Nature Phys. Sci.* **239,** 106 (1972).