Since, for reasons already stated, it seems preferable to use a molecular weight obtained from a measurement in one mixed solvent to one derived from several single solvents, we may insert a value of $M_C = 1.21 \times 10^3$ kg/mol as the left hand side of equation (6). However, it is found that the equation does not hold and M_C is smaller than the right hand side of the expression. Equation (6) does hold, if a value of 0.735 is taken for W_A which is not very different from the average analytical value of 0.71 used in this work.

The number-average molecular weight of the PS branches was 247 kg/mol, as measured with a Melabs membrane osmometer. It is not possible to calculate the grafting frequency (f) without a knowledge of M_n for the CTC backbone. If the latter is identical with its weight-average value (630 kg/mol), then $f = 0.99$ which must be regarded as the maximum possible value for f. Since M_n for the backbone is more likely to be of the order of ½ (630), a more realistic estimate of f is ~0.50. Grafting frequencies of value less than unity are not without precedent in the literature[15,16] and they preclude a simple backbone/graft model. They are indicative of crosslinking, presence of ungrafted substrate and also, possibly, block copolymer formation. The last two of these seem likely in the present system.

ACKNOWLEDGEMENTS

The award of a Science Research Council CAPS grant (to J. T. G.) is gratefully acknowledged. The authors thank Transparent Paper Company Limited, Bury, Lancashire, UK for providing the regenerated cellulose film.

REFERENCES

1 Guthrie, J. T., Huglin, M. B., and Phillips, G. O. *J. Appl. Polym. Sci.* 1972, **16**, 1017

2 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Polym. Sci. (C)* 1972, **37**, 205

3 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Eur. Polym. J.* 1972, 8, 747

4 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Appl. Polym. Sci.* 1971, **15**, 1033

5 J. T. Guthrie, Huglin, M. B. and Phillips, G. O. *IUPAC Int. Symp. Macromolecules Helsinki July 1972, Prepr. Vol 1 Paper II* – 26

6 Guthrie, J. T., Huglin, M. B., Richards, R. W., Shah, V. I. and Simpson, A. H. *Eur. Polym. J.* 1975, **11**, 527

7 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Makromol. Chem.* 1971, **149**, 309

8 Johnson, B. L. and Smith, J. in 'Light Scattering from Polymer Solution', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 2

9 Benoit, H. and Froelich, D. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 11

10 Tuzar, Z., Kratochvíl, P. and Straková, *Eur. Polym. J.* 1970, **6**, 1113

11 Strazielle, C. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London–New York, 1972, Ch 15

12 Sakurada, I., Ikada, Y. and Nishizaki, Y. *J. Polym. Sci. (C)* 1972, **37**, 265

13 Collins, R., Huglin, M. B. and Richards, R. W. *Eur. Polym. J.* 1975, **11**, 197

14 Chapiro, A., in 'Polymer Handbook', 2nd Edn, (Eds J. Brandrup and E. H. Immergut), Wiley, New York, 1975, p II–482

15 Taga, T. and Inagaki, H. *Angew, Makromol. Chem.* 1973, **33**, 129

16 Hamburger, C. J. *J. Polym. Sci. (A-1)* 1969, **7**, 1023

X-ray diffraction crystallinity measurements on mixtures of polyethylene and atactic polystyrene

Margaret A. McRae and William F. Maddams

Group Research and Development Department, The British Petroleum Company Ltd, Sunbury-on-Thames, Middlesex TW16 7LN, UK

(Received 11 November 1976; revised 4 January 1977)

Although X-ray diffraction is used widely for crystallinity measurements on a variety of polymers, particularly polyethylene, less attention has been paid to partly crystalline and partly amorphous composite systems. These may occur as block copolymers, with one type of block being substantially ordered and the other disordered, or as physical mixtures of the two types of polymer. It seems to have been tacitly assumed that the examination of such polymers is straight forward but the purpose of this Note, which reports crystallinity measurements on mixtures of high density polyethylene and atactic polystyrene, is to show that this may not always be the case.

EXPERIMENTAL

The near-linear polyethylene used in the blends was a BP Chemicals Ltd Rigidex experimental grade polymer containing about one butyl branch per thousand carbon atoms. The polystyrene was BP Chemicals Ltd EF grade, an amorphous, atactic polymer having M_w of about 240 000.

Ten mixtures of the two homopolymers, covering the composition range of 100% polyethylene/0% polystyrene to 10% polyethylene/90% polystyrene, in the form of hot pressed sheets, were examined with a Philips powder diffractometer over the 2θ range 14° to 26° using Ni-filtered CuKα radiation. The results were calculated by the method of Matthews, Peiser and Richards[1], as extended by Preedy[2], taking into account also the broad amorphous polystyrene peak at 19.5° 2θ which is almost coincident with the peak from amorphous polyethylene. This then gave the equation:

$$\%\ \text{Crystallinity} = \frac{I'_{110} + 1.36I'_{200}}{I'_{110} + 1.36I'_{200} + 0.81A'} \times 100$$

where I'_{110} and I'_{200} are the areas of the (110) and (200) polyethylene reflections and A' is the total area of the amorphous polyethylene and polystyrene broad peak at 19.5° 2θ. From the known compositions of the mixtures and the percentage crystallinity values obtained by the use of the above equation crystallinity values for the polyethylene may be calculated.

RESULTS AND DISCUSSION

The results for the ten mixtures are given in *Table 1*. The crystallinity values in the fourth column should be identical but they increase steadily

Table 1 Measured crystallinity values for ten polyethylene/polystyrene blends using X-ray diffraction scans over the range 14° to 26° 2θ

Composition of sample		Crystallinity of total blend (wt %)	Estimated crystallinity of polyethylene (wt %)
Polyethylene (wt %)	Polystyrene (wt %)		
100	0	75.3	75.3
99	1	74.4	75.2
95	5	72.7	76.5
90	10	70.6	78.4
85	15	68.6	80.7
80	20	67.7	84.5
70	30	61.8	88.4
50	50	48.1	96.2
30	70	36.0	112
10	90	15.5	155

with decreasing polyethylene content of the blend, reaching quite unrealistic values when polystyrene becomes the major component. This suggests the presence of a systematic error. The initial supposition that the specimens were not uniform in composition as a function of depth and that the proportion of polyethylene was greater nearer to the surface, thus biasing the reflection X-ray diffraction measurements, was disproved by measurements made in the transmission mode. These gave identical results. This suggests that the systematic error has its origin in considering the polystyrene component and, in particular, in the assumption that it has only the one broad amorphous peak at 19.5° 2θ.

Polystyrene was therefore examined over the range 3° to 26° 2θ. Measurements below about 10° are somewhat difficult because the X-ray beam is incident on the sample at near-glancing angles and it is necessary to use as large a polymer specimen as can be accommodated in the diffractometer. It is also advisable to use narrow slits but as these seriously attenuate the beam a compromise is necessary; 0.5° slits were selected. Satisfactory results were obtained, as shown in *Figure 1.* There is a second broad maximum at 9.5° 2θ, only marginally less intense than the one at 19.5° 2θ. This corresponds to a spacing of 8.84 Å. Krimm[3] has previously observed this peak and studied it at different temperatures in the context of obtaining structural information, as he did with the one at 19.5° 2θ, which corresponds to a spacing of 4.67 Å. He concluded that the 8.84 Å peak corresponds to quasi-order between adjacent chains, which are separated by 9 to 10 Å. The 4.67 Å spacing was tentatively assigned to two types of pseudoregularity; that between atoms in alternate phenyl groups in the same chain and that between atoms in phenyl groups and main atoms in neighbouring chains.

Although Challa, Hermans and Weidinger[4], in their work on isotactic polystyrene, disregard the peak at 9.5° 2θ without giving any clear reason, it is clearly necessary to take it into account to obtain correct crystallinity values. For example, it appears very clearly in blends containing polyethylene as the major component; *Figure 2* shows the diffractometer trace for a 70% polyethylene/30% polystyrene mixture. It is not difficult to resolve visually the two polystyrene peaks, which overlap somewhat, in order to apply the appropriate corrections for Lorentz polarization and the change of scattering factor with Bragg angle. Polyethylene shows negligible scattering from amorphous material at low Bragg angles and no additional correction term is necessary. The revised equation then becomes:

$$\% \text{ Crystallinity} = \frac{I'_{100} + 1.36I'_{200}}{I'_{110} + 1.36I'_{200} + 0.81A' + 0.18A''} \times 100$$

This has been used to obtain the values set out in *Table 2.* These are very satisfactory and the small trend towards higher crystallinity values for the mixtures containing substantial amounts of polystyrene may be the result of a systematic error in measuring the intensities of the (110) and (200) polyethylene reflections when they are weak and not well resolved from the relatively strong amorphous background signal. Alternatively, the trend may be real; although the hot pressed sheets of the various mixtures were prepared using seemingly constant conditions the melt viscosity will change with the composition and this may affect the effective thermal history of the sample and hence the crystallinity of the polyethylene. The general conclusion to be drawn from this study is that when X-ray diffraction crystallinity measurements are being made on polymer systems containing both crystalline and amorphous components care should be taken to define the background incoherent scattering from the latter over a wide Bragg angle range.

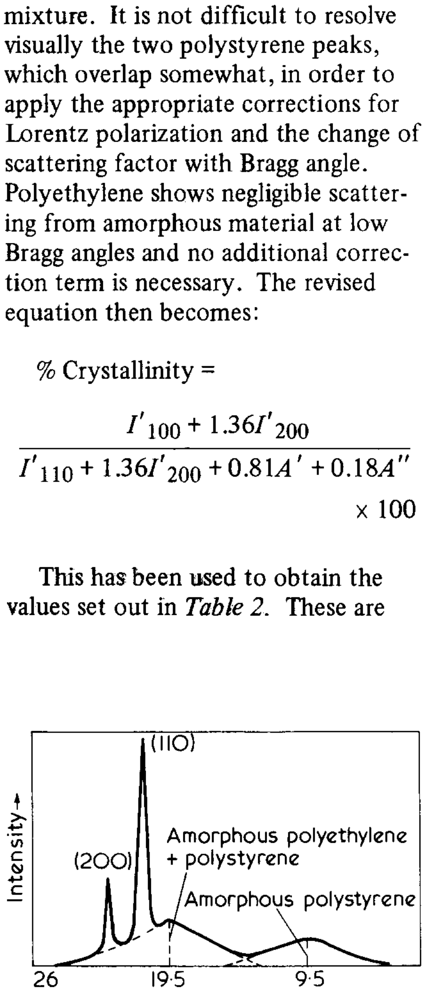

Figure 1 X-ray diffraction pattern of atactic polystyrene over the 2θ range 3° to 26°

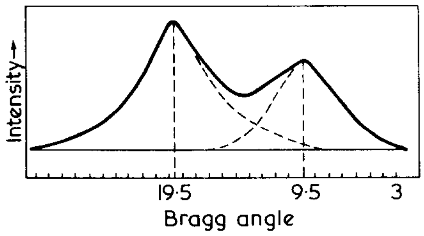

Figure 2 X-ray diffraction pattern of a blend of 70% polyethylene and 30% attactic polystyrene over the 2θ range 3° to 26°

Table 2 Measured crystallinity values for ten polyethylene/polystyrene blends using X-ray diffraction scans over the range 3° to 26° 2θ

Composition of sample		Crystallinity of total blend (wt %)	Estimated crystallinity of polyethylene (wt %)
Polyethylene (wt %)	Polystyrene (wt %)		
100	0	74	74
99	1	73	74
95	5	68	72
90	10	63	71
85	15	63	74
80	20	60	75
70	30	49.5	73
50	50	38.5	77
30	70	23	77
10	90	7.9	79

ACKNOWLEDGEMENTS

The authors wish to thank Dr J. E. Preedy for helpful suggestions. Permission to publish this paper has been given by The British Petroleum Company Limited.

REFERENCES

1 Matthews, J. L., Peiser, H. S. and Richards, R. B. *Acta Crystallogr.* 1949, 2, 85
2 Preedy, J. E. *Br. Polym. J.* 1973, 5, 13
3 Krimm, S. *J. Phys. Chem.* 1953, 57, 22
4 Challa, G., Hermans, P. H. and Weidinger, A. *Makromol. Chem.* 1962, 56, 169