Morphology of binary blends of linear and branched polyethylene: transmission electron microscopy

M. T. Conde Braña, J. I. Iragorri Sainz*, B. Terselius and U. W. Gedde†
Department of Polymer Technology, The Royal Institute of Technology,
S-100 44 Stockholm, Sweden
(Received 1 December 1987; revised 5 July 1988; accepted 22 September 1988)

Binary mixture of low molecular weight linear polyethylene (PE) ($M_w = 2500$, $M_w/M_n = 1.1$) and higher molecular weight branched PE ($M_w = 65\,000$–$146\,000$, ethyl- butyl and hexyl branches, 0–1.3 mol%), crystallized at 387–389 K at which both components of the blends crystallize, have been studied by transmission electron microscopy (TEM). TEM on thin sections treated with chlorosulphonic acid and uranyl acetate provides direct evidence for cocrystallization of the components. The absence of white unstained spots and the uniform lamellar structure (i.e. thickness of amorphous layer and local crystallinity) constitute the experimental evidence in favour of this view. TEM on the pure branched PE samples further supports this view. The correspondence between the crystallinity values obtained by TEM and d.s.c. indicates that the structural features obtained by TEM are representative of the samples studied.

(Keywords: linear polyethylene; branched polyethylene; binary mixtures; transmission electron microscopy; morphology; cocrystallization)

INTRODUCTION

Blends of linear and branched PE have aroused considerable scientific (e.g. refs. 1–5) and commercial interest during recent years. A central question being studied is whether or not the components cocrystallize. Norton and Keller[1] presented electron microscopy findings in favour of segregation of the components in a binary blend of unfractionated commercial grades of linear PE and ethyl-branched PE (1.4 mole% ethyl groups) crystallized at 397 K. They reported that the linear PE fraction crystallizes at the isothermal temperature in regular shaped sheets (so-called dominant lamellae) whereas the branched PE materials crystallize during the subsequent cooling phase forming finer, S-shaped subsidiary lamellae[1]. On the basis of d.s.c. data, these authors expect the microstructure of quenched samples to be less segregated, although no conclusive electron microscopy data in favour of such a view was presented in the paper.

Edwards[2] and Hu *et al.*[3] present data obtained by d.s.c., WAXS, SAXS and Raman spectroscopy indicating cocrystallization between linear and ethyl-branched PE. Both reports were based on blends of broad molecular weight samples of similar molecular weight. In the present paper which is a follow up of a recent paper[5], electron microscopy data for blends of fractions of linear PE and branched PE are presented. Low molecular weight linear PE ($M_w = 2500$) and relatively high molecular weight branched PE ($M_w = 65\,000$–$146\,000$) have been selected on the basis of their similar crystallization temperature ranges. In the previous paper[5], data from studies of crystallization kinetics and morphology indicated the existence of two regimes of crystallization. At high temperatures, the branched PE component crystallizes separately in relatively large spherulites. At lower temperatures, both the components crystallize and a very fine-textured spherulitic structure is obtained. The transition between the two regimes is very sharp in terms of temperature, of the order of 1 K. It is also accompanied by a sharp change in crystallization kinetics[5]. The samples used in this study have all been crystallized from the melt in the low temperature domain where cocrystallization of the components is possible. The question addressed in this paper is whether cocrystallization occurs in the blends.

EXPERIMENTAL

Binary 50/50 (w/w) mixtures of a linear PE sharp fraction ($M_w = 2500$, $M_w/M_n = 1.1$), referred to as L2.5, received from Polymer Laboratories Ltd, UK, and different branched PE fractions have been prepared by a solution mixing technique. The branched PE fractions (described in *Table 1*) were prepared from experimental LLDPE grades produced by Neste Polyethylene AB, Sweden, and Dow Chemical Corp. (Dowlex 2049) by gel permeation chromatography (g.p.c.) at Rapra Technology Ltd, UK. Each binary mixture was made by stirring a hot *p*-xylene solution containing both components for at least 20 minutes, and then rapidly precipitating the polymer by adding an excess amount of cold methanol, followed by cengtrifugation, decantation and drying in vacuum to constant weight. G.p.c. analysis showed that the molecular weight distributions of the components in the blends were the same as prior to blending and that the blended samples indeed were 50/50 mixtures.

The samples, both the binary mixtures and the pure BPE samples, were encapsulated in d.s.c. aluminium

---

* Present address: Department of Physical Chemistry, Polymer Group, Basque Country University, 644 Bilbao, Spain

† To whom all correspondence should be addressed

0032-3861/89/030410-06$03.00

Table 1 Molecular structure of branched polyethylene fractions and crystallization conditions for blends and pure BPE fractions

Sample	Branch	ε (%)[a]	[b]M_w	[b]M_n	[c]T_c/t_c	[d]T_c/t_c
BE1.3	ethyl	1.3	84 000	33 000	389/30	387/30
BE0.5	ethyl	0.5	146 000	76 000	389/30	389/30
BB0.4	butyl	0.4	64 000	10 000	387/30	392/30
BH0.8	hexyl	0.8	94 000	40 000	389/60	388/30

[a] Molar content of chain branches by i.r.
[b] By g.p.c.
[c] Crystallization conditions for blends: T_c in K and t_c in min
[d] Crystallization conditions for pure samples: T_c in K and t_c in min

pans, heated to 450 K, cooled at a rate of 80 K/min to a constant temperature (T_c), held at that temperature for t_c minutes and finally cooled at a rate of 80 K/min to 300 K. All thermal treatments were carried out in a temperature-calibrated Perkin–Elmer DSC-2 apparatus. The thermal treatment data for the different samples are presented in *Table 1*. The samples were treated according to the Kanig method[6]. Trimmed pieces were treated with chlorosulphonic acid for 1 day (L2.5/BE1.3, L2.5/BE0.5 and L2.5/BB0.4), 2 days (BE0.5 and BH0.8), 3 days (L2.5/BH0.8) or 7 days (BE1.3 and BB0.4) at 308 K, stained with 0.7% uranyl acetate for 24 h at 300 K, embedded in epoxy and sectioned with a glass-knife-equipped LKB ultramicrotome at room temperature. The 50–100 nm thick sections were examined in a JEOL JEM 100B electron microscope. The chosen conditions for the chlorosulphonic acid treatments were selected based on electron microscopy of a number of samples treated for different periods of time at 308 K with the acid. Martinez-Salazar *et al.*[7] have shown that the crystal thickness assessed by electron microscopy does not change with the chlorosulphonation time.

The measurements of the thickness of crystals and amorphous layers were carried out on magnified images of the negatives. The crystal lamellae and amorphous layers included in the analysis were selected by the intercept method, i.e. only those crossed by any of the introduced lines were chosen. The lines were always parallel and the line spacing was 100 nm. The accuracy of each measurement (reading) is 1 nm. Care was exercised so that only those crystal lamellae and amorphous layers which are parallel to the electron beam were evaluated. This was assured by only counting the crystals and amorphous layers appearing with sharp boundaries. The thickness of the boundary region ('grey zone') of the selected crystals is about 1 nm and the crystal thickness is in the analysis defined as the sum of the thickness of the white, unstained zone and the 'grey zone'. About 100 crystals and 100 amorphous layers were measured in this way in each sample.

RESULTS AND DISCUSSION

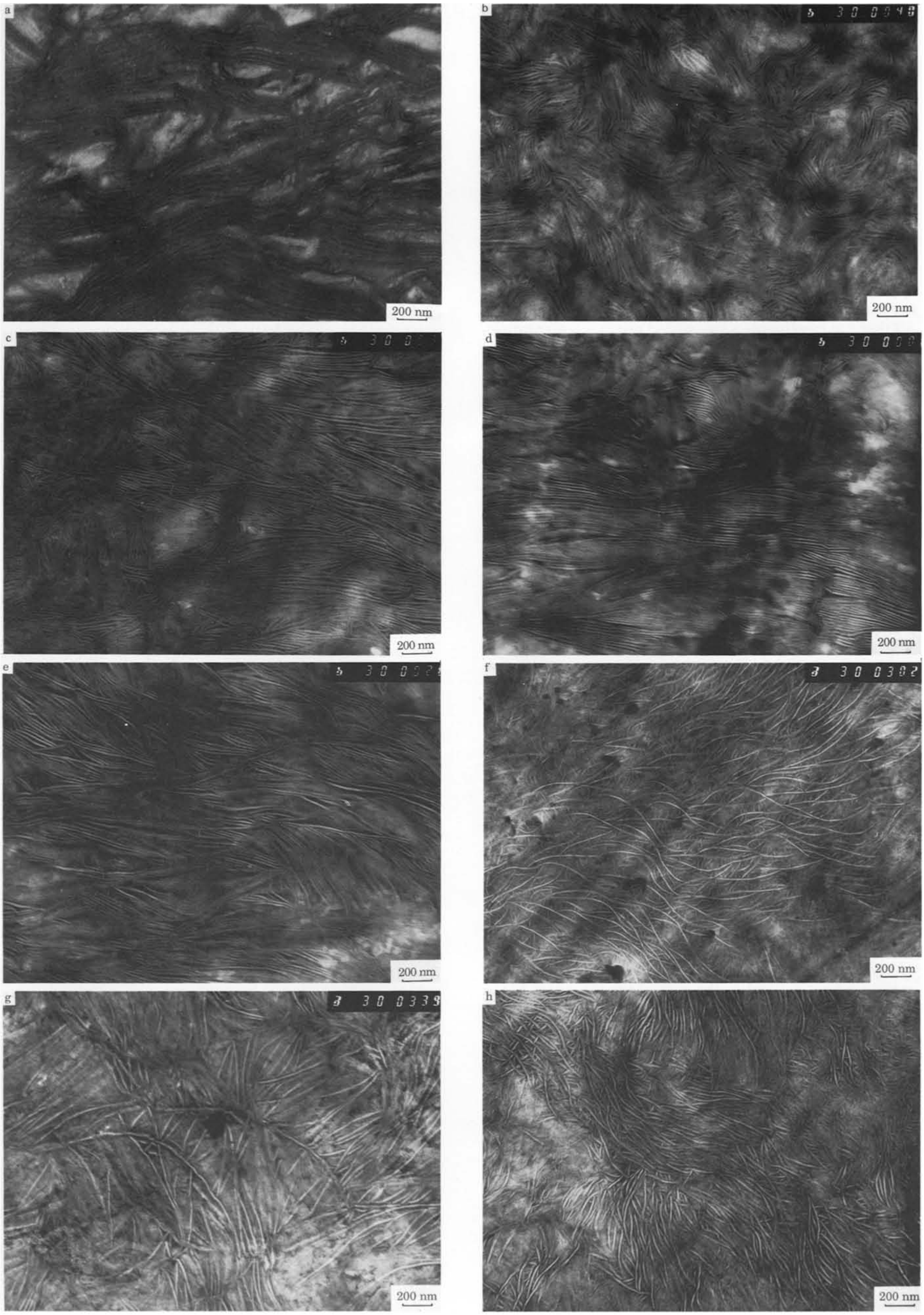
Electron micrographs of Kanig-treated sections are presented in *Figure 1*. The crystals appear light whereas the amorphous regions appear dark primarily due to the introduction of chlorine and sulphur in the less dense amorphous regions[8]. A generally striking feature is the major difference in the morphology between the LPE/LPE blend and the LPE/BPE blends (cf. *Figures 1a–e*). The low molecular weight component (L2.5) in the LPE/LPE blend is located in isolated domains in between the dominant lamellae (*Figure 1a*). The presence of the isolated L2.5 component in the structure is relatively easily detected as white, unstained areas in the micrographs[9]. There is, however, also another cause of the absence of contrast. If the stained surfaces of the crystal lamellae are tilted with respect to the beam their contours gradually disappear and the contrast is lost. A striking feature of the LPE/LPE blend is the presence of holes (*Figure 1a*) probably created by the sectioning process. Around those holes, areas without lamellar structure and thus composed of material enriched in L2.5 are observed. The existence of the holes demonstrates the anticipated brittleness of the low molecular weight material (L2.5). The LPE/BPE blends, on the other hand, display no signs of domains of segregated L2.5 (*Figures 1b–e*).

A number of important features are observed in the micrographs of the LPE/BPE blends shown in *Figures 1b–e*. The blends based on BE1.3 and BH0.8 exhibit a few, long (2.5 μm) S-shaped lamellae. Between these apparently dominant lamellae, shorter, almost equally thick lamellae are located. S-shaped crystal lamellae have been observed in LDPE samples by several researchers (e.g. refs. 1 and 10). The blends based on BE0.5 and BB0.4 display longer (2–4 μm) and straighter lamellae occasionally shaped as 'roof ridges'. The most common apex angles are 110°, 125° and 135°. Both Bassett *et al.*[10] and Voigt-Martin *et al.*[11] have observed roof ridge-shaped crystal lamellae in linear PE samples. The latter authors have identified the above apex angles with the crystallographic fold planes {201}, {302}, and {101} combined with {302} respectively. Chain tilt angles between 18° and 34° are indicated by the data obtained.

The transmission electron micrographs (*Figures 1f–i*) of the pure BPE samples display S-shaped and 1–2 μm long dominant lamellae. Between the dominant lamellae, S-shaped significantly shorter (0.02–0.4 μm) subsidiary lamellae are observed. The latter are of about the same thickness as the long dominant lamellae. Roof-ridged shaped crystal lamellae were not observed in these samples. The crystallinity of the pure BPE samples as judged from the density of crystal lamellae in the micrographs is significantly lower than in the corresponding LPE/BPE blends (cf. *Figures 1b–i*).

Figure 2 presents the distributions in thickness of the amorphous layers (L_a) and the crystals (L_c). Only crystal lamellae appearing with a good contrast in the micrographs were included in the analyses. The L_c distributions are generally more symmetrical than the L_a distributions. The latter are often skewed towards higher values.

The average crystal thickness ($\langle L_c \rangle$) is about the same, 12.5 nm, in the different blends (*Table 2*) which is as expected because the different samples have crystallized at about the same temperature (*Table 1*). The average thickness of the amorphous interlayer ($\langle L_a \rangle$) however, varies amongst the different samples (*Table 2*). The trend exhibits an increase in $\langle L_a \rangle$ with increasing degree of chain branching of the branched component of the blends (*Table 2*). The increase in $\langle L_a \rangle$ is significant and amounts to 70% of the lowest $\langle L_a \rangle$ value, which is obtained for L2.5/BB0.4. The pure BPE samples have significantly greater $\langle L_a \rangle$ values than in the LPE/BPE blends. The crystallinity values obtained from measurements of the thickness of the amorphous interlayer and of the crystals constitute a 'local' crystallinity value. There is a striking


a
200 nm
b
200 nm
c
200 nm
d
200 nm
e
200 nm
f
200 nm
g
200 nm
h
200 nm

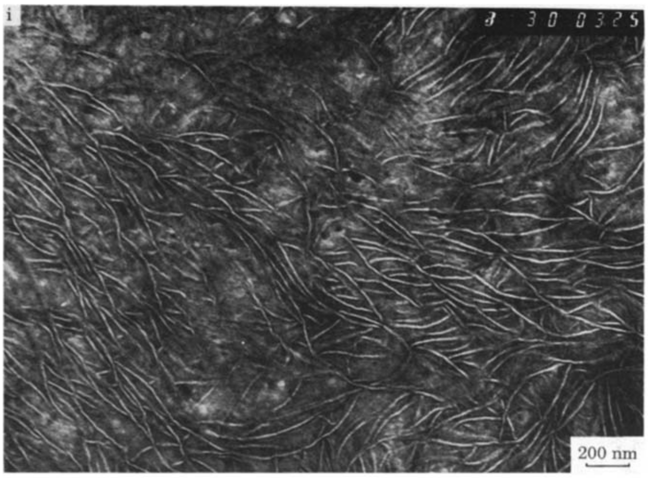


Figure 1 Transmission electron micrographs of samples treated according to the Kanig method. (a) L2.5/L66 crystallized from the melt at 392 K for three hours. (b) L2.5/BE1.3 (c) L2.5/BE0.5 (d) L2.5/BB0.4 (e) L2.5/BH0.8 (f) BE1.3 (g) BE0.5 (h) BB0.4 (i) BH0.8. The samples shown in *Figures 1b–e* have been crystallized under the conditions given in *Table 1*

correspondence between these local crystallinity values and the overall crystallinity as determined by d.s.c. (*Table 2*). This finding supports a hypothesis of intimate mixing and cocrystallization of the components in the blends. The high local crystallinity values recorded for the blends in comparison with the values obtained for the pure BPE samples also support this hypothesis.

A calculation of the thickness of an extended chain crystal based on L2.5 ($M_w = 2500$) assuming a chain tilt of 35° and a crystallinity of 90% gives a value of 16 nm which is significantly higher than the value (12.5 nm) obtained by TEM. However, the discrepancy amounting to 3.5 nm can be accounted for by considering the following items. The weight based molecular weight average is, in the present analysis, compared with the number based crystal thickness average. The use of a weight based crystal thickness average decreases the discrepancy by about 0.2 nm. The crystal thickness is underestimated by TEM due to the fact that the crystal lamellae are not perfectly perpendicular to the electron beam. A limited penetration of the crystals by the chlorosulphonic acid is also possible. The importance of these factors can be significant. The molecular weight determination by g.p.c. is associated with an uncertainty of about 10%. This is thus equivalent with a reduction in the discrepancy by about 2 nm.

Table 2 Thickness of amorphous interlayer (L_a) and crystals (L_c)

Sample	$\langle L_a \rangle^a$ (nm)	$\langle L_c \rangle^a$ (nm)	w_c(TEM)[b]	w_c(d.s.c.)[c]
L2.5/BE1.3	5.7	12.1	0.71	0.65
L2.5/BE0.5	3.7	12.3	0.79	0.75
L2.5/BB0.4	4.1	12.7	0.78	0.78
L2.5/BH0.8	6.9	12.5	0.68	0.66
BE1.3	14.7	9.5	0.43	0.40
BE0.5	12.8	13.3	0.55	0.54
BB0.4	9.3	13.3	0.62	0.62
BH0.8	13.4	9.4	0.45	0.44

[a] Arithmetic average

[b] By TEM according to equations 1 and 2:

$$V_c = \langle L_c \rangle / [\langle L_c \rangle + \langle L_a \rangle] \quad (1)$$

$$w_c = 1/[1 + \rho_a/\rho_c(1 - V_c)/V_c] \quad (2)$$

where V_c is the volume crystallinity, w_c is the weight crystallinity, ρ_a and ρ_c are the densities of the amorphous and crystalline phases, respectively. Values from the literature[12] for ρ_a and ρ_c are inserted in equation (2) to calculate w_c

[c] By d.s.c.

CONCLUSIONS

Binary mixtures of low molecular weight linear PE ($M_w = 2500$) and branched PE ($M_w \approx 60\,000$–$146\,000$) have been crystallized at temperatures at which both components crystallize (see ref. 5). Transmission electron microscopy of thin sections of samples treated with chlorosulphonic acid and stained with uranyl acetate provide direct evidence for cocrystallization of the components at these temperatures (387–389 K). The absence of white unstained spots in these samples (cf. linear PE/linear PE blends) and the relatively uniform estimated 'local' crystallinity constitute experimental evidence in support of this view. The correspondence in the crystallinity values obtained from TEM and d.s.c. indicate that the structural features revealed by TEM are representative of the samples. The invariance of crystal thickness (12.5 nm) in the different linear PE/branched PE samples is expected and is due to the similarity in crystallization temperature of the samples (*Table 1*). The conclusion that cocrystallization occurs in the linear PE/branched PE mixtures is further substantiated by the TEM data obtained for the pure branched PE samples. The latter show a significantly lower density of lamellar crystals, i.e. lower crystallinity in comparison with the binary mixtures.

ACKNOWLEDGEMENTS

This study has been sponsored by the Swedish Natural Science Research Council (NFR) grant K-RT 1910-100, the Swedish Board for Technical Development (STU) grant 85-3479 and Swedish Plastics Federation. The PE grades provided by Neste Polyethylene AB and the Dow Chemical Corp, the preparative g.p.c. work carried out by Dr S. Holding, RAPRA Technology Ltd, UK and the Spanish scholarships for M.T.C. and J.I.I.S. are gratefully acknowledged.

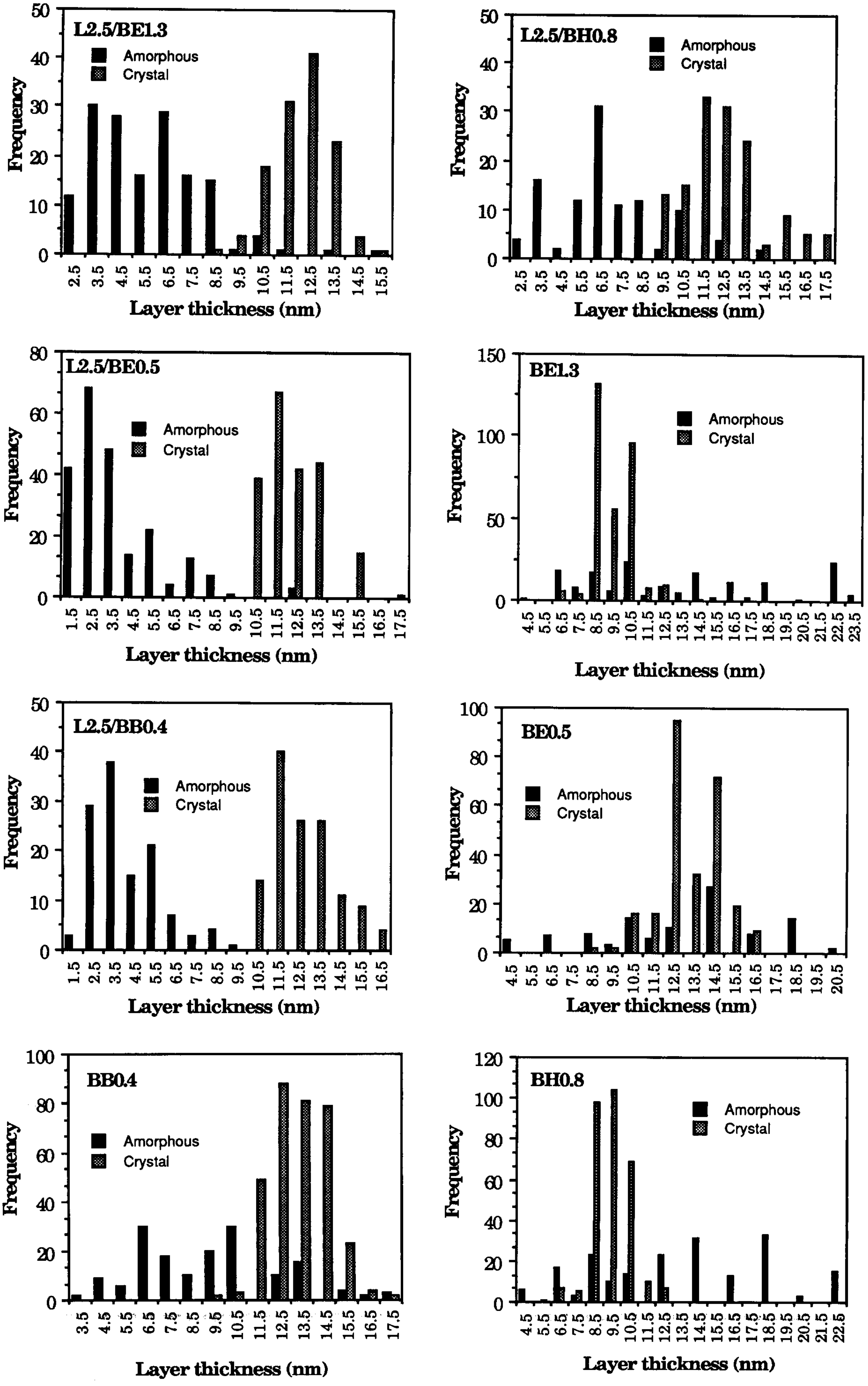


Figure 2 Histograms showing the distribution in amorphous layer thickness and crystal thickness for the different samples as are shown in the diagrams

REFERENCES

1 Norton, D. R. and Keller, A. *J. Mater. Sci.* 1984, **19**, 447

2 Edwards, G. H. *Brit. Polymer J.* 1986, **18**, 88

3 Hu, S.-R., Kyu, T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1987, **25**, 71

4 Rickinger, C., Larbi, F. C. and Rault, J. *J. Macromol. Sci.–Phys.* 1984, **B24**, 511

5 Rego Lopez, J. M. and Gedde, U. W. *Polymer* 1988, **29**, 1037

6 Kanig, G. *Colloid Polym. Sci.* 1977, **255**, 1005

7 Martinez-Salazar, J., Keller, A., Cagiao, M. E., Rueda, D. R. and Baltá Calleja, F. J. *Colloid Polym. Sci.* 1983, **261**, 412

8 Hodge, A. M. and Bassett, D. C. *J. Mater. Sci.* 1976, **12**, 265

9 Rego Lopez, J. M., Conde Braña, M. T., Terselius, B. and Gedde, U. W. *Polymer* 1988, **29**, 1045

10 Bassett, D. C., Hodge, A. M. and Olley, R. H. *Disc. Faraday Soc.* 1979, **68**, 218

11 Voigt-Martin, I. G., Fischer, E. W. and Mandelkern, L. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 2347

12 Wunderlich, B. in 'Macromolecular Physics, volume 1: crystal structure, morphology and defects', Academic Press, New York, 1973