

Relating Microhardness of Poly(ethylene Terephthalate) to Microstructure

C. SANTA CRUZ,¹ F. J. BALTÁ CALLEJA,^{1*} H. G. ZACHMANN,² N. STRIBECK,² and T. ASANO³

¹Instituto de Estructura de la Materia C.S.I.C., Serrano 119. 28006 Madrid, Spain, ²Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstraße 45, 2000 Hamburg 13, Germany,

³Department of Physics, Faculty of Science, Shizuoka University, Shizuoka 422, Japan

SYNOPSIS

The microhardness (H) of poly(ethylene terephthalate) (PET) containing catalysts, as well as of PET without catalysts has been investigated. Two types of morphologies have been examined: (a) structures where spherulitic growth is incomplete, resulting from a primary crystallization from the glassy state and (b) samples in which spherulitic crystallization is completed. It is shown that for the former materials, H is an increasing linear function of the volume of the spherulites and depends on annealing time and catalyst content. For the latter materials, H is nearly constant with increasing annealing temperature (T_A). Results are discussed in the light of three principal structural factors which determine the microhardness behavior: (1) the volume content of spherulites within the material; (2) the value of crystallinity within the stacks of the lamella, which turns out to be a constant; (3) the average thickness of the crystals, which increases slightly with T_A after crystallization is completed. An expression which takes into account the above parameters and offers a description of the H of polyethylene terephthalate is proposed.

INTRODUCTION

The use of microindentation hardness (H) is now well established as a powerful technique to accurately determine changes in morphology and microstructure of polymers which, in turn, are monitoring the macroscopic mechanical properties of these materials.^{1,2} The stress-strain behavior under the indenter is known to depend upon the test duration^{3,4} (viscoelasto-plastic behavior); and previous work on polymers has concentrated on time-dependent properties.⁵⁻⁹ Thus, in order to make a complete analysis of the H behavior of polymer materials it is important to separate the plastic component (given by the area of the impression after immediate load removal) from the elastic, and time-related components.^{10,11} From a macroscopic viewpoint H , measured after short loading times ($t \rightarrow 0$), is directly correlated with the yield stress (Tabor's relation)^{1,2} and to the modulus of the material.^{1,2,9,12}

On the other hand, on a microscopic scale, H is related to the critical stresses required for irreversible deformation of solidified molecular aggregates (crystalline lamellae, microfibrils, etc.).^{2,13} Hence microhardness can be considered as a bridging parameter between microstructural quantities (crystal thickness, etc.), on the one hand, and bulk properties (yield stress, elastic modulus, etc.) on the other.¹⁴ A generalized Tabor relation taking into account the influence of crystal thickness, crystallinity, and temperature has been proposed.¹³ Furthermore, H has been shown to be capable of detecting crystal phase^{15,16} and molecular orientation changes in polymers,¹⁷ as well as changes in polymer blends with composition.¹⁸ The increase, both in hardness and elastic recovery with increasing draw ratio, has been observed in polyethylene fibers.^{6,7} Finally, a strong correlation has been also shown to exist among microhardness, crystalline texture, and processing conditions.^{17,19,20}

A great number of the microhardness results mentioned make reference to polymer materials exhibiting a high degree of crystallinity (polyethylene, polypropylene, polyvinylidene fluoride copolymers,

* To whom correspondence should be addressed.

etc.), having transition temperatures (T_g) well below room temperature. In these systems the H value of the amorphous regions measured at room temperature is negligible.^{1,11} Microhardness studies of amorphous polymers, as a function of temperature, below and above T_g , have also been reported.²¹

The aim of the present study is to extend the above investigations to examine the correlation of H and the microstructure of polyethylene terephthalate (PET), a polyester of typically low crystallinity having a T_g value well above room temperature. The plastic, elastic, and flow properties of the near-surface region of amorphous and uniaxially drawn PET measured by means of a submicroindentation technique has been recently reported by Ion, Pollock, and Roques-Cames.²² PET can be prepared easily in the form of a glassy amorphous material by quenching from the melt. The mechanism of crystallization from the glassy state has been thoroughly investigated by many researchers.²³⁻²⁷ Specifically, the use of synchrotron radiation offers the possibility to perform time-resolved measurements of small- and wide-angle x-ray scattering (SAXS and WAXS) during crystallization of PET.^{28,29} By adequately varying the catalyst content, the temperature, time and the rate of crystallization, we have prepared materials with a wide range of crystallinities, spherulitic morphologies, different crystal thickness and various levels of crystal distortions. The influence of these structural parameters on the microhardness value and the detection of specific changes after controlled crystallization are of special interest.

EXPERIMENTAL

The following types of PET samples were investigated: (a) materials synthesized using the method of Günther and Zachmann²⁴ containing manganese acetate as catalyst; (b) samples synthesized from oligo (ethylene terephthalate) without a catalyst, as described by Asano et al.³⁰; (c) samples containing manganese acetate as a catalyst, and sodium montanate as a crystal nucleating agent. All samples were melt pressed to 150–200 μm thick films and then quenched in ice water. The films were finally isothermally annealed in the 70–240°C range for various periods of time.

Density was measured at 23°C by a density gradient column filled with hexane/tetrachloromethane. From the density, the degree of crystallinity was estimated, assuming for the density of the crys-

tals a value of $\rho_c = 1.4895 \text{ g/cm}^3$ and for the amorphous density a value $\rho_a = 1.3379 \text{ g/cm}^3$.

Small-angle x-ray scattering (SAXS) patterns were obtained first with a Rigaku camera with point collimation. The long periods were calculated from the first maximum using Bragg's law after subtraction of the continuous scattering. Later a Kratky compact camera was also used. Scattering was measured using two different slit heights in overlapping angular region with slit heights of 60 and 130 μm , respectively. Ruland's interface distribution function method was used for data evaluation.³¹

Microhardness was measured at room temperature using a microhardness tester with a Vickers square pyramidal diamond indenter. The H value (in MPa) was derived from the residual projected diagonal impression using: $H = kp/d^2$; where d is the mean diagonal length of the indentation in mm, p the applied force in N, and k a geometrical factor equal to 1.854. Loads of 0.15, 0.25, 0.5, and 1 N to correct for instantaneous elastic recovery were used. A loading cycle of 0.1 min to minimize creep of the material under the indenter was adopted. Some of the samples which were not fully crystallized exhibited a much harder outer skin, a few microns thick, which falsified the H measurement of the bulk. To measure the true value of the bulk H , the skin of these samples was removed.

RESULTS AND DISCUSSION

All samples investigated were crystallized from the glassy state for different times at different temperatures. To explain the results obtained, it is necessary to distinguish between two types of morphologies depending on the crystallization conditions: (a) structures in which the growth of spherulites is not completed, obtained by interrupting the primary crystallization after different times of crystallization at a constant temperature and (b) structures in which such a growth is completed, obtained by crystallization at different temperatures beyond the end of primary crystallization.

Microhardness of PET Samples in which Spherulitic Growth is Incomplete

In order to obtain samples in which the growth of spherulites is not completed we have crystallized amorphous PET at 117°C for different times. Spherulites grow from existing nuclei, gradually filling the volume of the material. The results will be discussed in light of three salient morphological ele-

ments: the crystalline lamellae, the intercrystalline disordered layers, and the interspherulitic amorphous regions. Figure 1 shows the gradual increase in H as a function of crystallization time at $T_A = 117^\circ\text{C}$, and a final leveling off after 5–20 min, depending on whether the samples contain a catalyst. It is seen that the samples containing a catalyst show an earlier and faster microhardness increase than the samples without a catalyst. This is due to the fact that catalyst particles act as nucleating agents and contribute to an earlier development of crystallinity, as shown in Figure 2. Here the degree of crystallinity determined from density is plotted as a function of time for both samples. A value of 25% is reached at the end of crystallization in agreement with previous investigations.^{24,25} Larger crystallinity values can only be obtained at higher temperatures (see Fig. 6). It is noteworthy that the stepwise increase of H versus t of Figure 1 resembles the trend shown for the scattering power (Q) derived from SAXS, during primary crystallization.²⁹ The invariant, Q , has been shown, in fact, to be mainly a function of the volume fraction Φ of spherulites during the main crystallization process:

$$Q = \alpha\Phi \quad (1)$$

Thus, it seems plausible to expect that H should be proportional to Q . Figure 3 supports this contention, showing that H is indeed an increasing linear function of the volume fraction of crystallized spherulites $\Phi = \alpha/\alpha_0$ (α being the measured crystallinity after a given time t , and α_0 the degree of crystallinity at which H levels off when crystallization is completed):

$$H = H_a + k\Phi \quad (2)$$

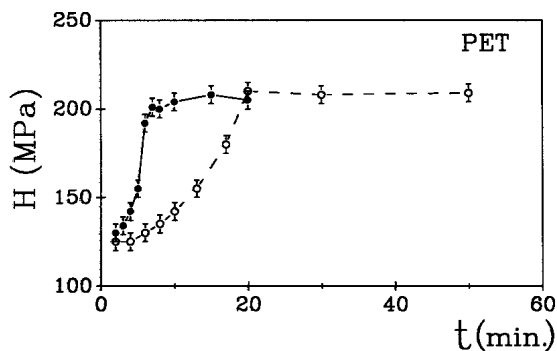


Figure 1. Change of microhardness of PET isothermally crystallized at $T_A = 117^\circ\text{C}$ from the glassy state for various periods of time. Solid symbols: samples with Mn catalyst without nucleating agent. Open symbols: samples without catalyst.

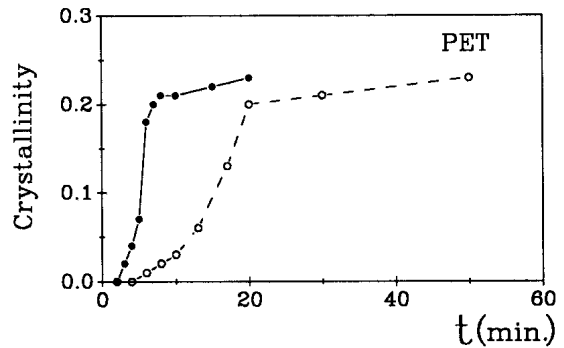


Figure 2. Degree of crystallinity of PET isothermally crystallized from the glassy state at $T_A = 117^\circ\text{C}$ for different times. Symbols as in Figure 1.

where the intercept, H_a , represents the microhardness of the amorphous glassy material which, of course, has no counterpart in eq. (1). It is to be noted that eq. (2) applies only for samples prepared in the primary crystallization range. The proportionality constant k in eq. (2) is equal to the difference in hardness values of the fully crystallized spherulitic material and the amorphous polymer: $H_{sph} - H_a$. Therefore, eq. (2) can also be written as:

$$H = H_{sph}\Phi + H_a(1 - \Phi) \quad (3)$$

This equation represents a generalization of hardness additivity, which is typical for high-crystallinity polymers.¹ However, H_{sph} and H_a instead of describing the crystal and amorphous hardness now represent the hardness values of the spherulites ($H_{sph} \approx 200$ MPa) and interspherulitic regions ($H_a \approx 120$ MPa), respectively.

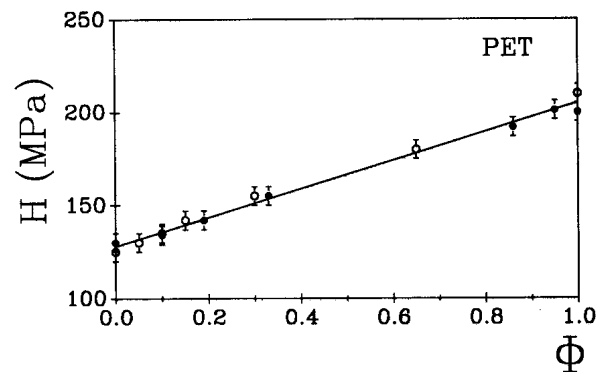


Figure 3. Plot of microhardness of PET as a function of volume fraction of spherulites [eq. (2)]. For $\Phi = 1$ the spherulites fill the volume of the sample and $H = H_{sph}$. Symbols as in Fig. 1.

Microhardness of PET Samples in Which Spherulitic Growth is Completed

Amorphous PET samples were crystallized at different temperatures in the range of 120–240°C for 1, 9, and 24 h respectively. Under these crystallization conditions the samples are always completely filled up by spherulites. Thus different degrees of crystallinity are associated with different states of crystalline perfection within the spherulites. Figure 4 shows the variation of H as a function of annealing temperature for different annealing times. One observes again a conspicuous stepwise increase at $T_A \approx 120^\circ\text{C}$ from a value of $H_a \approx 120$ MPa for the amorphous samples up to $H_{sph} \approx 200$ MPa for the crystallized material. Most intriguing, however, is the question of why H_{sph} remains practically constant for the fully crystallized samples, in contrast with the gradual long-period increase (Fig. 5) and concurrent macroscopic crystallinity rise with T_A (Fig. 6) observed above $T_A \approx 120^\circ\text{C}$. At this temperature the material is completely filled with spherulites. In high crystallinity polymers it is known that crystal hardness, H_c , is an increasing function of crystal thickness, l_c , within the lamellar stacks.^{2,13,14} To derive the value of l_c we used Ruland's interface distribution function method.³¹ Figure 5 illustrates the slight increase of l_c with increasing T_A , which is the result of the concurrent increase of L and slight decrease of the amorphous layer. If we consider the linear degree of crystallinity within the stacks of crystals, $\alpha_L = l_c/L$, it is immediately seen that the α_L values do not depend on T_A (Fig. 7), a result which is, in good agreement with the H constancy with T_A observed in Figure 4 for $T_A > 120^\circ\text{C}$. This seems to indicate that H mainly de-

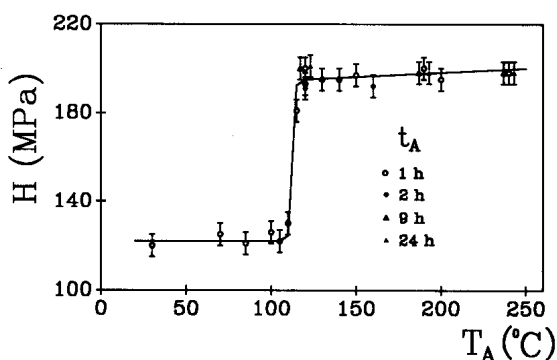


Figure 4. Microhardness for samples of PET (with Mn catalyst and nucleating agent) as a function of crystallization temperature T_A , isothermally crystallized at various temperatures from the glassy state for different annealing times (t_A).

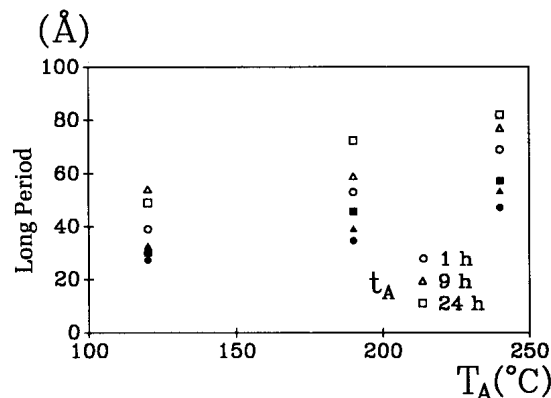


Figure 5. Long period (L) (open symbols) and average crystal thickness (l_c) (filled symbols) derived from SAXS for samples of PET isothermally crystallized at various temperatures for different annealing times t_A , as functions of crystallization temperature T_A . Samples as in Fig. 4.

fects the yielding of the stacks of crystals within the spherulites acting as hard cooperative elements. The difference between α_L , derived from SAXS, and α , as deduced from density measurements, is presumably due to the existence of amorphous domains which do not form layers between the crystal lamellae.³² These amorphous domains probably form larger regions outside the lamellae stacking, or even outside of the spherulites. It is surprising to find such a large difference between α and α_L , specially at low temperatures. Of course there is, in principle, the ambiguity whether α_L or $1 - \alpha_L$ is chosen to be the degree of crystallinity.³¹ However, we made the choice under the assumption that α_L cannot be smaller than α and that α_L cannot decrease with increasing temperature. Furthermore, one sees that the content of amorphous domains (proportional to

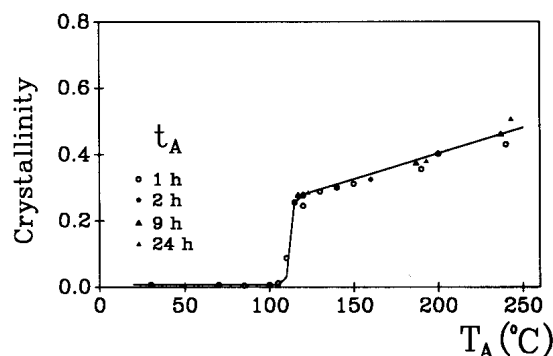


Figure 6. Degree of crystallinity derived from density as a function of crystallization temperature T_A for samples of PET isothermally crystallized from the glassy state for different annealing times. Samples and symbols as in Fig. 4.

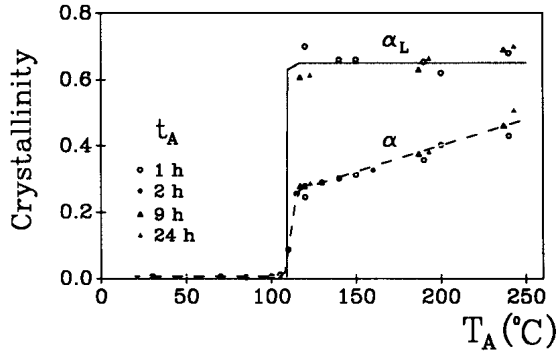


Figure 7. Linear degree of crystallinity, $\alpha_L = l_c/L$, derived from SAXS and crystallinity α derived from density for PET samples isothermally crystallized from the glassy state at various temperatures (T_A). Symbols and samples as in Fig. 4.

$\alpha_L - \alpha$), decreasing with T_A , does not contribute to depression of the hardness of the stacks of crystals. Additionally, as in our samples, α_L did not vary with T_A , we cannot make any statement concerning the influence of α_L upon H . It is interesting to note that independent l_c values computed from the coherent diffracting domains in the [001] direction derived from the analysis of the integral width of the (011) and (010) reflections yield α_L values in agreement with the data of Figure 7.

If we use the hardness additivity law which applies for semicrystalline polymers:^{1,2,11}

$$H_{sph} = H_c \alpha_L + H_a (1 - \alpha_L), \quad (4)$$

since H_{sph} , H_a , and α_L are experimentally determined quantities, we can calculate the hardness H_c of the crystal lamellae within the stacks for each annealing temperature. Table I illustrates the slight increase of H_c with l_c so obtained, which is similar to that found in high-crystallinity polymers like PE.^{2,13,15} According to previous investigations^{2,13} the dependence of H_c upon l_c can be assumed to be given by:

$$H_c = H_c^\infty / (1 + b/l_c) \quad (5)$$

where H_c^∞ is the hardness value for infinitely large crystals and b is a parameter. The parameter b measures, in fact, the hardness depression from H_c^∞ and has been shown to be equal to $2\sigma/\Delta h$,³³ where σ is the surface free energy of the crystal lamellae and Δh is the energy for crystal destruction. If we assume for H_c^∞ a value of 380 MPa (derived from *ab initio* calculations,¹ using for the heat of fusion of PET a value of $\Delta h_f = 135 \text{ J/g}^{34}$), values for b increasing with T_A , in the 17–28 Å range are obtained. The

obtained data for b suggest that the surface free energy (which is proportional to the density of surface defects)³³ increases with T_A . Additionally, from Table I it is seen that in PET crystal thickness apparently plays a smaller role than in high-crystallinity polymers in influencing the crystal hardness. Consequently, the macroscopic hardness values in Figure 4 are nearly independent of annealing temperature.

CONCLUDING REMARKS

From the above results, using eqs. (3) and (4), the following expression which offers a useful description of the microhardness of PET in relation to its salient morphological features can be derived:

$$H = [H_c \alpha_L + H_a (1 - \alpha_L)] \Phi + H_a (1 - \Phi) \quad (6)$$

Depending on the structure of the material, microhardness of PET can consequently be characterized as follows: (a) For the starting *amorphous glassy material*, $\Phi = 0$ and $H = H_a$. (b) For *samples crystallized from the glassy state where spherulitic growth is incomplete*, $0 < \Phi < 1$. In this range of materials, $l_c = \text{const}$, $\alpha_L = \text{const}$, and hence, $H_c = \text{const}$. Therefore, the first bracket in eq. (6) is constant and H is directly proportional to the volume occupied by the spherulites. The use of a catalyst induces the formation of a larger number of spherulitic nuclei leading to higher crystallinities, and consequently to a faster H increase. (c) For *samples crystallized from the glassy state in which spherulitic growth is completed*, then $\Phi = 1$, and eq. (6) simplifies to eq. (4). Here the crystal thickness increases slightly with T_A , leading to a concurrent small increase of the crystal hardness H_c . However, since α_L remains

Table I. Variation of Crystal Hardness H_c as a Function of Crystal Thickness, l_c for PET Annealed at $T_A > 120^\circ\text{C}$

H_c (MPa)	l_c (Å)
232	27.2
235	32.7
236	30.0
240	34.6
241	39.2
235	45.8
250	46.9
250	53.4
245	57.5

constant with T_A , and the rise of H_c is small, the resulting end effect is that one hardly does observe any H variation with T_A . Finally, it is noteworthy that the amorphous domains outside the lamellar stacks do not influence the value of H .

The authors express their thanks to the internacionales Büro, Kernforschungsanlage, Kerlsruhe and to CSIC, Madrid for the generous support of this Cooperation Project. Grateful acknowledgment is also due to CICYT, Spain for the support of this investigation (Grant MAT88-0159).

REFERENCES AND NOTES

1. F. J. Baltá Calleja, *Adv. Polym. Sci.*, **66**, 117 (1985).
2. F. J. Baltá Calleja and H. G. Kilian, *Coll. Polym. Sci.*, **263**, 697 (1985).
3. O. H. Wyatt and D. Dew-Hughes, *Metals Ceramics and Polymers*, Cambridge University Press, Cambridge, 1974.
4. I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed., Wiley, New York, 1983.
5. P. Grodzinski, *Plastics*, 312 (September 1953).
6. F. J. Baltá Calleja, *Colloid Polym. Sci.*, **254**, 258 (1976).
7. F. J. Baltá Calleja, W. T. Mead, and R. S. Porter, *Polym. Eng. Sci.*, **20**, 393 (1980).
8. R. J. Crawford, *Polym. Testing*, **3**, 37 (1982).
9. B. Darlix, B. Monasse, and P. Montmitonnet, *Polym. Testing*, **6**, 107 (1986).
10. I. L. Loubet, J. M. Georges, and G. Meille, in *Microindentation Technique in Materials Science and Engineering*, P. J. Blau and B. R. Lawn, Eds., ASTM STP889, Philadelphia, 1986, p. 72.
11. F. J. Baltá Calleja, J. Martínez-Salazar, and D. R. Rueda, *Encycl. Polym. Sci. Eng.*, **7**, 614 (1987).
12. B. Martín, J. M. Pereña, J. M. Pastor, and J. A. de Saja, *J. Mater. Sci. (Lett.)*, **5**, 1027 (1986).
13. F. J. Baltá Calleja and H. G. Kilian, *Coll. Polym. Sci.*, **266**, 29 (1988).
14. F. J. Baltá Calleja, D. R. Rueda, J. Garcia, F. P. Wolf, and V. H. Karl, *J. Mater. Sci.*, **21**, 1139 (1986).
15. F. J. Baltá Calleja, J. Martínez-Salazar, and T. Asano, *J. Mater. Sci. (Lett.)*, **7**, 165 (1988).
16. J. M. Salazar, J. C. Canalda, E. Lopez Cabarcos, and F. J. Baltá Calleja, *Coll. Polym. Sci.*, **266**, 41 (1988).
17. D. R. Rueda, R. K. Bayer, F. J. Baltá Calleja, and H. G. Zachmann, *J. Macromol. Sci. Phys.*, **B22**(2), 265 (1989).
18. J. M. Martínez-Salazar, J. Garcia Tijero, and F. J. Baltá Calleja, *J. Mater. Sci.*, **23**, 862 (1988).
19. J. Bowman, N. Harris, and M. Bevis, *J. Mater. Sci.*, **10**, 63 (1975).
20. J. Bowman and M. Bevis, *Coll. Polym. Sci.*, **255**, 954 (1977).
21. F. Ania, J. Martínez-Salazar, and F. J. Baltá Calleja, *J. Mater. Sci.*, **24**, 2934 (1989).
22. R. H. Ion, H. M. Pollock, and C. Roques-Cames, *J. Mater. Sci.*, **25**, 1444 (1990).
23. H. G. Zachmann and H. A. Stuart, *Makromol. Chem.*, **41**, 131 (1960).
24. B. Günther and H. G. Zachmann, *Polymer*, **24**, 1008 (1983).
25. A. Keller, G. Lester, and L. B. Morgan, *Phil. Trans. Roy. (London)*, **(A)247**, 1 (1954).
26. G. E. Yeh and P. H. Geil, *J. Macromol. Sci.*, **B1**, 235 (1967).
27. G. Althen and H. G. Zachmann, *Macromol. Chem.*, **180**, 2723 (1979).
28. G. Elsner, C. Rickel, and H. G. Zachmann, *Adv. Polym. Sci.*, **67**, 1 (1985).
29. G. Elsner, M. H. J. Koch, J. Bordas, and H. G. Zachmann, *Makromol. Chem.*, **182**, 1263 (1981).
30. T. Asano, A. Dzeick-Pickuth, and H. G. Zachmann, *J. Mater. Sci.*, **24**, 1967 (1989).
31. W. Ruland, *Coll. Polym. Sci.*, **255**, 417 (1977).
32. G. Konrad and H. G. Zachmann, *Kolloid Z. Z. Polym.*, **247**, 851 (1971).
33. F. J. Baltá Calleja, C. Santa Cruz, R. Bayer, and H. G. Kilian, *Coll. Polym. Sci.*, **268**, 440 (1990).
34. D. J. Blundell and B. N. Osborn, *Polymer*, **24**, 953 (1983).

Received January 9, 1990

Accepted September 18, 1990