JOURNAL OF MATERIALS SCIENCE 31 (1996) 5691–5695

Effect of $CaCO_3$ on the crystallization behaviour of polypropylene

A. KHARE, A. MITRA, S. RADHAKRISHNAN*
Polymer Science and Engineering, National Chemical Laboratory, Pune 411 008, India

The effect of $CaCO_3$ on the crystallization behaviour and the modification of structure in polypropylene (PP) has been investigated using X-ray diffraction and optical microscopy. The crystallization half time deduced from spherulitic growth rate was found to vary sharply and decreased considerably from 5–6 min for pure polymer to less than 2 min in the presence of $CaCO_3$. The ultimate spherulite size also decreased considerably for PP containing $CaCO_3$. Its dependance on composition however, showed a plateau region at about 10–15 wt % of additive. The intensities of certain reflections especially the 130 and 040 of the α phase were greatly affected by the presence of $CaCO_3$ and large variations in the crystallinity (*Ci*) values were observed with composition. The ratio of intensities of 130 and 040 reflections and the *Ci* revealed a maximum at a certain concentration of $CaCO_3$. The above results can be explained on the basis of nucleation and preferential growth of the α phase of PP crystallites.

1. Introduction

The crystallization behaviour and structure development of polymers has received considerable attention due to its potential use in tailoring commodity plastics with properties equivalent to other engineering polymers [1–4]. Pigments and particulate fillers are routinely added to polymers to impart colour or to reduce the cost of the product. However, these additives can by themselves affect crystallization and induce certain structural or morphological features which can produce modifications in many properties such as the impact and mechanical strengths. Some authors have found that the impact strength of polyolefines such as high density polyethylene (HDPE) and PP containing calcium carbonate or talc depends on the additive concentration in a peculiar manner and also shows a maximum value at a particular concentration [5–7]. Although the effect of additives on crystallization behaviour of PP has been reported for some cases [8, 9], the effect of the incorporation of varying percentages of $CaCO_3$ has not been previously reported in detail. It is thought that the peculiar variation in the impact strength of PP containing $CaCO_3$ could be associated with corresponding changes in the structure and morphology of the polymer matrix. We report here our detailed studies on the morphological and structural features induced in PP by the presence of $CaCO_3$.

2. Experimental procedure

In order to study the effect of $CaCO_3$ on the crystallization behaviour, polypropylene (grade SM85N) was first precipitated in the form of fine powder by dropping PP dissolved in xylene into acetone and subsequently drying in vacuum (1.333 Pa) for 24 h at 40 °C. The obtained powder had a particle size ranging from 30–60 μm (as measured by an optical microscope coupled to an image analyser Video Pro 32). The powder was then mixed with $CaCO_3$ and a desired quantity of methanol in order to facilitate better dispersion. The $CaCO_3$ was also in fine particulate form (average particle size 6 μm). Uniformity of the dispersion was ensured by grinding the mixture with an agate mortar and pestle for 2 h. The mixed powder was further dried for 5 h. The crystallization behaviours of powders containing different concentrations of $CaCO_3$ (ranging from 0–50 wt %) were studied. The premixed polymer powder was melted at 200 °C on microscopic slides using a thermostated hot plate and the slides were then quickly transfered to the hot stage of an optical polarizing microscope which had been preheated to the desired crystallization temperature. The spherulitic growth was recorded with respect to time at a constant crystallization temperature (isothermal case).

In order to investigate the structure by wide angle X-ray (WAX) diffraction powders containing different concentrations of $CaCO_3$ ranging from 0–50 wt % were first pelletised in a single ended compaction die at 294 MPa for 30 s. These pellets were subsequently held between glass slides by use of a slight hand pressure and were melted at 200 °C on a thermostated hot plate. The melted samples then underwent isothermal crystallization in the hot stage of the optical polarizing microscope. The crystallization time was

NCL Communication No. 6255

*To whom correspondence should be addressed.

10 min and the process was stopped by quenching the samples in distilled water. The samples appeared uniform with the filler being homogenously dispersed due to the fine particulate nature of the starting material. The samples were then scanned with the help of Philips X-ray Diffractometer (PW1730) and the WAX data was analysed in the same manner as reported in references [10–12].

3. Results and discussion

The spherulitic growth rate in PP isothermally crystallised at 115 °C was observed using an optical polarizing microscope. Fig. 1 shows the spherulite size as a function of time for pure PP as well as that containing various concentrations of $CaCO_3$. It can be seen that in the case of pure PP the spherulites grow to a large size over a long period of time (9–10 min) to attain an ultimate value of 90.5 μm. However, in the case of PP containing $CaCO_3$, the growth is smaller in a much shorter duration and that the ultimate size obtained is also reduced. The crystallization half time i.e., the time required to attain a spherulite size of half its ultimate value was derived from such curves as those shown in Fig. 1 for different isothermal crystallization temperatures (T_c). Fig. 2 shows the $t_{1/2}$ values for three T_c values of 110, 115 and 120 °C with respect to the concentration of $CaCO_3$. It is interesting to note that the crystallization half time decreases considerably for all the T_c values and that the extent to which this reduction occurs depends on T_c in that the higher the T_c the greater the reduction. This suggests that the $CaCO_3$ produces an increase in the nucleation rate.

It was observed from Fig. 1 that the ultimate spherulite size depended on the $CaCO_3$ content in the polymer. This was further investigated in detail and Fig. 3 shows the ultimate spherulite size obtainable at three different isothermal T_c values as a function of composition. The three curves correspond to T_c values of 110, 115 and 120 °C. It is interesting to note that although there is an overall decrease in the spherulite dimension with an increase in concentration of $CaCO_3$, this is not a continuous increase. There appears to be a region of composition in which the spherulite size exhibits a plateau region. This is especially noticeable at T_c values of 110 and 120 °C.

The crystallization phenomenon in polymers consist of two processes namely nucleation and growth which are both dependant on temperature and exhibit a maxima at a certain T_c value which exists between the glass transition temperature, T_g and the melting temperature T_m. The T_g and T_m [13, 14] values together decide the ultimate crystallinity value, spherulite size etc. However, at higher T_c values close

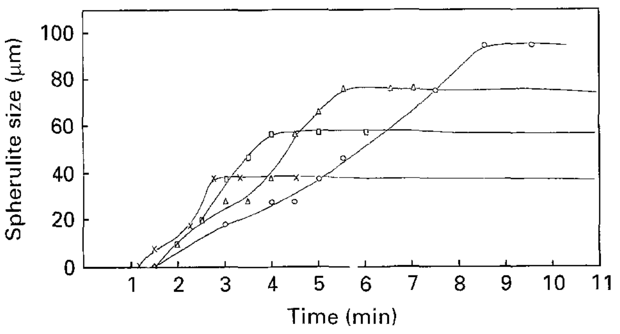

Figure 1 Isothermal crystallization of PP at 115 °C containing (○) 0, (△) 2, (□) 10 and (×) 20 wt % $CaCO_3$.

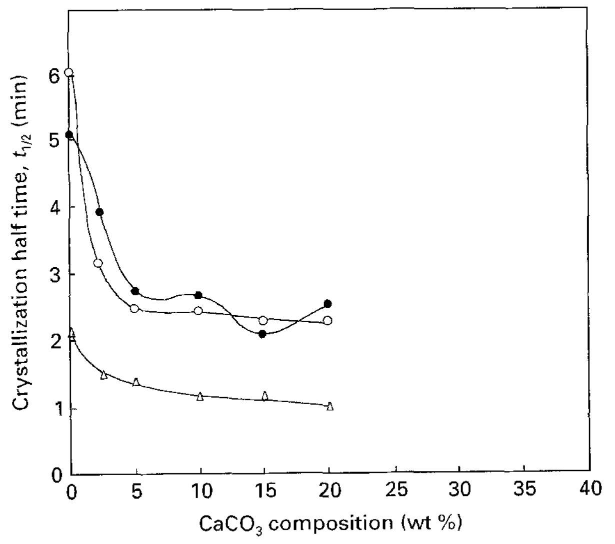

Figure 2 The crystallization half time $t_{1/2}$ as a function of composition for PP–$CaCO_3$ at different crystallization temperatures of; (△) 110, (●) 115 and (○) 120 °C.

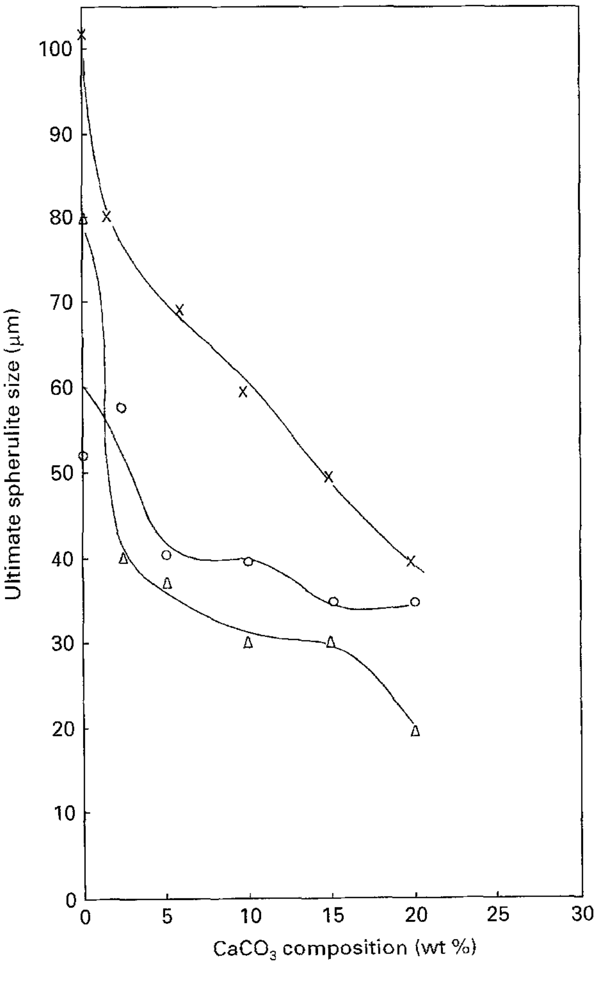

Figure 3 Variation of ultimate spherulite size in PP–$CaCO_3$ with composition at T_c of (△) 110 ° (×) 115 ° and (○) 120 °C respectively.

to the melting point it is nucleation which is the dominant factor and hence any additive which enhances nucleation has a strong effect on the crystallization at these temperatures. This was observed in Fig. 3. A large nucleation density or rate also affects the ultimate spherulite size due to restrictions on their growth. Hence one expects the spherulite size to decrease with an increase in concentration of the additive. However, it is seen in the present case, that the variation of spherulite size with composition is more complex. Nucleation is no doubt important in the crystallization process but it is only the initial step in generating the crystallites. The subsequent growth of the crystallites is an important factor in deciding the ultimate size of the spherulite. It appears that the growth is not restricted by an increase in the concentration of the additive in a certain range of compositions in the PP–$CaCO_3$ system. This suggest that there is clustering of nuclei giving rise to more available space for spherulitic growth in the polymer melt. When the growth rate and the nucleation rate are at the maximum value for the polymer at a particular T_c, they override the secondary effects due to the presence of an additive. This is observed in the data plotted in Fig. 3.

The detailed structural investigations were carried out by X-ray diffraction studies of these samples. Fig. 4 shows the WAX diffraction patterns of compression moulded samples prior to melt crystallization. It is seen that in all cases the diffraction angles of the various diffraction peaks remain the same but that their relative intensities change considerably with an increasing concentration of additive. The reflections observed in the 2θ region of 12–24° correspond to diffraction from polymer crystallites and none are observed that can be attributed to the $CaCO_3$; which exhibits diffraction peaks only at 2θ values greater than 30°. Further analysis of these various peaks reveals that they correspond to the α crystal structure of PP. The various interplanar spacings (*d* values) derived from these peaks, their relative intensities and corresponding *hkl* values are given in Table 1. It is interesting to note that there is a large change in intensity of the peak occurring at a 2θ value of 21.1° with an increase of $CaCO_3$ in these samples. It may be noted that the samples were made by a high pressure compaction technique which is equivalent to solid state processing during which the polymer is subjected to cold crystallization [15, 16]. Under these conditions recrystallization or structural ordering takes place as reported for many other polymers [17–19] and a similar explanation can be proposed in the present case.

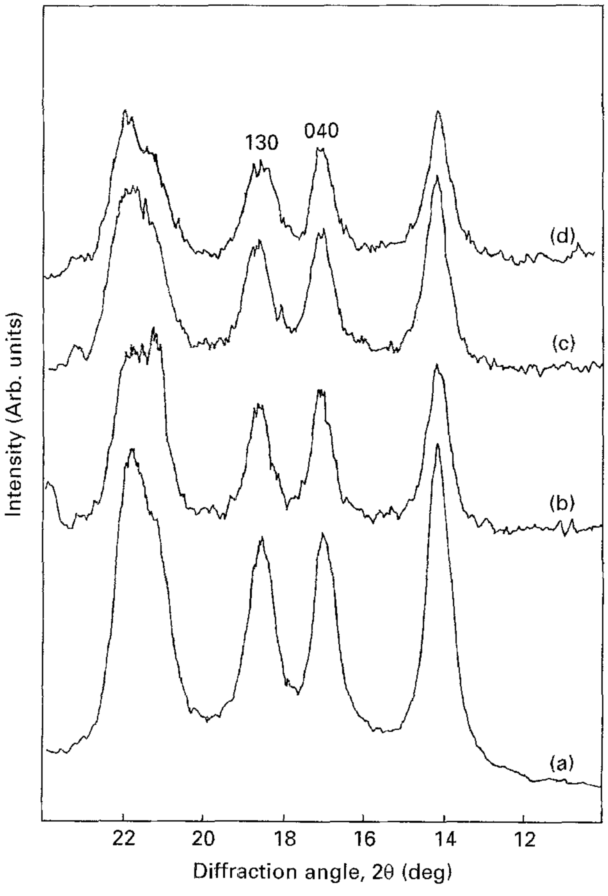

Figure 4 WAX scans for PP containing (a) 2, (b) 20, (c) 30 and (d) 40 wt % of $CaCO_3$, prior to melt crystallization.

The samples subjected to melt crystallization revealed very interesting features in the WAX scans. Figs. 5 and 6 show the X-ray diffraction patterns in the 2θ region of 12–34° for PP samples containing various concentrations of $CaCO_3$ subjected to isothermal crystallization at 120 °C. It can be seen that although the overall nature of the diffraction patterns remains the same, there is a large variation in the intensity of the 130 and 040 reflections. This suggests that the crystalline phase remains the same in all cases but that there is relative orientation of the crystallites in presence of the additive. The most interesting feature which emerges from these studies is that this orientation depends on the composition of the samples. Fig. 7 shows the ratio of the relative intensities of the peaks corresponding to 130 and 040 reflections as a function of composition. It is evident that this ratio of the intensities is a maximum at $CaCO_3$ concentrations of about 15–20 wt %.

Fig. 8 shows the crystallinity index (*Ci*) values plotted as a function of PP–$CaCO_3$ composition prior to melt crystallization and after melt crystallization at T_c values of 110 and 115 °C. It was observed that the *Ci* values for samples after melt crystallization show an initial increase, with a maximum at a certain

TABLE I Analysis of wide angle X-ray diffraction of polypropylene containing $CaCO_3$

PP–$CaCO_3$			α phase PP reference [19]		
2θ	d_{obs} ($\times 10^{-1}$ nm)	I/I_o obs	d_{rep} ($\times 10^{-1}$ nm)	I/I_o	*hkl*
14.1	6.282	100	6.54	100	110
17.1	5.186	74.6	5.32	70	040
18.5	4.796	74.6	4.84	56	130
21.8	4.077	98.50	4.25	40	131
25.1	3.540	13.43	4.10	58	041
25.6	3.482	17.91	3.50	20	060
26.1	3.414	17.91			
27.3	3.267	14.92			
28.3	3.154	3.154	3.10	08	220

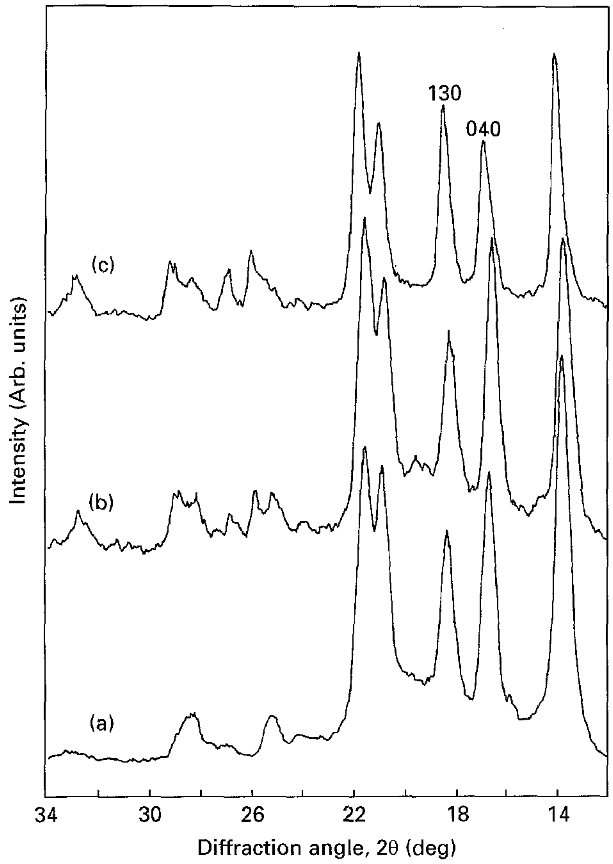

Figure 5 WAX scan for melt crystallized PP samples (T_c 120 °C) containing (a) 0, (b) 5 and (c) 10 wt % of $CaCO_3$.

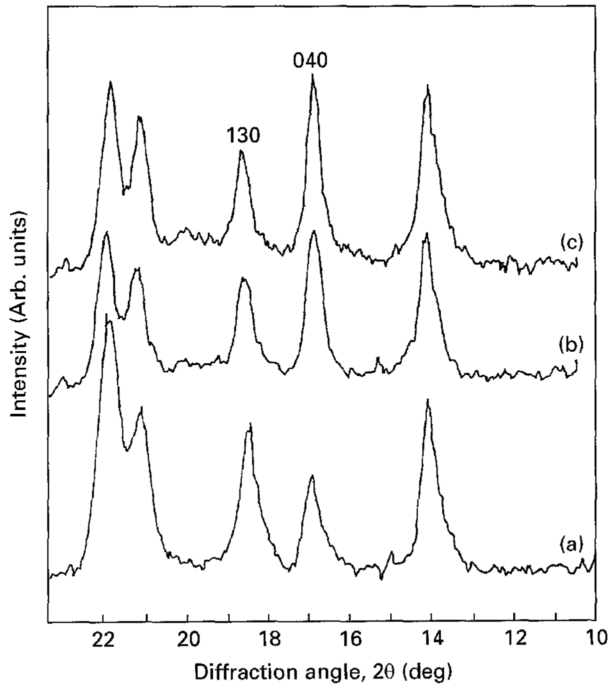

Figure 6 As for Fig. 5 but for melt crystallized samples of PP containing (a) 20, (b) 30 and (c) 40 wt % of $CaCO_3$.

$CaCO_3$ concentration (about 10 wt %) but a decrease at a certain higher concentration (about 20 wt %). These variations were found to be less prominent in the case of the samples prior to melt crystallization. These findings suggest that the impact strength of PP filled with $CaCO_3$ would depend strongly on the concentration of the filler. It is interesting to note that these expectations are in accordance with the variation of impact strength of PP containing different concentration of $CaCO_3$ reported by number of authors. [5–7].

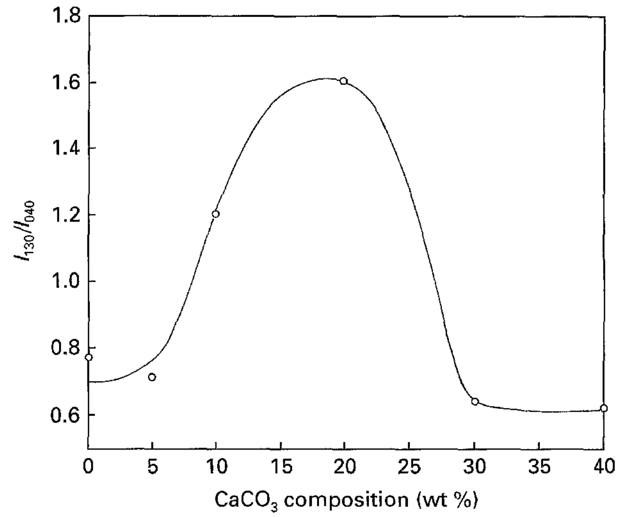

Figure 7 The ratio of the intensities of the 130 and 040 reflections as a function of PP–$CaCO_3$ composition.

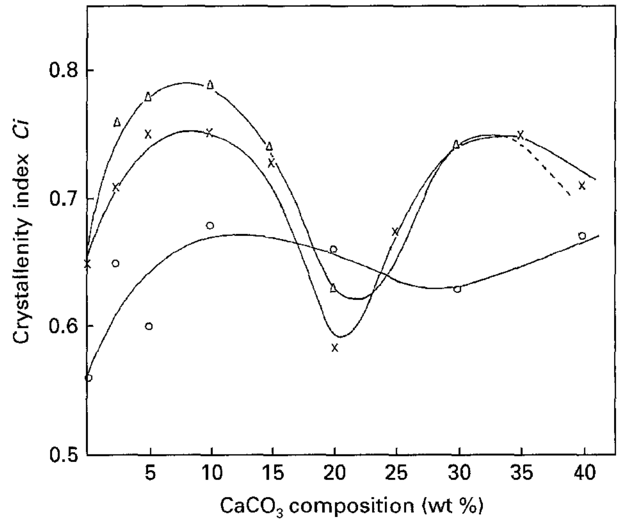

Figure 8 Variations in the *Ci* of samples; (○) prior to melt crystallization and after melt crystallization at T_c values of (×) 110 °C and (△) 115 °C.

It is seen from the above studies that $CaCO_3$ makes an effective nucleating agent for the crystallization of PP. This additive itselt exists in different crystalline forms such as calcite, vaterite and aragonite. A separate study on the structure of $CaCO_3$ powder used by us indicated that it mainly contained aragonite ($a = 0.797, b = 0.574, c = 0.496$ nm). The α form of PP crystallites are monoclinic with $a = 0.665$, $b = 2.09$, $c = 0.65$ nm and $\beta = 99$ °C. [20] Crystal mismatch theory for nucleation suggests that the lattice parameters or their integral multiples should be as close as possible for effective nucleation [21]. A comparison of the two structures in the present case, indicates that only one of the axes have a close match in this respect. This can give rise to preferential nucleation and hence orientation of certain crystalline planes of PP during crystallization.

We have carried out similar studies with other grades of $CaCO_3$ including laboratory synthesized *in situ* deposited $CaCO_3$, surface treated $CaCO_3$ etc. The results of these studies will be published in the near future.

4. Conclusion

It is seen from the present studies that the incorporation of $CaCO_3$ in polypropylene affects the crystallization behaviour to a large extent. In presence of the filler the spherulitic growth rate is faster, the ultimate spherulite size smaller and the crystallinity higher than without it. The compositional dependence of these parameters is complex. These results may be able to throw some light on the peculiar variation of mechanical properties reported in the past for talc or calcium carbonate filled polypropylene.

References

1. I. M. WARD, "Developments in Oriented Polymers" Vol. 1, 2, (Applied Science Publishers, London, 1982).
2. A. E. ZACHARIADES and R. S. PORTER, "High Modulus Polymers", (Marcel Dekker, New York, 1988).
3. G. GRUENWALD, "Plastics-How Structure Determines Properties", (Hanser Verlag, Munich, 1993).
4. J. C. SEFERIS and P. S. THEOCARIS, (ed), "Interrelations Between Processing, Structure and Properties of Polymeric Materials", (Elsevier, Amsterdam, 1984).
5. H. S. KATZ and J. V. MILEWSKI, "Handbook of Fillers for Plastics", (Van Nostrand Reinhold, New York, 1987) pp. 139–140.
6. S. F. XEVIER, J. M. SCHULTZ and K. FRIEDRICH, *J. Mater. Sci* **25** (1990) 2411.
7. R. HERZIG and W. E. BAKER, *Ibid* **28** (1993) 6531.
8. G. ZOU, Z. HE, J. YU and Z. HAN, *Makromol. Chem.* **187** (1986) 633.
9. P. CORRADINI and G. GUERRA, *Adv. Polym. Sci.* **100** (1992) 185.
10. S. RADHAKRISHNAN and S. G. JOSHI, *Eur. Polym. J.* **23** (1987) 819.
11. S. RADHAKRISHNAN and R. JOSEPH, *Ferroelectrics* **142** (1993) 189.
12. S. RADHAKRISHNAN and J. M. SCHULTZ, *J. Cryst. Growth* **116** (1992) 378.
13. J. M. SCHULTZ, "Polymer Material Science", (Prentice-Hall, New York 1974).
14. B. WUNDERLICH, "Macromolecular Physics", Vol. 1 and 2, (Academic Press, New York, 1976).
15. R. S. STEIN and G. L. WILKES, in "Structure and properties of Oriented Polymers", edited by I. M. Ward, (Applied Science Publishers, London, 1975) p. 76.
16. M. T. SHAW, *Annual Rev. Mater. Sci.* **10** (1980) 19.
17. S. RADHAKRISHNAN and V. M. NADKARNI, *Polym. Engng Sci.* **24** (1984) 1383.
18. S. RADHAKRISHNAN, *Angew. Macromol. Chem.* **141** (1986) 49.
19. S. RADHAKRISHNAN and V. M. NADKARNI, *Inter. J. Polym. Mater.* **11** (1986) 79.
20. S. BRUCKNER, S. V. MEILLE, V. PETRACONNI and B. PIROZZI, *Progr. Polym. Sci.* **16** (1991) 361.
21. K. MAURITZ, E. BAUER and A. HOPFINGER, *J. Macromol. Sci. Macromol. Rev.* **8** (1978) 1.

*Received 10th April 1995
and accepted 18th March 1996*