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Poly(phenylene sulfide)/liquid crystalline polymer blends: 1. Non-isothermal crystallization kinetics

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The non-isothermal crystallization behaviour of poly(phenylene sulfide) (PPS) in blends with thermotropic liquid crystalline polymer (TLCP) was studied by means of differential scanning calorimetry. The TLCP chosen for the investigation was poly(oxybenzoate-*co*-ethylene terephthalate). It was observed that the Ozawa equation is valid not only for neat PPS, but also for the blends. The PPS crystallization temperature was found to increase markedly upon addition of the TLCP. A notable reduction in Avrami exponents for the PPS/LCP blend systems suggests that the nucleated process leads to rod-shaped growth with thermal nucleation. The cooling crystallization function, which represents the rate of non-isothermal crystallization, was found to decrease with decreasing temperature and/or increase in LCP content. It has been concluded that the non-isothermal crystallization of PPS is strongly accelerated by the presence of TLCP. © 1997 Elsevier Science Ltd.

(Keywords: poly(phenylene sulfide); thermotropic liquid crystalline polymer; polymer blend)

INTRODUCTION

Poly(phenylene sulfide) (PPS) is an important high strength/high temperature engineering thermoplastic with dual properties of thermoplastic and thermoset. During fabrication of thermoplastic composites, the polymer invariably undergoes repeated melting, quenching and crystallization. The mechanical and physical properties of the moulded and extruded products of crystalline polymers are governed by the supermolecular morphology, which in turn is controlled by the crystallization process. The properties of semicrystalline polymers such as PPS depend on the crystallization behaviour of the polymer. It is important, therefore, to understand the effects of these process cycles on the crystallization kinetics of PPS. Thus, the study of the kinetics of crystallization is necessary for optimizing the process conditions and establishing the structure–property correlations in polymers.

Liquid crystalline polymer (LCP) blends have been studied extensively in recent years[1,2]. The motivation was first to use the high-tensile modulus of the LCPs in the solid state to reinforce the matrix polymers. Secondly, the low viscosity of the LCPs can reduce the overall viscosity of the blend and thus act as a good processing aid. The thermotropic liquid crystalline polymer (TLCP), which is initially dispersed as spheres or droplets, can be elongated in adequate flow fields to give an *in situ* reinforcement. Elongated fine fibrils can effectively reinforce the matrix polymer. Moreover, the LCP phase has been shown to influence the crystallizability of the matrix[3–7].

The crystallization behaviour of neat PPS[8], of PPS filled with solid fillers[9–11] and of PPS blended with thermoplastic polymers[12,13] has been studied extensively by isothermal methods. The study of the non-isothermal crystallization of polymers is of great technological significance, since most practical processing techniques proceed under non-isothermal conditions. The non-isothermal experiments would provide greater insight into the understanding of the crystallization behaviour of polymers because the more frequently used isothermal methods are often restricted to narrow temperature ranges[14]. The nonisothermal crystallization kinetics of linear and branched PPSs was studied by Lopez and Wilkes[8]. They have found that the Avrami exponents, determined by the Ozawa equation[15] from non-isothermal measurements, are in good agreement with those achieved by isothermal methods. Minkova *et al.*[16] found that blending PPS with Vectra-B, a wholly aromatic commercial LCP from Hoechst Celanese, leads to an increase of the non-isothermal crystallization temperature without any reduction in the degree of crystallinity. Minkova and Magagnini[14] found that the non-isothermal crystallization of PPS is strongly accelerated by Vectra-B950 without any change in the type of nucleation and

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the geometry of crystal growth. Hong *et al.*[17] have studied non-isothermal crystallization kinetics of PPS/Vectra-B950 blends. This study reveals a notable reduction in the Avrami exponent, which indicates that the nucleated process leads to rod-shaped growth with thermal nucleation.

In the present paper, we present the results of our investigation on the effects of an aliphatic–aromatic thermotropic liquid crystalline copolyester, poly(oxybenzoate-*co*-ethylene terephthalate) (POB–PET), on the non-isothermal crystallization kinetics of PPS/LCP blends by differential scanning calorimetry (d.s.c.) data, adopting the Ozawa equation[15].

EXPERIMENTAL

The PPS used was a commercial grade Ryton V-1 (M_w about 60 000) manufactured by Phillips Petroleum Co. This material shows a melting point of 282°C and melt flow index of 79.8 g per 10 min (ASTM 1238, 5 kg, 316°C). Thermotropic liquid crystalline POB–PET was synthesized from PET and 4-acetoxy benzoic acid according to the procedure reported in our previous study[18]. The intrinsic viscosity of the PET used in the synthesis was 0.6 dl g^{-1}. The composition of POB–PET was 30–70, and it was termed P37. P37 exhibited birefringence when it was heated to 300°C and then cooled down. P37 shows a glass transition temperature of 65.1°C and crystal to nematic transition at 197.7°C.

Preparation of blends

Powders of the liquid crystalline P37 and PPS were dried at 130°C under vacuum for 8 h prior to the mixing. The PPS/P37 blends, with a P37 content in the range 3, 5, 10, 20 and 30 wt% were prepared in a 30 ml mixer attached to a Brabender Plasticorder, at 290°C and 100 rev min^{-1} for 5 min, under nitrogen. Blank samples of both PPS and P37 were subjected to the same treatment.

Thermal analysis

Thermal properties were measured by a Mettler TA4000 series differential scanning calorimeter. The heat of fusion and heat of crystallization were determined from the peak area of the d.s.c. thermograms. The apparatus was calibrated with indium at different scanning rates. The lag between sample and pan holder temperature was also taken into account, and computed through indium crystallization tests described by Elder and Wlochowicz[19].

Non-isothermal crystallization kinetics

About 10 mg of the polymer sample was weighed very accurately in the aluminium d.s.c. pan and placed in the d.s.c. cell. It was heated from 30°C to the melt temperature of 320°C at a rate of 10°C min^{-1} under nitrogen atmosphere.

The sample was kept for 10 min at this temperature to destroy any residual nuclei, before cooling at a specified cooling rate. Constant cooling rates of 10, 15, 20, 25 and 30°C min^{-1} were applied. The thermograms corresponding to heating and cooling cycles were recorded and analysed to estimate the non-isothermal crystallization kinetics.

RESULTS AND DISCUSSION

The d.s.c. thermograms obtained at a cooling rate of 10°C min^{-1} for neat PPS and its blends with P37 contents of up to 30% are shown in *Figure 1*. The exothermic crystallization peaks are monomodal and their shapes indicate that secondary crystallization does not play an important role in these blends. Also observed was the fact that the blend exotherms are much sharper than that of pure PPS and are located at a higher temperature with respect to the latter. The PPS crystallization temperature was found to increase from 241 to 251°C upon addition of 3–30% P37.

The crystallization temperature, T_c, the half-widths of the crystallization peaks ΔT and the degree of crystallinity α of the PPS phase obtained at different cooling rates for the blends with P37 content in the range 3–30% are presented in *Table 1*. The crystallization temperatures T_c are those corresponding to the exothermic peak maxima, corrected as described by Elder and Wlochowicz[19]. The degree of crystallinity α has been calculated from the enthalpy of crystallization normalized to the PPS content, assuming that the contribution of the TLCP phase is negligible[20]. The value of 146.2 J g^{-1} was estimated by Maemura *et al.*[21] for the enthalpy of

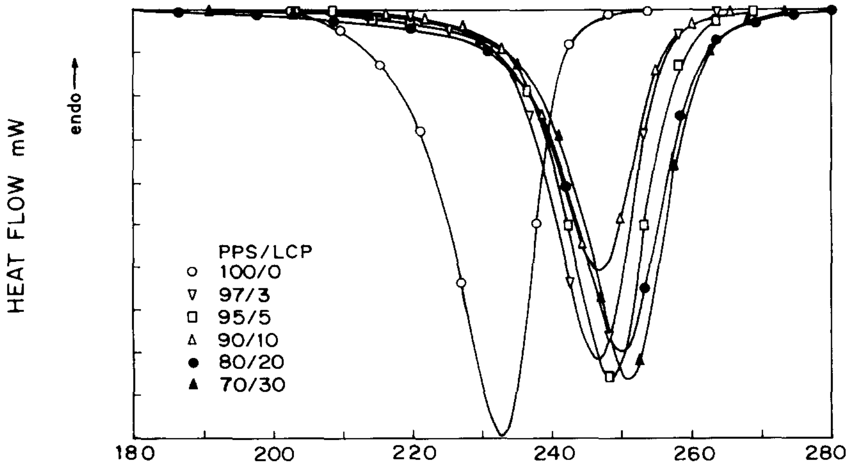

Figure 1 D.s.c. cooling traces of PPS/POB–PET blends, recorded at 10°C min^{-1}

Table 1 Effect of POB–PET on the crystallization temperature (T_c), degree of crystallinity (α), half-width of crystallization peak (ΔT) and Avrami exponent (n) of PPS in PPS/POB–PET blends

Blend PPS/POB–PET		10°C min^{-1}			15°C min^{-1}			20°C min^{-1}			25°C min^{-1}			30°C min^{-1}			
No.	% (wt/wt)	T_c (°C)	α	ΔT (°C)	T_c (°C)	α	ΔT (°C)	T_c (°C)	α	ΔT (°C)	T_c (°C)	α	ΔT (°C)	T_c (°C)	α	ΔT (°C)	n
1	100/0	242.3	0.30	21.4	239.4	0.28	23.5	237.1	0.31	26.7	235.2	0.31	29.3	232.0	0.31	36.6	2.97
2	97/3	250.9	0.31	14.4	250.1	0.28	16.0	249.6	0.30	15.3	248.9	0.29	16.4	247.7	0.29	16.9	2.68
3	95/5	252.2	0.29	14.0	250.6	0.30	16.0	250.8	0.29	15.5	250.3	0.30	16.4	249.8	0.30	16.4	2.50
4	90/10	253.0	0.30	14.5	252.6	0.29	15.7	252.1	0.29	14.9	251.3	0.30	15.3	250.8	0.29	14.8	2.45
5	80/20	253.9	0.28	11.4	252.1	0.29	12.4	251.3	0.30	14.4	250.0	0.32	14.9	249.6	0.31	13.4	2.23
6	70/30	254.2	0.29	12.4	253.9	0.29	12.4	252.8	0.29	13.2	251.6	0.28	14.2	250.8	0.30	12.3	2.01

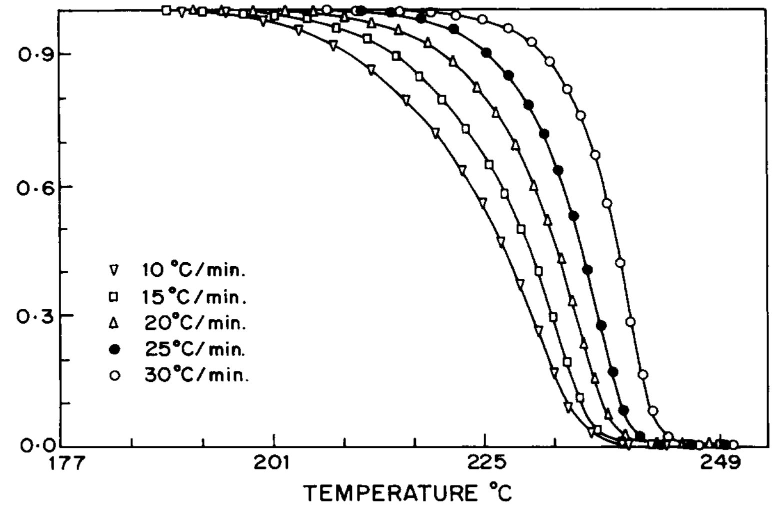

Figure 2 Fraction of crystallized PPS *versus* crystallization temperature

fusion of 100% crystalline PPS. It is noticed that α remains constant, which suggests that the addition of P37 does not affect the degree of crystallinity of PPS. At a fixed P37 level, the crystallization peak temperature (T_c) decreased with increasing cooling rate, whereas at a given cooling rate the T_c increased as the LCP content increased.

The crystallization temperature increases upon addition of P37 to PPS whereas it decreases on increasing the cooling rate, as could be expected for the polymer crystallization controlled by nucleation[22]. The sharpness of the crystallization peaks, as measured by ΔT is considerably higher for the blends than for pure PPS. These suggest that the rate of non-isothermal crystallization of PPS is increased appreciably by the presence of P37.

The overall non-isothermal crystallization kinetics of PPS and its blends with P37 was studied using the Ozawa equation (1)[15]:

$$\ln\{-\ln[1 - X(T)]\} = \chi - n \ln \phi \qquad (1)$$

where X is the volume fraction of material crystallized at temperature T, ϕ is the constant cooling rate, n is the Avrami exponent, which depends on the nucleation density and on the spherulitic radial growth rate, for both instantaneous and sporadic nucleation, and χ is the cooling crystallization function. The amorphous fractions $[1 - X(T)]$ of the PPS phase of PPS/P37 blends with P37 content between 0 and 30% were calculated from the d.s.c. traces and plotted against T for different cooling rates. The plots drawn for pure PPS and for 90/10 PPS/P37 blend are shown in *Figures 2* and *3*, respectively. The Ozawa plots can be obtained by plotting the double logarithm of the reciprocal amorphous fractions of the PPS phase against cooling rate, for different temperatures, as shown in *Figures 4* and *5*, respectively for PPS and for 90/10 PPS/P37 blend. It can be seen that these plots as well as those of all other blends studied represent straight lines, which means that the Ozawa equation describes the non-isothermal crystallization behaviour of the blends investigated satisfactorily.

The intercept of the Ozawa plots give the cooling crystallization function (χ), which represents the rate of non-isothermal crystallization[15,22,23]. The plot of cooling crystallization function against temperature is presented in *Figure 6*. The function decreased with a decrease in temperature or increase in LCP content. The values of χ measured are in good agreement with those given by Ozawa[15] for PET, Kozlowski[23] for nylon, Elder and Wlochowicz[19] for PP and Lopez and Wilkes[22] for PPS. The χ values measured for the blends are of the same order of magnitude as those obtained for pure PPS, but they appear on the plot in a higher temperature range due to the higher crystallization temperature of the blends.

The Avrami exponent, n, was obtained from the slope of the Ozawa plots. The Avrami exponents so obtained are plotted against temperature in *Figure 7*. PPS gives a value of 3, suggesting that the nucleated process leads to

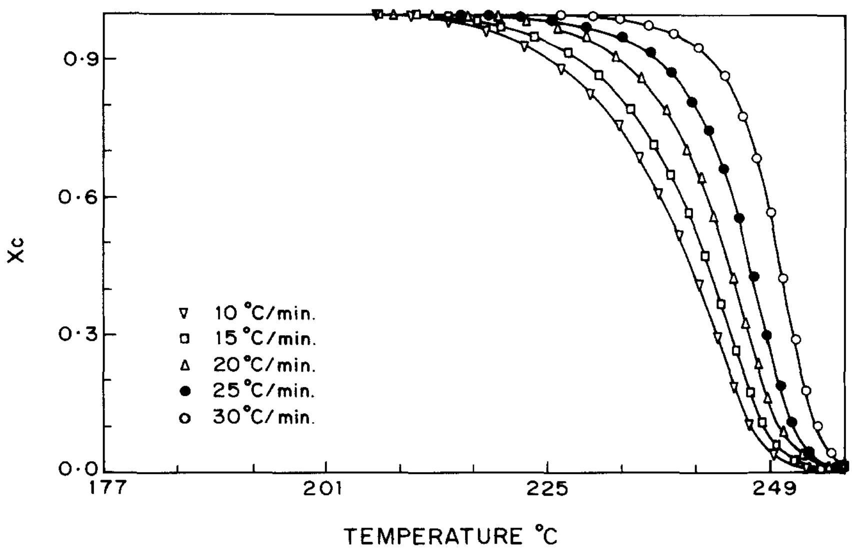

Figure 3 Fraction of crystallized PPS phase in PPS (90%)/LCP (10%) *versus* crystallization temperature

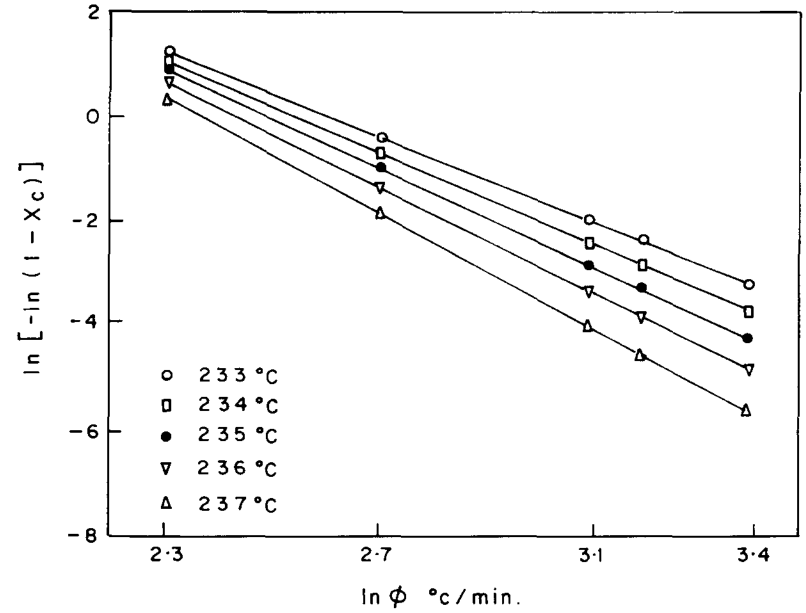

Figure 4 Ozawa plots of non-isothermal crystallization for neat PPS

a spherulitic growth with thermal nucleation[24-26]. In the case of PPS/LCP blend systems, however, the Avrami exponent decreases with the temperature decrease, particularly at low temperatures. This clearly indicates that the nucleated process leads to rod-shaped growth with thermal nucleation[24,25]. Hong *et al.* reported[17] similar results for PPS/Vectra B 950 blends. Two factors may lower the value of Avrami exponent, n: (1) fast crystallization rate of the blend systems at lower temperatures prevents the spherulite from developing into three-dimensional crystallites[22]; (2) growth site impingement, truncation of spherulites, impurity segregation and slightly slow secondary crystallization[19,22,27-29] may change the crystallization mechanism if the crystalline weight fraction is higher than 0.5. However, at higher crystallization temperatures, e.g. 246–247°C, the Avrami exponent becomes approximately 3 because the predetermined nuclei grow into three-dimensional spherulites before cooling[30]. This finding shows that the type of nucleation and the geometry of crystal growth markedly change in the presence of P37. The deviation of Avrami exponent n could be attributed to factors such as time-dependent nucleation, variant growth rate constant as well as a combination of homogeneous and heterogeneous nucleation. However, in general, it is difficult to elucidate the growth of geometry and the type of nucleation solely from the value of n. On the basis of Mandelkern's analysis[31] the crystallization of PPS may involve homogeneous nucleation whereas the blends might involve heterogeneous nucleation with two-directional diffusion controlled growths.

CONCLUSIONS

The non-isothermal crystallization behaviour of PPS in blends with TLCP was studied by means of d.s.c. It was shown that the Ozawa equation is valid not only for neat PPS, but also for the blends. The PPS crystallization temperature was found to increase markedly upon

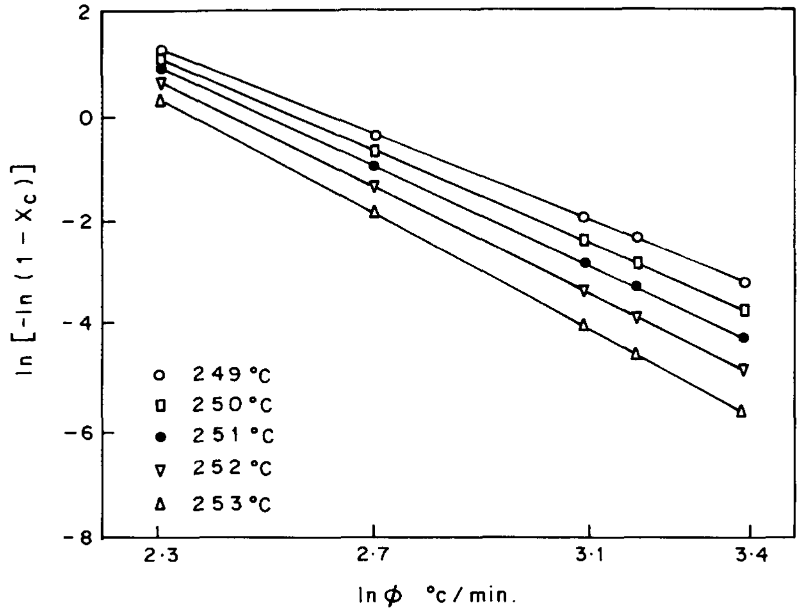

Figure 5 Ozawa plots of non-isothermal crystallization for neat PPS/POB–PET blends

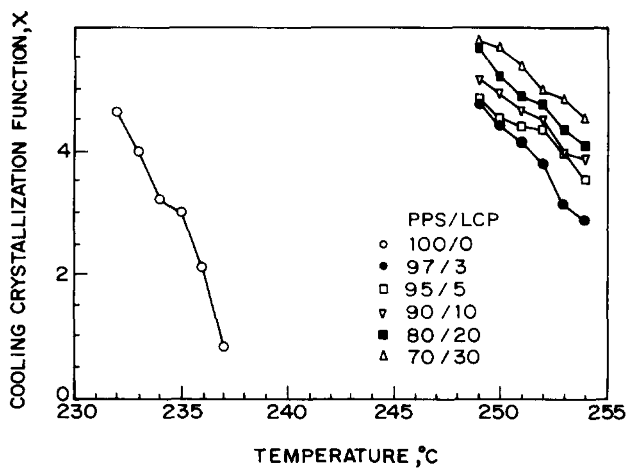

Figure 6 Plot of cooling crystallization function *versus* temperature for PPS/POB–PET blends

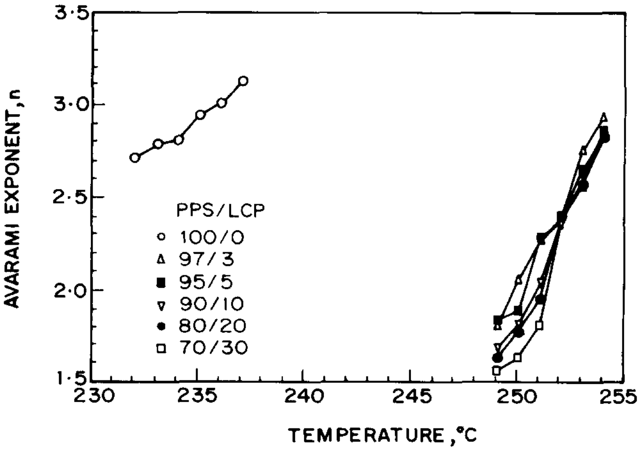

Figure 7 Plot of Avrami exponent (n) *versus* temperature of PPS/POB–PET blends

addition of 3–30% LCP. A notable reduction in Avrami exponents for the PPS/LCP blend systems suggests that the nucleated process leads to rod-shaped growth with thermal nucleation. The cooling crystallization function, which represents the rate of non-isothermal crystallization, decreases with decreasing temperature or increase in LCP content. It has been concluded that the non-isothermal crystallization of PPS is strongly accelerated by the presence of LCP.

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REFERENCES

1 Kiss, G. *Polym. Eng. Sci.* 1987, **27**, 410
2 Kolhi, A., Chung, N. and Weiss, R. A. *Polym. Eng. Sci.* 1989, **29**, 573
3 Kimura, M., Porter, R. S. and Salee, G. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 367
4 Joseph, E. G., Wilkes, G. L. and Baird, D. G. in 'Polymer Liquid Crystals' (Ed. A. Blumstein), Plenum Press, New York, 1984
5 Bhattacharya, S. K., Tandolkar A. and Misra, A. *Mol. Cryst. Liq. Cryst.* 1987, **153**, 501
6 Paci, M., Barone, C. and Magagnini, P. L. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1595
7 Pracella, M., Chielini, E. and Dainelli, D. *Die Makromol. Chem.* 1989, **190**, 175
8 Lopez, L. C. and Wilkes, G. L. *Polymer* 1988, **29**, 106
9 Nadkarni, V. M. and Jog, J. P. *J. Appl. Polym. Sci.* 1985, **30**, 997
10 Desio, G. P. and Rebenfeld, L. *J. Appl. Polym. Sci.*, 1990, **39**, 825
11 Song, S. S., White, L. J. and Cakmak, M. *Polym. Eng. Sci.* 1990, **30**, 994
12 Nadkarni, V. M., Shingankuli, V. L. and Jog, J. P. *Int. Polym. Process.* 1987, **2**, 53
13 Shingankuli, V. L., Jog, J. P. and Nadkarni, V. M. *J. Appl. Polym. Sci.* 1988, **36**, 335
14 Minkova L. I. and Magagnini, P. L. *Polymer* 1995, **36**, 2059
15 Ozawa, T. *Polymer* 1971, **12**, 150

16 Minkova, L. I., Paci, M., Pracella, M. and Magagnini, P. L. *Polym. Eng. Sci.* 1992, **32**, 57

17 Hong, S. M., Kim, B. C., Kim, K. U. and Chung, I. J. *Polymer J.* 1992, **24**, 727

18 Mathew, J., Bahulekar, R. V., Ghadage, R. S., Rajan, C. R., Ponrathnam, S. and Prasad, S. D. *Macromolecules* 1992, **25**, 7338

19 Elder, M. and Wlochowicz, A. *Polymer* 1983, **24**, 1593

20 Minkova, L. I., De Petris, S., Paci, M., Pracella, M. and Magagnini, P. L. 'Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends', Chem Tec Publishing, Ontario, Canada, 1993, p. 153

21 Maemura, E., Cakmak, M. and White, L. J. *Int. Polym. Process.* 1990, **3**, 79

22 Lopez, L. C. and Wilkes, G. L. *Polymer* 1989, **30**, 882

23 Kozlowski, W. *J. Polym. Sci. C* 1970, **38**, 47

24 Day, M., Suprunchuk, T., Cooney, J. D. and Wiles, D. M. *J. Appl. Polym. Sci.* 1988, **36**, 1097

25 Deslandes, Y., Dat, M., Sabir, N. F. and Suprunchuk, T. *Polymer Composites*, 1989, **10**, 360

26 Kumar, S., Anderson, D. P. and Adams, W. W. *Polymer* 1986, **27**, 329

27 Cebe, P. and Hong, S. D. *Polymer* 1986, **27**, 1183

28 Tobin, M. C. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 2253

29 Kim, S. P. and Kim, S. C. *Polym. Eng. Sci.* 1990, **31**, 110

30 Jabarin, S. A. *J. Appl. Polym. Sci.* 1987, **34**, 85

31 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964