

Influence of Molecular Weight on the Ordered State in Poly(ethylene Terephthalate)

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Synopsis

WAXS, DSC, and IR methods have been employed to follow the crystallization of poly(ethylene terephthalate) as a function of molecular weight. The degree of order, which is a measure of the extent of crystallization, decreased with increasing molecular weight. The degree of reduction in the molecular order with increasing molecular weight differed depending on the technique employed to measure it. Crystallinity indices obtained by x-ray diffraction methods show an almost linear relationship with molecular weight. The Trans-Gauche ratio inferred from the IR spectrum tends to decrease at a very rapid rate with increasing molecular weight. The heat of fusion, computed from the melting endotherm in DSC thermograms, shows a smaller but a definite decreasing trend with increasing molecular weight. Besides, the thermograms themselves showed distinct changes related to the molecular weight differences. The results have been discussed in terms of two different possible influencing factors known to affect the crystallization process in almost all polymers. Up to certain molecular weights, random coiling of molecules appears to be the more dominant factor, but in a much higher range of molecular weights, entanglement in the molecular network may become predominant.

INTRODUCTION

The influence of molecular weight on the physical and chemical properties of polymers is well known and well documented.¹⁻⁶ Tensile strength, fatigue life, and impact strength are positively influenced and stiffness, tear strength, and elongation at break are negatively influenced by increasing molecular weight.² For poly(ethylene terephthalate) fibers it has been shown that high molecular weight of the polymer leads to higher spin line stress, which accelerates oriented crystallization during melt spinning, and the optimum stretching temperature is determined by its molecular weight.⁵ Fiber strength, initial modulus, and pliability of polyester (PET) are shown to increase with increasing molecular weight.⁶ There have been a number of attempts in the past to study the influence of molecular weight on crystallinity and crystallization kinetics.⁷⁻¹⁹ Veda and Nakushima¹⁷ found that the density of poly(ethylene terephthalate) is limited by its molecular weight in its extent of increase because of thermal treatments. The higher the molecular weight, the lower is the limiting density after maximum possible crystallization by thermal treatments. The crystallite nuclei induction time is also longer with increasing molecular weight. It is inferred from these results that molecular chain aggregation proceeds less easily as the chain length is increased.

Structure and properties of PET have been well investigated by employing different analytic tools, such as x-ray diffraction,²⁰⁻³³ thermal analysis,³⁴⁻³⁹ and infrared spectroscopy.⁴⁰⁻⁴⁹ The structure sensitivity of each of these

techniques is known to be different because structural elements respond differently to the different methods of analysis. It is therefore often suggested that these methods are supplementary techniques to be used together so that a more logical approach can be followed to obtain a better understanding of the structure of polymeric materials. The same idea prompted us to investigate the effect of molecular weight on the crystallinity of PET using these three different techniques for the characterization of molecular order, and the results obtained are presented here.

EXPERIMENTAL

Polyester (PET) dried chips of four known molecular weights were kindly supplied by Dr. Siesler (Bayer & Co., West Germany). These chips were prepared under well-controlled and identical conditions by rapidly quenching the polymer from the molten state. Annealing of these chips was carried out at 200°C and in an atmosphere of inert gas. The chips were then conditioned at standard conditions of temperature and humidity.

X-ray powder diffractograms were obtained by using the chips directly in the form of pellets employing a Philips powder diffractometer, Model (PW 1050) with nickel-filtered $\text{CuK}\alpha$ radiation.

Thin films of these four different samples were cast from a solvent mixture of phenol-tetrachloroethane. These films were thoroughly washed with warm water until the last traces of the solvent were removed and then air dried and conditioned before spectral analysis. A Perkin-Elmer double-beam Infrared spectrophotometer, Model 180, was employed to record the spectra of these films.

Differential scanning calorimetry (DSC) thermograms were obtained employing a Perkin-Elmer DSC, Model-2C, equipped with a data station for analysis of spectra. A heating rate of 40°C/min was used.

RESULTS AND DISCUSSION

Since DSC thermograms are known to be sensitive to sample mass, scanning rate, and other factors, care has been taken so that the differences observed are not due to the variations in experimental conditions. It has been observed that, although increasing or decreasing the sample mass and scanning rate influenced the thermograms considerably, when the differences are examined in relation to sample molecular weight, the general trends observed have not been altered. However, in order that the different thermal transitions could be distinctly observed, and also conveniently interpreted, the sample mass and the scanning rate were carefully chosen after a number of trials to obtain the best thermograms. These conditions were then fixed for all the samples investigated. Figures 1 and 3 show the observed thermograms in two different temperature ranges for polyester chips of different molecular weights.

Poor molecular order in high-molecular-weight polymers is evident from the less distinct glass transition, from the appearance of exothermic crystallization transition, and from the broad melting range, all of which are known to be characteristic of an initially amorphous polyester. The heat of fusion, which is calculated from the area under the melting (T_m) endotherm (Fig. 1) after suitable calibrations, showed a linear decrease with

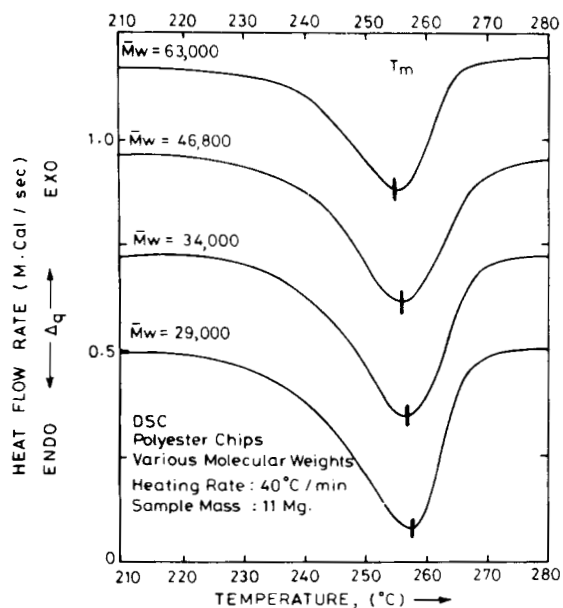


Fig. 1. DSC thermograms covering melting region.

increasing molecular weight (Fig. 2). An important observation from these thermograms is that both the onset and peak temperature of melting shifted slightly to lower values with increasing M_w .

M_w	Melting temperature	
	Onset ($^{\circ}\text{C}$)	Peak ($^{\circ}\text{C}$)
29,000	240	260
34,000	239	256
46,800	237	254
63,000	236	252

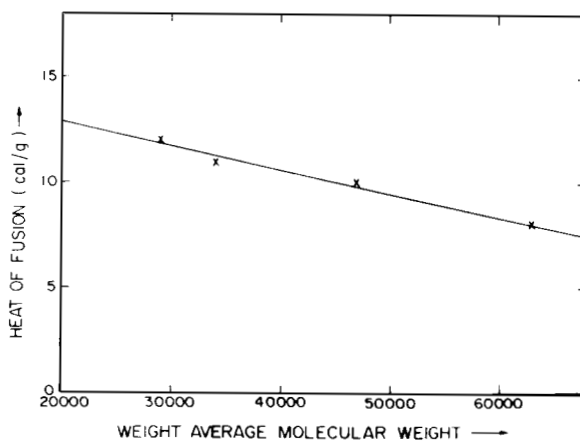


Fig. 2. Heat of fusion versus molecular weight.

When different scanning rates were used, these trends persisted, indicating that they are not fortuitous. The glass transition temperature T_g , as shown in Figure 3, on the other hand, seems to be much less affected by the M_w or M_n . Lower melting temperatures and lower enthalpy of fusion are both suggestive of a more disordered state in the higher molecular weight polymers.

Wide-angle x-ray diffractograms (WAXS) obtained both before and after thermal treatment of these different molecular weight poly(ethylene terephthalate) samples are shown in Figure 4. The unannealed high-molecular-weight polymer gave a broad unresolved diffraction curve (broken line) known to be typical of amorphous poly(ethylene terephthalate). The unannealed lower molecular weight polymers (broken lines), on the other hand, showed better and gradually improving resolution of individual peaks with decreasing molecular weight. Annealing at 200°C improved the order in all the samples investigated, but the extent of this improvement appears to be dependent on the molecular weight, as can be deduced from the gradual reduction in resolution of the crystalline peaks (full lines) with increasing molecular weight.

A parameter of order, namely, crystallinity index, calculated using the correlation x-ray crystallinity method, also decreased linearly with increasing molecular weight (Fig. 5), as was the case with heat of fusion. After annealing, the decrease in crystallinity index became nonlinear with increasing molecular weight (Fig. 6), but the trends remained the same. Hence, high molecular weight does not seem to inhibit crystallization altogether, although it appears to set a limit to the extent of crystallization that can take place after thermal treatment at a particular temperature.

Infrared spectroscopy (IR) has been employed for assessing the order-disorder situation in PET several times in the past.⁴⁰⁻⁴⁹ The difficulty often

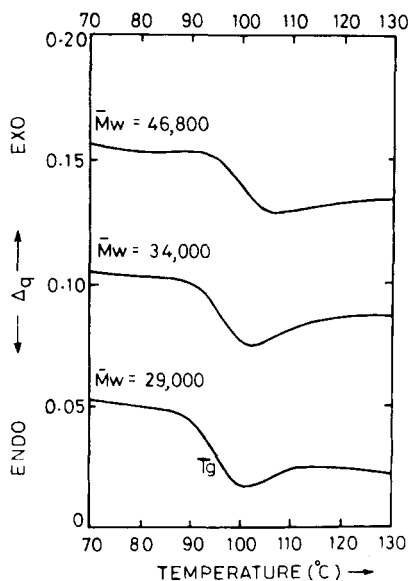


Fig. 3. DSC thermograms in glass transition region alone.

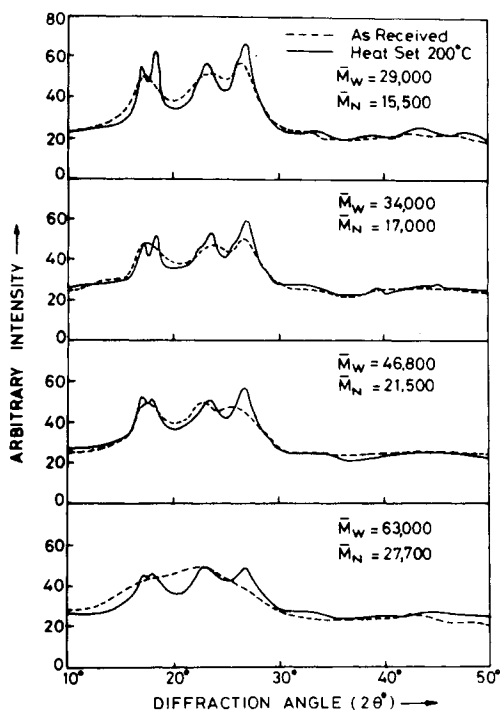


Fig. 4. X-ray diffractograms.

faced in these studies is that there is no known absorption band in the IR spectrum of PET that can be confidently assigned to the crystalline phase alone. One method normally employed is to estimate the gauche contribution and use this as a measure of the amorphous content because the gauche form is the most likely configuration of molecular chains in the noncrystalline regions. The trans sensitive absorption bands are normally

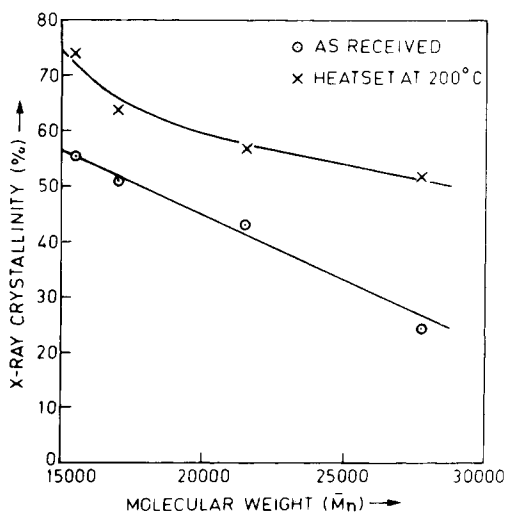


Fig. 5. Crystallinity versus number-average molecular weight.

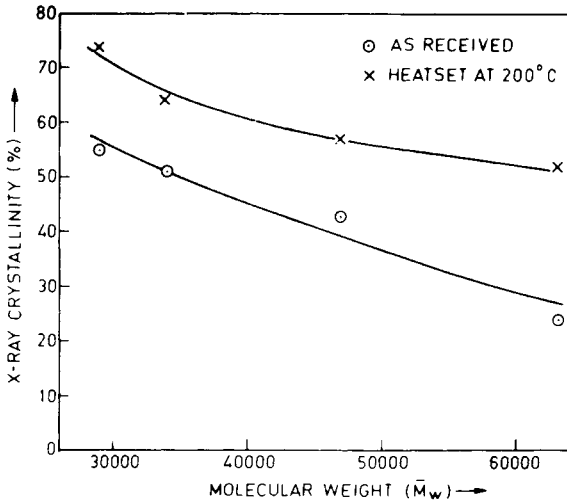


Fig. 6. Crystallinity versus weight-average molecular weight.

designated only as regularity bands, because trans is a likely configuration of molecular chains in the crystalline as well as noncrystalline regions in PET.

The trans configuration is considered representative of extended chain segments, and the gauche configuration is representative of the random coiled or folded, chain segments of molecular chains in the polymer. The trans content or trans-gauche ratio will then give the ratio of extended chain segments to the random coiled segments in a polymer.

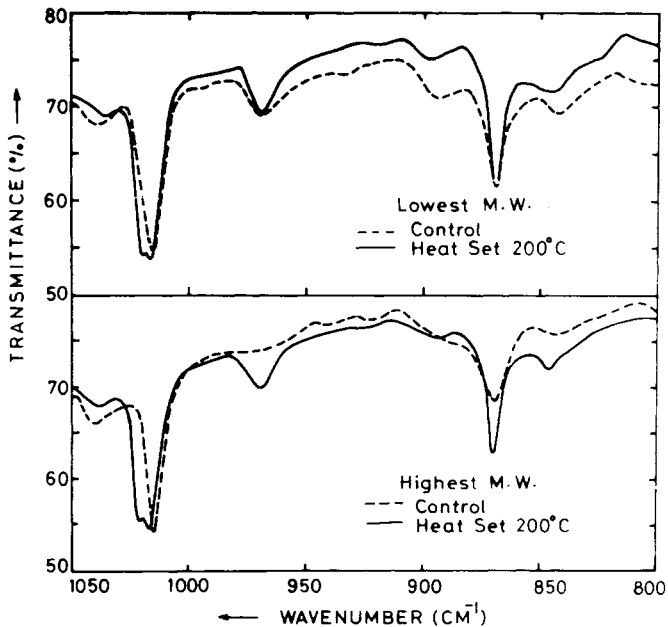


Fig. 7. Infrared spectra in the region 800–1050 cm^{-1} .

Figures 7, 8, and 9 show the effect of molecular weight on the trans absorption bands in an IR spectrum of PET in three different regions: 800–1000, 1000–1200, and 1300–1600 cm^{-1} , respectively. The two very good order sensitive trans absorption bands at 975 and 848 cm^{-1} are seen only as weak shoulder bands (broken curve) for the highest molecular weight control sample before annealing (Fig. 7). The trans-gauche absorption pairs at 1120/1100 (Fig. 8), and at 1340/1370 cm^{-1} (Fig. 9) show that the trans-gauche ratio is very low in the highest molecular weight polymer before annealing (broken curve) compared with that in the lowest molecular weight polymer. This trend persisted even after thermal treatment at 200°C (full curves).

The relative trans contents were computed as the ratio of absorbance of corresponding trans-sensitive bands to the absorbance of a structure-insensitive thickness reference standard at 795 cm^{-1} . The relative trans contents in all cases showed initially a very rapid decrease with increasing molecular weight (Figs. 10 and 11), but thereafter a proportional reduction in relative trans content is observed at higher molecular weights. This initial rapid reduction in trans content with even a small increase in molecular weight indicated an increasing tendency for molecular chains to become more randomly coiled due to even a small increase in chain length initially.

It appears from these results that the molecular chains tend to coil more with increasing molecular weight, and this makes it difficult to provide an extended parallel chain segment for incorporation into growing crystal nuclei, which is a prerequisite for unhindered growth of crystallites. However, orientation, or uncoiling of molecular chains, can easily occur during such processes as filament extrusion and drawing, and the crystallinity, as well as crystallite size, can be more in a high-molecular-weight polymer than in a low-molecular-weight polymer under such circumstances. But when the polymer in its unoriented and unstressed form is annealed, the

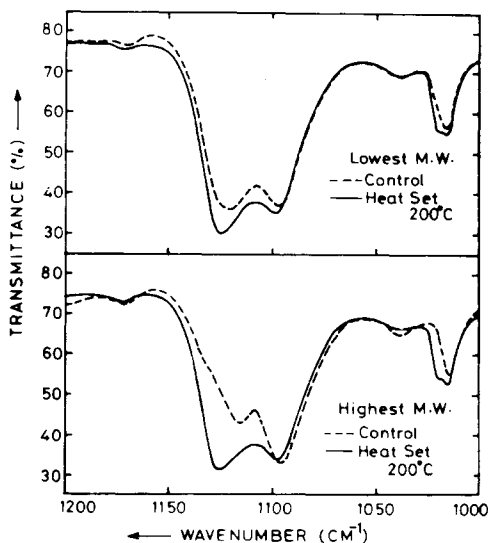


Fig. 8. Infrared spectra in the region 1000–1200 cm^{-1} .

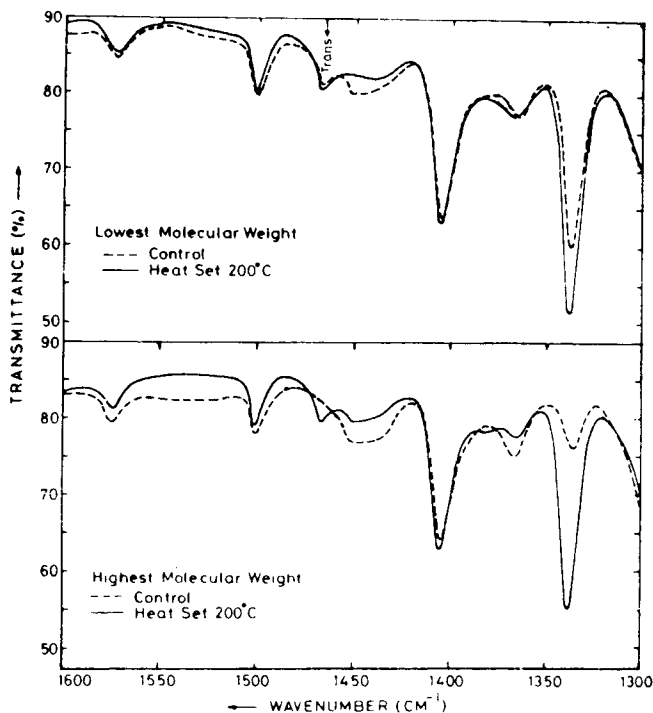


Fig. 9. Infrared spectra in the regions 1300–1600 cm^{-1} .

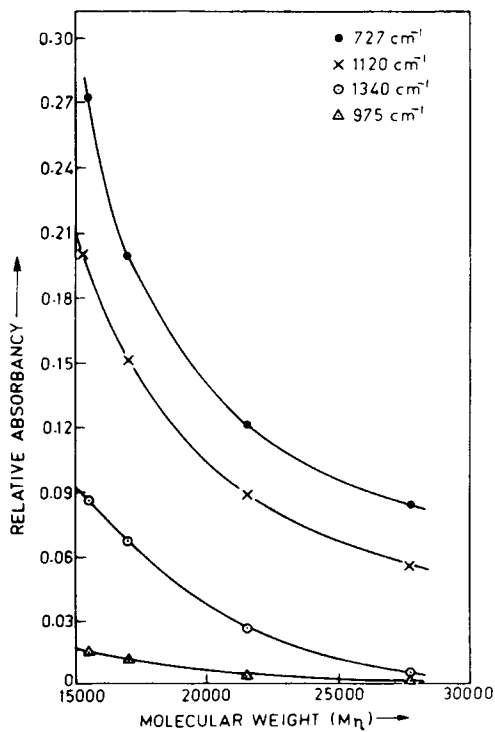


Fig. 10. Relative trans absorbance versus number-average molecular weight.

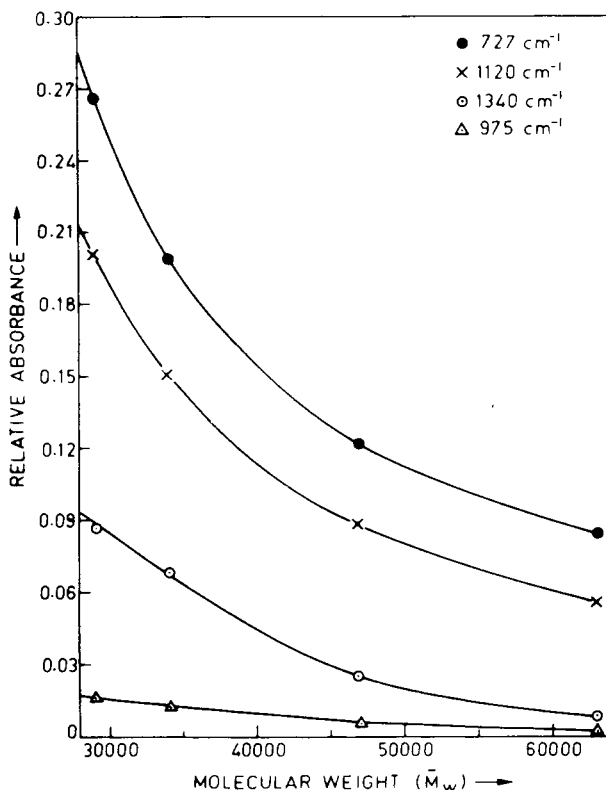


Fig. 11. Relative trans absorbance versus weight average molecular weight.

low-molecular-weight polymers possess higher crystallinity and higher crystallite perfection than high-molecular-weight polymers. This is probably more due to extensive random coiling of molecular chains than to chain entanglements.

From rheological studies on polymer melts, it was observed that, above a certain degree of polymerization, most polymers begin to undergo intermolecular entanglements in the melt. It was therefore reasoned that, with increasing molecular weight, these entanglements increase the hindrances to molecular organization. If this is the case, one expects an increase in glass transition because of a reduction in chain mobility likely with increasing entanglement. However, no spectacular change in glass transition temperature occurred within the range of molecular weight distribution investigated here. Second, increasing entanglements should always cause a large reduction in breaking elongation, but for most polymers the reverse of this is true; that is, an increase in breaking elongation with increasing molecular weight has usually been observed.

It was only at very high molecular weight that a reduction in breaking elongation occurred for many polymers, but this has always been for oriented polymers, not for undrawn or unoriented material. Hence, random coiling or irregular folding of molecular chains appears to give a better alternative explanation for reducing the capacity for molecular organization with increasing polymer molecular weight. A gradual reduction in heat of fusion and crystallinity, a gradual reduction in melting onset and peak

temperature with very little change in glass transition temperature, and a rapid reduction in trans content with increasing molecular weight, all lend support to this argument. It may be that entanglements may become dominant only at very high molecular weights, maybe at levels much higher than the range investigated here.

The authors express their gratitude to Dr. T. Radhakrishnan, Director of ATIRA for permission to publish this work. One of us (Rao) is also grateful to the CSIR India, for financial assistance in the form of a research fellowship.

References

1. A. Ziabick, *Fundamentals of Fibre Formation*, Wiley-Interscience, New York, 1976.
2. R. W. Nunes, J. R. Martin and J. F. Johnson, *Polym. Eng. Sci.*, **22**, 4 (1982).
3. T. Bhattacharya, A. Mukherjee, and A. Sengupta, *Tex. Res. J.*, **48**, 261 (1978).
4. S. Fakirov and N. Abranova, *Acta Polym.*, **33**, 271 (1982).
5. H. H. George, A. Holt, and A. Buckley, *Polym. Eng. Sci.*, **23**, 95 (1983).
6. E. M. Aizenstein and B. V. Petukhov, *Khim. Volokna.*, **6**, 18 (1984).
7. R. B. Richards, *J. Appl. Chem.*, **1**, 370 (1951).
8. L. H. Tung and S. Buckser, *J. Phys. Chem.*, **62**, 1530 (1958).
9. J. G. Fatou and L. Mandel Kern, *J. Phys. Chem.*, **69**, 417 (1965).
10. R. Chiang and R. J. Flory, *J. Amer. Chem. Soc.*, **83**, 2857 (1961).
11. W. Banks, M. Gordon, R. J. Roe, and A. Sharples, *Polymer*, **4**, 61 (1963).
12. H. Kojima and K. Yama Guchi, *Kobunshi Kagaker*, **19**, 715 (1962).
13. J. M. Barrales-Rienda and J. G. Fatou, *Polymer*, **13**, 407 (1972).
14. E. Erogz, J. G. Fatou, and L. Mandelkern, *Macromolecules*, **5**, 146 (1972).
15. J. Imorel, *J. Polym. Sci.*, **A1**, 2697 (1963).
16. A. Keller et al., *Philod. Trans. Roy. Soc. London, A*, **247**, 1 (1954).
17. N. Veda and Nakushima, *Chem. High Polym.*, **23**, 673 (1966).
18. F. Van Antwooten and D. W. Van Krevevelen, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2423 (1972).
19. T. Suwa, M. Takelisa, and S. Machi, *J. Appl. Polym. Sci.*, **11**, 3253 (1973).
20. L. E. Alexander, *X-ray Diffraction Methods in Polymer Science*, Wiley-InterScience, New York (1969).
21. J. H. Dumbleton, *J. Polym. Sci.*, **A2**, 667 (1969).
22. R. Bonart, *Kolloid Z., Z. Polym.*, **231**, 438 (1969).
23. D. C. Prevorsek and J. P. Sibilia, *J. Macromol. Sci. Rev., Macromol. Phys.*, **5**, 617 (1971).
24. J. J. Klement and P. H. Geil, *J. Macromol. Sci. Rev., Macromol. Phys.*, **5**, 505, 535 (1971).
25. E. Liska, *Kolloid Z., S. Polym.*, **251**, 1028 (1973).
26. H. Berg, *Chemifasern* **3**, 1 (1972).
27. A. M. Hindeh and D. J. Johnson, *Polymer*, **15**, 697 (1974).
28. W. L. Lindner, *Polymer*, **14**, 9 (1973).
29. V. B Gupta and S. Kumar, *Ind. J. Tex. Res.*, **1**, 72 (1976).
30. T. Asano and T. Seto, *Polymer (Japan)*, **5**, 72 (1973).
31. A. Misra and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 235 (1979).
32. T. Kunugi, A. Suzuki, and M. Hascrimoto, *J. Appl. Polym. Sci.*, **26**, 1951 (1981).
33. R. Huismann and H. M. Heuvel, *J. Appl. Polym. Sci.*, **22**, 943 (1978).
34. J. G. Fatou, Differential thermal analysis and themeograrimetly of Fibres, Chapter 2 in *Applied Fibre Science (London)* Vol. 3, Ed. by F. Happy, 1979, pp. 24-125.
35. S. Fakirov, E. W. Fischer, R. Hoffmann, and G. F. Schmidt, *Polymer*, **18**, 1121 (1977).
36. H. D. Weigmann, M. G. Scott, and A. C. Ribnick, *Text. Res. J.*, **47**, 761 (1977); **48**, 4 (1978).
37. E. Ito et al., *Polymer*, **19**, 39 (1978).
38. R. Hagege, *Text. Res. J.*, **47**, 229 (1977).
39. H. Jameel, H. D. Noether, and L. Rebenfeld, *J. Appl. Polym. Sci.*, **27**, 773 (1982).
40. D. J. Carlsson and D. M. Wiles, *Applied Fibre Science (London)*, Vol. 1, Ed. by F. Happy (1978), p. 272.

41. P. G. Schmidt, *J. Polym. Sci.*, **A1**, 1271 (1963).
42. C. J. Hebbinger and P. G. Schmielt, *J. Appl. Polym. Sci.*, **9**, 2661 (1965).
43. J. P. Sibilía, P. J. Harget, and G. A. Tirpak, Amer. Chem. Soc. 167th meeting *Polym. Preprints*, **15**, (1), 660 (1974).
44. G. Farrow and J. M. World, *Polymers*, **1**, 330 (1960).
45. A. Parisot and P. Bouriot, *Bull. Just Text. Fr.*, **23**, 789 (1969).
46. K. Edelmann and H. Wyden, *Kaut. Gummi, Kunst St.*, **25**, 353 (1972).
47. G. W. Urbanczkgk, *J. Polym. Sci., Polym. Symp.*, **58**, 311 (1977).
48. G. A. Tirtuk and J. P. Sinilia, *J. Polym. Symp.*, **17**, 643 (1973).
49. A. Garton, D. J. Carlsson, and D. M. Wiles, *Text. Res. J.*, **51**, 28 (1981).

Received November 29, 1984

Accepted April 25, 1985