

Electron-Microscopical Investigation of the Morphology of Segmented Polyurethanes

J. FOKS, *Technical University of Gdańsk, Institute of Organic and Food Chemistry and Technology, 80-952 Gdańsk, Poland*, and G. MICHLER, *Wissenschaftliches Forschungs- und Koordinierungszentrum für Plast- und Elasterzeugung und -anwendung (WKZ) der chemischen Industrie im Kombinat VEB Chemische Werke Buna, DDR-4212 Schkopau, East Germany*

Synopsis

Segmented polyurethanes obtained by two-step synthesis were studied by electron microscope on specimens prepared as replicas from the brittle surface of the polymer and on thin sections cut with a cryo-ultramicrotome. Each of the specimens showed two different kinds of dispersed phase. Information obtained on morphology complemented each other. The continuous phase observed on the thin section directly by microscope showed no structure of its own and was similar in all polymers investigated, whereas the surface of the brittle fracture showed two kinds of continuous phase.

INTRODUCTION

A great deal of research work has been done in the field of segmented polyurethanes in the last few years. Their behavior and their favorable mechanical properties are attributed to their domain structure,¹⁻³ which is directly observed by electron microscopy⁴⁻⁷ and confirmed by X-ray diffraction studies.⁷⁻¹¹ Though still more information is provided by infrared spectroscopy and thermal studies,^{9,11-13} there still remains a lot to be elucidated regarding structure and interdependence between structure and properties.

Recently the application of light and electron microscopy has revealed the presence of further morphological elements, mainly spherulites,^{6,10,14-17} globular structures,¹⁷ or granular aggregates,¹⁸⁻²⁰ of sizes exceeding domains.

Investigation morphology by electron microscopy requires several steps of preparation. Microscopical specimens have to be sufficiently thin (ca. 50–100 nm) to yield adequate contrasts, and not to undergo changes while being investigated in the electron microscope. A variety of techniques are used to satisfy these requirements. A traditional one uses brittle fractures of the material: Often the fracture path runs along the characteristic structural elements causing a corresponding relief on the fracture surfaces.

Techniques to investigate these surfaces use replicas that can be observed in transmission electron microscopy. The morphology of the fracture can also be directly observed in scanning electron microscope. The development of a relief showing the morphology is sometimes possible by selective etching

(by ions or by gas discharge, or chemically) of a smooth or brittle fracture surface.

A useful technique is ultramicrotomy. In order to obviate plastic deformations during the cutting process and to enhance the contrast between structural details, it is usually necessary to harden and stain the sample by physical or chemical means.

In the case of polymers high voltage electron microscopy (usually accelerating voltage of 1000 kV) is of great use since it facilitates the examination of objects of up to several micrometers thickness providing a better spatial presentation of structural details and permitting an easier preparation.²¹

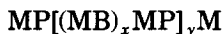
The morphology of segmented polyurethanes described in the present study was obtained by applying various electron-microscopical techniques. Results obtained from the investigations on brittle fracture surfaces were compared with those obtained from investigations on cryo-thin sections and chemically stained thin sections using a high voltage electron microscope.

EXPERIMENTAL

Polymer Synthesis

Segmented polyurethanes were obtained from poly(ethylene-adipate) glycol, diisocyanate 4,4'-diphenylmethane (MDI), and 1,4-butanediol. Syntheses were performed in two steps with 5% MDI excess. After solidifying the polymers were annealed at 385 K for 24 h.

The chemical structure of the PU obtained is shown in the following scheme



where M = MDI, B = butanediol, and P = polyester with M_w of ca. 2000.

The four PUs which were prepared have a different percentage of hard elements each (owing to varied molar ratios of reagents) and differ in temperatures used in the second step of synthesis. Sample PU 4 is a PU 3 which had been additionally annealed at 425 K for 5 h. The differences between the samples are shown in Table I.

TABLE I
Molar Composition of the Investigated Polyurethanes and Annealing Temperatures

Polymer	P:M:B	Temperature in the 2nd step (K)	Additional annealing
PU 1	1:4:3	325	—
PU 2	1:4:3	385	—
PU 3	1:4:3	365	—
PU 4	1:4:3	365	425 K
PU 5	1:8:7	365	—

Preparation of Samples for Electron-Microscopical Studies Fracture Surface Replicas

Brittle fractures of the samples were prepared in liquid nitrogen. A matrix of a layer of 7% aqueous poly(vinyl alcohol) solution was coated with platinum and then with coal at an oblique angle. After the matrix had been removed, the remaining Pt/C replica was examined by a BS 613 Tesla, Brno/CSSR electron microscope (accelerating voltage of 80 kV).

Ultramicrotome Thin Sections. Being too soft to be cut with an ultramicrotome, the material had to be hardened. This was attempted by using various media. Phosphortungsten acid (PTA) was not active enough, and chlorosulfonic acid partially destroyed the samples; only osmiumtetroxide led to partial hardening. Samples treated with osmiumtetroxide in association with cryo-ultramicrotomy permitted, however, the preparation of thin sections yielding electron-microscopical pictures with well-contrasted spherulites. Cryo thin sections were also prepared from untreated material. The cutting temperature was 150 K; the knife temperature 220 K. A diamond knife was used. The cryo thin sections were investigated in a high voltage electron microscope at 1000 kV.

RESULTS

Investigation of Polymer Fracture Surfaces

The fractures show characteristic elements of the morphology: A continuous and a dispersed phase are distinctly discernible. The dispersed phase appears in form of two types of granular aggregates: Type I consists of equally sized granular elements with grains distributed statistically on the flat surface of the fracture. The grains of type II are only slightly larger than the former ones and show a certain centripetal orientation.

The first aggregate type appears in sample PU 1 (Fig. 1), the second in

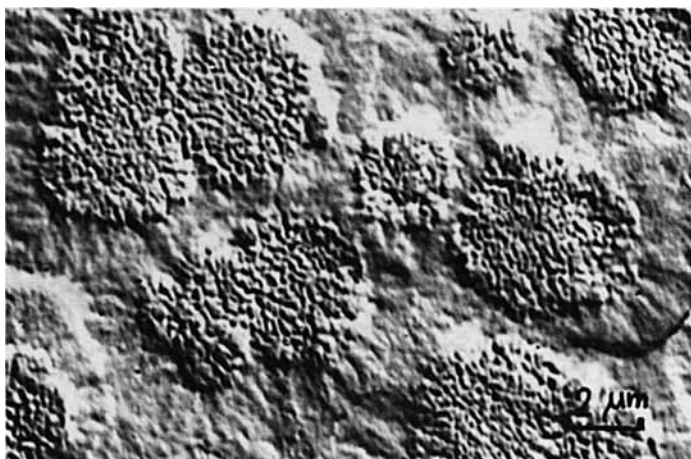


Fig. 1. Granular aggregates of type I in sample PU 1 (replica of fracture surface).



Fig. 2. Granular aggregates of type II in sample PU 2 (replica of fracture surface).

sample PU 2 (Fig. 2). Both types appear in sample PU 3, with structures of type I being markedly smaller than those of type II (Fig. 3). Only sample PU 4 (sample PU 3 after annealing at 425 K for 5 h) shows a different structure in the matrix of the polymer and remains a form of two continuous mutually interpenetrating phases. The dispersed form remains unchanged (Fig. 4). The fracture surfaces of sample PU 5, which has a higher percentage of hard segments, show a larger number of granular elements (Fig. 5).

Investigation of Thin Sections in HEM

High voltage electron microscopy (HEM) together with highly sensitive photographic material facilitates the study of beam-induced changes in polymers.²² Also the thin sections of segmented polyurethanes show changes in the initial phase of the electron irradiation. The slightly contrasted, hardly discernible forms at the beginning change into clearly discernible, radially arranged spherulites after intense irradiation. These effects are

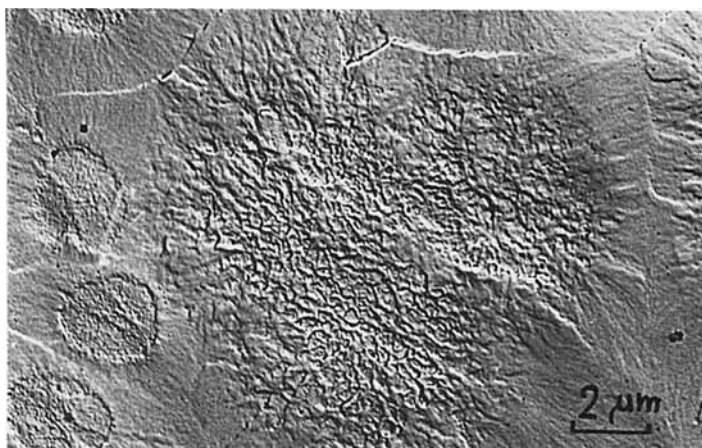


Fig. 3. Both types of granular aggregates in sample PU 3 (replica of fracture surface).



Fig. 4. Different structure of the continuous phase in sample PU 4 (sample PU 3 after annealing at 425 K for 5 h) (replica of fracture surface).

shown in Figure 6 for PU 2 and Figure 7 for PU 3. The "beam-induced development of contrast" in spherulites can be accounted for by dilatation and contraction of radial fibrils, as known for lamellae in polyethylene.²³

The hardening of samples has a decisive influence on the quality of the thin sections and the discernibility of their structures. At a cutting temperature of 190 K in the cryo-ultramicrotome, the samples are still slightly smeared as the boundaries between the structural elements are only dimly visible (blurred contrasts). Structural elements obtained at a cutting temperature of 150 K are markedly more distinct, but compression of the material in front of the knife edge (so-called chatter) may occur (Fig. 8). Artefact-free and more contrasted structures of the thin sections (Fig. 9) can only be obtained from a more intense hardening of the material by treating it with osmiumtetroxide before being cut. The quality of the structures is also influenced by the thickness of the thin sections. The use of



Fig. 5. Larger number of granular elements in sample PU 5 (replica of fracture surface).

sections with thicknesses of up to a few micrometers is advantageous because large sections are to be prepared, allowing the spatial distribution of structural elements to be more easily analyzed, even though details are less clearly visible. The most distinct spherulite structures are obtained when the sections are not thicker than 1 μm .

The PU samples investigated showed three morphological elements: two types of dispersed phase and one continuous phase. The matrix of sample PU 1 shows dispersed areas with more intense contrast but without structures of their own (Fig. 10). PU 2 shows spherulites with pronounced radially arranged fibrils (Fig. 11). In sample PU 3 either dispersed phase is represented (Fig. 12). Sample PU 4 showed the same morphology as sample PU 3. Sample PU 5, which has a higher percentage of hard segments, shows a fibrillar structure without a pronounced presence of spherulites (Fig. 13). The continuous phase was uniform in all samples also for PU 4 and had no structure of its own.

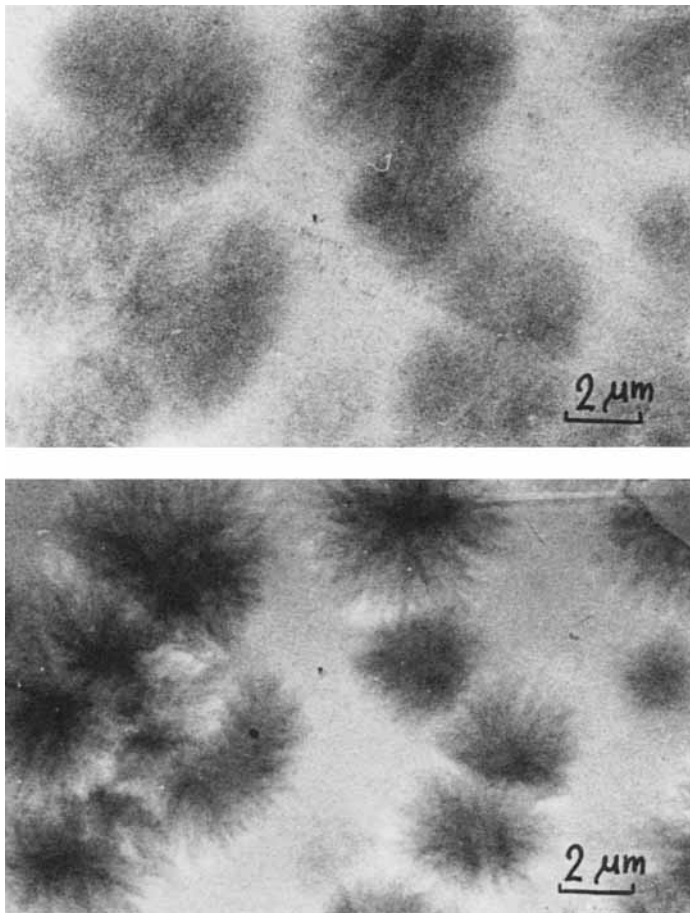


Fig. 6. Development of "beam-induced contrast" in the HEM of thin sections of sample PU 2. Micrographs: (a) at the beginning of irradiation; (b) after intense irradiation.

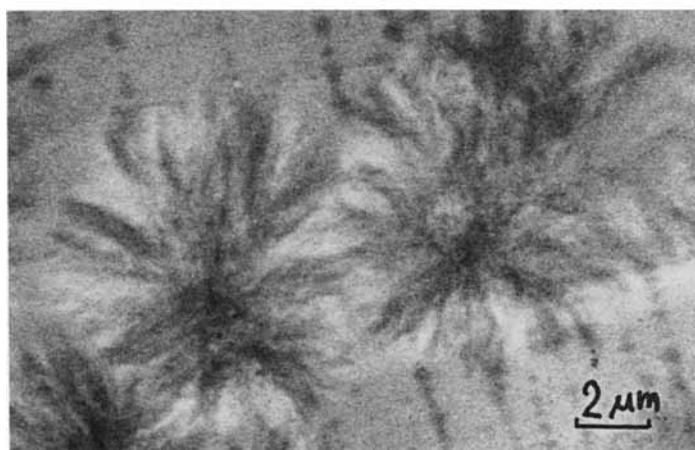
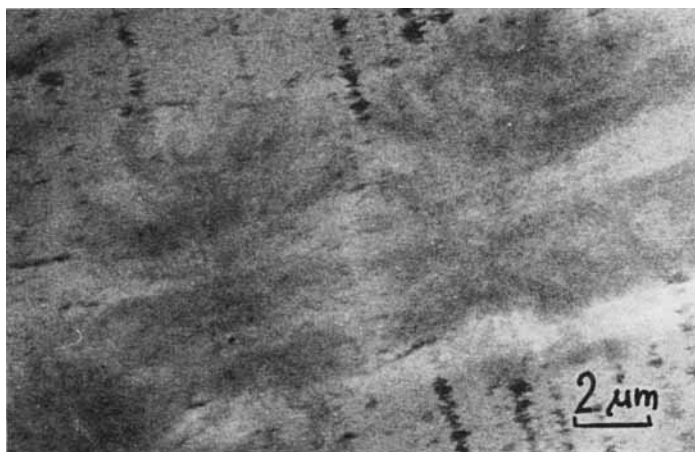


Fig. 7. As Figure 6, for sample PU 3.



Fig. 8. Structural elements in a thin section, cutting temperature 150 K.

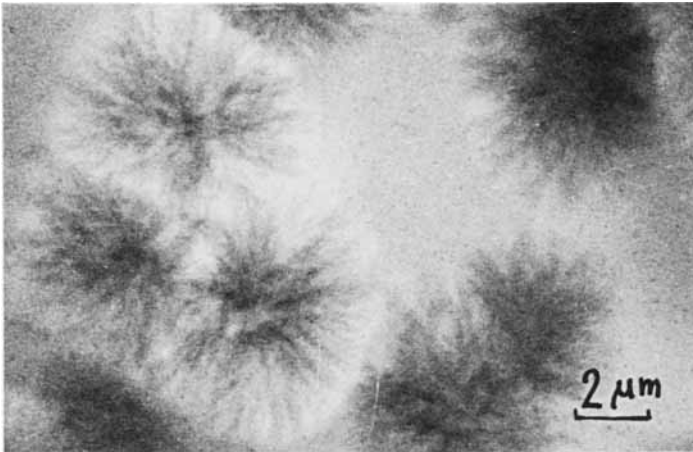


Fig. 9. Artefact-free and more contrasted structures of a thin section in the HEM hardening of the material by osmium-tetroxide and cutting at 150 K.

DISCUSSION OF RESULTS

The PU fracture surfaces investigated show distinctly varied structures. Many of the PU samples previously investigated had shown characteristic morphology, similar to that presented in Figure 3. The relationships found between synthesis and morphology²⁰ allowed us to obtain a PU with only one single type of dispersed phase. In connection with a study by Wilkes et al., who had investigated films obtained from polymer solution,^{6,14,15} in our samples we had primarily supposed the fracture to be running only across the spherulites. We consequently supposed that there were two types of spherulites filling up the whole volume of the samples and differing from one another only in their central areas. This erroneous conclusion was corrected by analyzing the morphology of PU 4 and by investigating the morphology of the thin sections of the remaining samples. These clearly show that the well-formed spherulites do not fill up the whole space of the

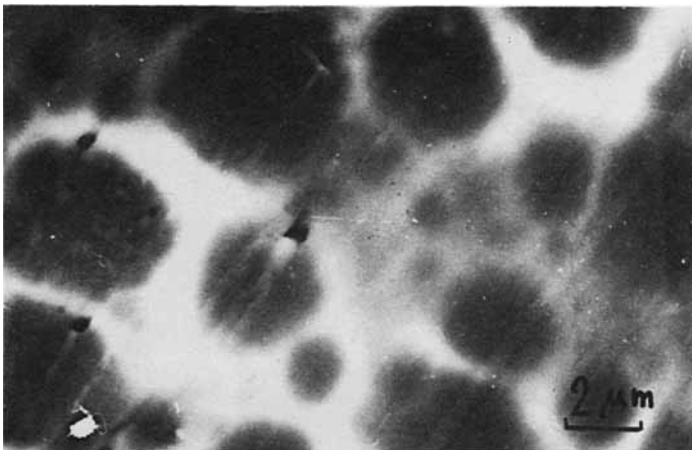


Fig. 10. Dispersed areas with intense contrast in sample PU 1 (thin section in HEM).

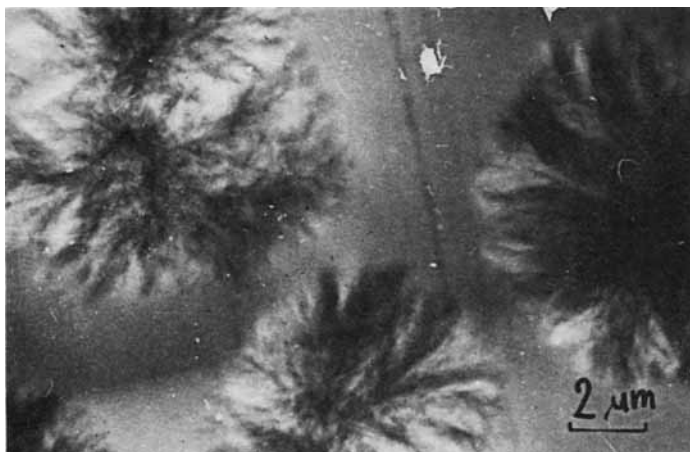


Fig. 11. Spherulites with well pronounced radially arranged fibrils in sample PU 2 (thin section in HEM).

sample, but are isolated from one another (Fig. 11). They touch each other only in some places, their spheric forms changing into polyeders (Fig. 9). The actual spherulitic structure of the fracture surfaces are the granular aggregates of type II. This result is confirmed by investigations applying light microscopy.²⁰ These spherulites have a melting temperature of about 475 K. In the thin sections granular aggregates of type I appear only in forms of darker spots having no internal structures. Also investigations carried out by light microscopy prove the presence of spherulites, of the melting temperature about 445 K.

HEM investigations of thin sections prove spherulites occurring either separately or in groups of a few. Three areas varying in contrast are discernible: radial fibrils in spherulites with the most intense contrast, inter-fibrillar areas with the weakest contrast, and interspherulitic areas with medium contrast. This can be accounted for as follows: spherulities contain

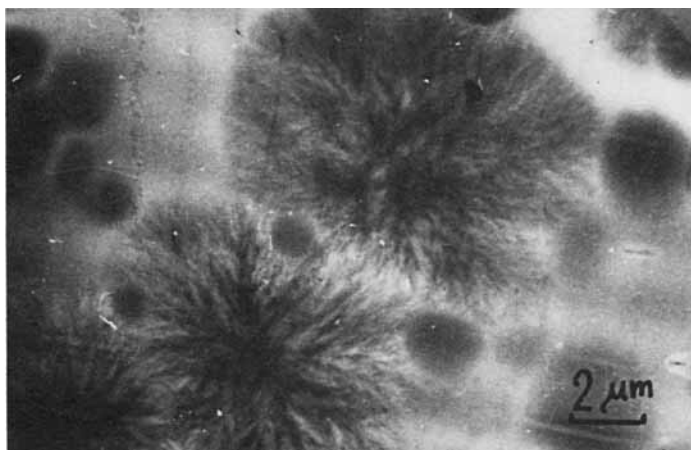


Fig. 12. Two types of dispersed phases in sample PU 3 (thin section in HEM).

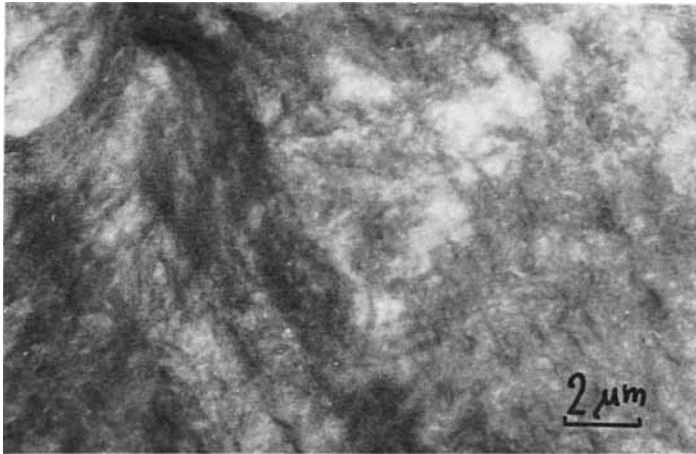


Fig. 13. Fibrillar structure without pronounced spherulites (thin section in HEM).

polymer chains with a higher percentage of hard material form fibrils, whereas the interfibrillar areas are filled with soft segments. The difference in contrast between fibrils and interspaces does not correspond to differences in density between the two areas, since differences in the thickness of the thin sections are also brought about by beam-induced effects at the beginning of electron irradiation, which, however, also allows us to presume a greater compactness of the structure of radial fibrils in comparison with that of the intermediate material (i.e., a higher percentage of hard segments). The interspherulitic areas contain polyurethane macromolecules of lower percentage of hard segments, in which the two segments are homogeneously mixed with each other (compatibility of the two kinds of segments percentages). Correspondingly, in these areas the contrast lies between the regions of hard and soft segments.

From these micrographs it obviously follows that the investigated samples are not homogenous. The formation of spherulites is due to the microphase separation of longer hard segments from the soft polyester matrix.

There is considerable similarity between the micrographs of the thin sections here described and those quoted in the literature. For example polyurethane investigated by Fridman and al.¹⁷ obtained in a different manner and contained a different polyol each, but they all consisted of the same hard segment. The synthesis ran at the ratio of P:M:B = 1:6:5. According to the authors, spherulites are formed from hard segments. A greater percentage of hard segments in these urethanes (M + B) is the reason why spherulites fill up the whole polymer volume. Amorphous areas with a greater percentage of soft segments are supposed to lie between the fibrils.

The thin sections showed no differentiation of the continuous phase. Structure formation was observed only on replicas of brittle fracture surfaces. As follows from our earlier investigations,¹⁹ some mechanical properties are connected with this type of morphology.

The authors are indebted to Professor Dr. H. Bethge for the possibility of performing the investigations with the High-Voltage Electron Microscope in the Institute of Solid State Physics and Electron Microscopy of the Academy of Science of the GDR in Halle/S. and to Mrs. G.

Hörig Technische Hochschule für Chemie, Leuna-Merseburg, Sektion Physik, for preparing the cryo-ultramicrotome sections.

References

1. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
2. T. L. Smith, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1825 (1974).
3. R. W. Seymour, G. M. Estes, and S. L. Cooper, *Macromolecules*, **3**, 579 (1970).
4. J. A. Koutsky, N. V. Hien, and S. L. Cooper, *J. Polym. Sci.*, **8**, 353 (1970).
5. S. L. Aggarwal, *Polymer*, **17**, 938 (1976).
6. G. L. Wilkes, S. L. Samuels, and R. Crystal, *J. Macromol. Sci., Phys.*, **10**, 203 (1974).
7. R. R. Lagasse, *J. Appl. Polym. Sci.*, **21**, 2489 (1977).
8. R. Bonart, *J. Macromol. Sci. Phys.* **2**(1), 115 (1968).
9. S. B. Clough and N. S. Schneider, *J. Macromol. Sci. Phys.*, **2**(4), 553 (1968).
10. N. S. Schneider, C. R. Desper, J. L. Illinger, A. O. King, and D. L. Barr, *J. Macromol. Sci.*, **11**, 527 (1975).
11. C. S. Paik Sung and N. S. Schneider, *J. Mater. Sci.*, **13**, 1689 (1978).
12. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
13. T. R. Hesketh, J. W. C. van Bogart, and S. L. Cooper, *Polym. Eng. Sci.*, **20**, 190 (1980).
14. S. L. Samuels and G. L. Wilkes, *J. Polym. Sci. B*, **9**, 761 (1971).
15. S. L. Samuels and G. L. Wilkes, *J. Polym. Sci. Symp.*, **43**, 149 (1973).
16. I. D. Fridman and E. L. Thomas, *Polymer*, **21**, 388 (1980).
17. I. D. Fridman, E. L. Thomas, and C. W. Macosko, *Polymer*, **21**, 393 (1980).
18. J. Foks, Proc. 8th Europhys. Conf. Macromolec. Phys., Bristol, 1978, p. 10.
19. J. Foks, H. Janik, and S. Winiecki, *J. Appl. Polym. Sci.*, **21**, 645 (1982).
20. J. Foks and H. Janik, Proc. 27th Inst. Symp. Macromolecules, Strasbourg, 1981, Vol. II, p. 923.
21. G. H. Michler, *Acta Polym.*, **31**, 709 (1980).
22. G. H. Michler and Ch. Dietzsch, *Cryst. Res. Technol.*, **17**, 1141 (1982).
23. G. H. Michler, B. Tiersch, and H. J. Purz, *Acta Polym.*, **30**, 529 (1979).

Received September 7, 1983

Accepted June 17, 1985