PII: S0032-3861(96)00643-X

Polymer Vol. 38 No. 6, pp. 1409–1414, 1997

0032-3861/97/$17.00+0.00

Monoclinic polyethylene revisited

K. E. Russell, B. K. Hunter and R. D. Heyding*
Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada
(Received 15 February 1996; revised 18 April 1996)

The monoclinic modification of linear polyethylene has been prepared by battering samples of the orthorhombic modification. The X-ray diffraction pattern, the CP/MAS ^{13}C n.m.r. spectrum, and the thermal stability of the phase are re-examined. The efficacy of WAXS and n.m.r. analyses in identifying this phase in the presence of the orthorhombic and amorphous phases and in reactor powders and PE copolymers is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: monoclinic polyethylene; WAXS; CP/MAS ^{13}C n.m.r.)

INTRODUCTION

The monoclinic modification of linear polyethylene, first described by Teare and Holmes[1] and by Turner-Jones[2], is formed when the polymer is subjected to stress beyond the yield point. The stress may be due to tension[3–7] or compression[8–10]. It was also identified some years ago by Flory[11] and by Mandelkern[12,13] in a number of samples which had been annealed for very long periods at *ca.* 130°C and cooled rather slowly to room temperature. More recently it has been identified in low temperature reactor powders[14–18] which were also not subject to stress in the usual macroscopic sense.

This phase is usually identified by wide angle X-ray diffraction or by magic angle n.m.r. spectroscopy. It gives rise to a ^{13}C n.m.r. resonance at 35 ppm, 1.4 ppm down field from the orthorhombic resonance at 33.6 ppm[20], and to three strong reflections between 19° and 26° 2θ (CuK_α radiation)[8,20], that is, at 4.56, 3.84 and 3.55 A, compared with 4.13, 3.72 and 2.98 A for the three strongest reflections of the orthorhombic form. In most instances, when both techniques have been used on the same sample, only one reflection—the reflection at 19.4°—is in evidence, as a result of overlap of the other monoclinic reflections with the second orthorhombic reflection. Moreover, the monoclinic phase seldom constitutes more than ten percent of the total crystalline content of the polymer, and for polymers that are not highly crystalline, identification by either technique can be uncertain.

In this study we have attempted to maximize the monoclinic content of a variety of PE samples by subjecting them to massive trauma. The objectives were to review some of the properties of this phase and to gain confidence in the use of a single X-ray reflection at 4.56 A and/or a ^{13}C n.m.r. signal at or near 35 ppm to identify the presence of the monoclinic phase.

EXPERIMENTAL

Polyethylene samples were prepared by striking them sharply, usually only once, in a diamond mortar. Hot extruded and hot rolled linear polyethylene samples provided by Frank Maine Consulting[21] were used in the majority of the studies reported here. In polyethylene so treated the molecules are highly oriented, with the chain axis parallel to the extrusion/roll direction[22,23]. Diffraction and n.m.r. samples can be split from the bulk polymer with ease, and the orientation direction is unambiguous. In a typical preparation, a rectangular specimen 2 mm × 4 mm × 20 mm (the chain axis) was placed in a diamond mortar which was struck once perpendicular to the smallest dimension, reducing that dimension by 40%, and increasing the width proportionately. The length of the specimen was reduced by 2%. Specimens for X-ray diffraction and magic angle n.m.r. spectroscopy were cut or split from the battered samples.

Diffraction patterns were obtained on a STOE STADI 2/PL diffractometer primarily in Debye–Scherrer mode using Cu radiation and an incident beam monochromator. For hot extruded samples, the beam was perpendicular to the specimen draw axis, that is, perpendicular to the orthorhombic *c* axis, and the data collected in the *a*, *b* plane. The specimens were roughly rectangular in cross-section, 1.0–1.5 mm, and rotating during exposure. Isotropic samples were melted to form sheets or lenses prior to battering, and examined in transmission mode, with the beam along the trauma axis.

Powdered specimens were held in Lindemann capillaries, for which scattering corrections were applied. The WAXS program used to analyse the patterns was described in an earlier paper[24].

Solid state ^{13}C n.m.r. spectra were obtained using a Bruker CXP-200 spectrometer operating at 50.31 MHz. Spectral parameters for these cross polarization experiments were: 3.6 μs (90°) pulses, 1 ms contact time, and a recycle time of 7 s. The spinning speed was about 2000 Hz.

RESULTS AND DISCUSSION

X-ray diffraction studies

A large number of linear polyethylene samples, both isotropic and stress oriented, were battered in a variety of orientations. The diffraction pattern of one of these

---

* To whom correspondence should be addressed

samples is given in *Table 1*, and illustrated in *Figure 1*. The monoclinic pattern is in agreement with those reported by Turner-Jones[3] and by Seto[8].

Trauma that produce the monoclinic phase also increase the amorphous content. In general, the greater the trauma, as indicated by the change in the dimensions of the sample, the greater the resulting monoclinic content. The quantity of the monoclinic phase seldom exceeds half that of the orthorhombic phase, that is, one third of the original orthorhombic phase. This limit is not improved by multiple blows, or by changing the direction of second or subsequent blows. It appears that mechanical stress can convert the interchain configuration of the monoclinic form back into the orthorhombic configuration. For samples of dimensions greater than a few millimetres, the monoclinic content is greater at the centre of the sample than at the edges, as one would expect. In the hot drawn samples, in which the crystallite orientation is random in the orthorhombic *a*, *b* plane, the resulting monoclinic crystallites as well as the remaining orthorhombic crystallites are oriented with respect to the trauma axis. This effect has been demonstrated before, and the orientations used in devising transformation mechanisms[4,5,7,8,10]. Our samples were too large and the application of the trauma too crude to allow us to contribute to that discussion.

Relaxation in battered polyethylene begins immediately after trauma. The process is very slow at room temperature (*Table 2*). The rate is, of course, increased by increasing the annealing temperature. On relaxation, the orthorhombic content recovers partially, and the total crystallinity increases. At temperatures below *ca.* 100°C recovery is arrested before the transformation is complete. The implication is that some monoclinic sites are more effectively constrained by their environments than are others.

Table 1 Diffraction pattern of battered polyethylene

Monoclinic: *C*2/*m* (#12) Seto *et al.*[8]
$a = 8.085\ (4)$; $(b = 2.544)$; $c = 4.808\ (6)$ A; $\beta = 108.64\ (5)°$
F30 = 34.8 (0.011, 19)
Orthorhombic: *Pnam* (#62) Bunn[19]
$a = 7.422\ (4)$ A; $b = 4.949\ (6)$; $(c = 2.544)$
F30 = 9.6 (0.029, 29)
WAXS analysis: Monoclinic, 23.5%; orthorhombic, 42.7%

I/I_m (WAXS)	I/I_m (Peak)	2θ	d (A)	$(h\,k\,l)_{mono}$	$(h\,k\,l)_{orth}$
24.6	30	19.45	4.563	0 0 1	
100	100	21.50	4.131		1 1 0
21.2	18	23.17	3.839	2 0 0	
44.1	35	23.90	3.721		2 0 0
11.2	8	25.11	3.546	−2 0 1	
2.6	1	30.01	2.977		2 1 0
1.8	2	35.08	2.559	2 0 1	
4.7	5	36.28	2.476		0 2 0
3.4	3	40.75	2.214		3 1 0
2.3	2	43.95	2.059		2 2 0
1.3	1	45.08	2.011	−4 0 1	
1.0	1	47.43	1.915	4 0 0	
1.1	1	49.07	1.856		4 0 0

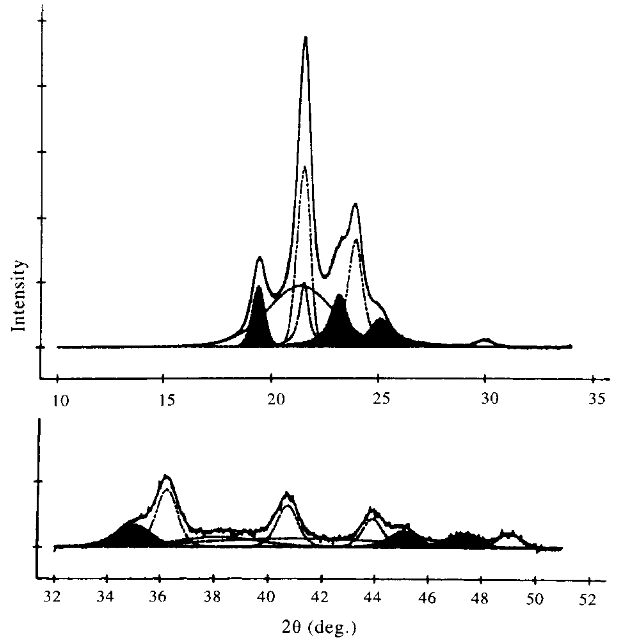

Figure 1 The WAXS pattern of a battered polyethylene. Detailed analysis given in *Table 1*. Monoclinic reflections are shaded. Intensities are arbitrary and not scaled

Table 2 Relaxation of battered polyethylene samples

Sample A: Dow UHMW PE, $\rho = 0.96$; disc in transmission, X-ray beam parallel to direction of trauma. Anneal temperature 22°C

Time	% Mono	% Ortho	% Xtalline
Unbattered	–	73.8	73.8
1 h	16.4	40.7	57.1
4 d	12.4	47.5	59.9
14 d	12.1	51.5	63.6
126 d	10.8	49.4	60.2
252 d	10.2	50.6	60.8
371 d	10.9	51.4	62.3

Sample B: Maine hot drawn PE, draw ratio 9.0 at *ca.* 125°C; transmission mode, X-ray beam parallel to direction of trauma, perpendicular to molecular chain (draw) axis; sample stationary. Anneal temperature 22°C

Time	% Mono	% Ortho	% Xtalline
Unbattered	–	81.1	81.1
1 h	22.3	50.5	72.8
12 d	18.2	54.1	72.3
124 d	18.2	58.6	76.9

Sample C: Maine/Symplastic hot extruded PE; Debye–Scherrer mode, X-ray beam perpendicular to the molecular (extrusion) axis, sample rotating. Anneal temperature 70°C

Time	% Mono	% Ortho	% Xtalline
Unbattered	–	82.6	82.6
1 h	20.6	43.9	64.5
44 h	10.6	56.4	66.0
68 h	8.3	60.2	68.5
140 h	8.3	60.5	68.8

Sample D: Maine hot drawn PE; draw ratio 9.0 at *ca.* 125°C; Debye–Scherrer mode, X-ray beam parallel to direction of trauma, perpendicular to molecular (draw) axis; sample rotating. Anneal temperature 105°C; annealing time 1.5 h

Status	% Mono	% Ortho	% Xtalline
Battered	9.0	70.4	79.4
Annealed		86.3	86.3
Rebattered	11.8	59.5	71.3
Reannealed	–	84.6	84.6

At annealing temperatures above 100°C the phase is eliminated, but the original degree of crystallinity is not recovered. Subsequent battering and annealing cycles result in a monotonous decline in crystallinity (see *Table 2*, sample D). The conversion of the monoclinic form to the orthorhombic form at 90–100° has been documented repeatedly. Appearance of the phase in samples heated above this temperature is less common. In several years of melting, quenching and annealing linear polyethylenes from a variety of sources, we have not found the monoclinic phase in any sample which had not been subjected to physical stress.

N.m.r. studies

The ^{13}C n.m.r. spectrum for a battered polyethylene sample is shown in *Figure 2A*, and the diffraction pattern of a slice of the same sample in *Figure 3A*. In *Figure 2B*, the n.m.r. spectrum is given for an identical sample, with an identical prior history to the sample in *Figure 2A*, but following an anneal for 1 h at 90°C, while *Figure 3B* shows the diffraction pattern of the same sample used to obtain *Figure 3A* following a 1 h 90°C anneal. This confirms VanderHart and Khoury's assignment of the n.m.r. signal at 35.0 ppm (34.3 ppm here) to the monoclinic phase.

The fractions of the three phases, monoclinic, orthorhombic, and amorphous, calculated from the WAXS and n.m.r. data for the polymers represented by *Figures 2* and *3* are in reasonable agreement with one another.

Marginal cases

When the monoclinic content of a polyethylene is relatively large and the quality of the crystallites is such that sharp diffraction patterns and n.m.r. signals are obtained, the presence of the phase can be verified, and the relative concentration estimated, by either technique. When the content is small and the crystallites less well developed, the data obtained by either technique may be ambiguous.

Residual monoclinic phases in battered samples annealed below 100°C show interplanar spacing consistent with those given in *Table 1*, although the relative WAXS intensities can vary widely as the data in *Table 3A* indicate. In patterns of samples with this degree of crystallinity and monoclinic content, the second and third monoclinic reflections are not present as shoulders on the orthorhombic (2 0 0) reflection but as widening in the base (*Figure 4*). Some confidence in the WAXS profile fitting programme and in the determination of monoclinic content can be drawn from the observation if, even at these relatively low monoclinic concentrations, the reflections, orthorhombic as well as monoclinic, are where they are expected to be, as they are in these polymers.

The n.m.r. spectra for the same samples (e.g. *Figure 5*) are less convincing and, as separate bits of evidence, should be regarded as ambiguous.

Two further examples of analyses producing ambiguous results are cited here. The first concerns catalytic

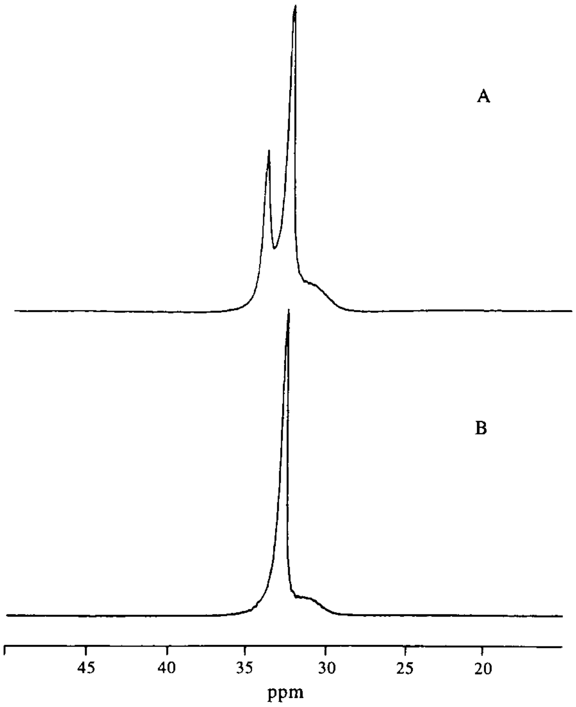

Figure 2 (A) The ^{13}C n.m.r. spectrum of a battered polyethylene. The signals are at 34.27 and 32.80 ppm downfield; the shoulder due to the amorphous component is at *ca.* 31.77 ppm. Monoclinic component, 27%; orthorhombic, 46%. The WAXS diffraction pattern for this sample is shown in *Figure 3A*. (B) The ^{13}C n.m.r. spectrum for the sample in *Figure 2A* after annealing 1 h at 90°C. The signal due to the orthorhombic component is at 32.80 ppm downfield, and the shoulder at *ca.* 31.3 ppm. Orthorhombic component, 71%. The WAXS diffraction pattern for this sample is shown in *Figure 3B*

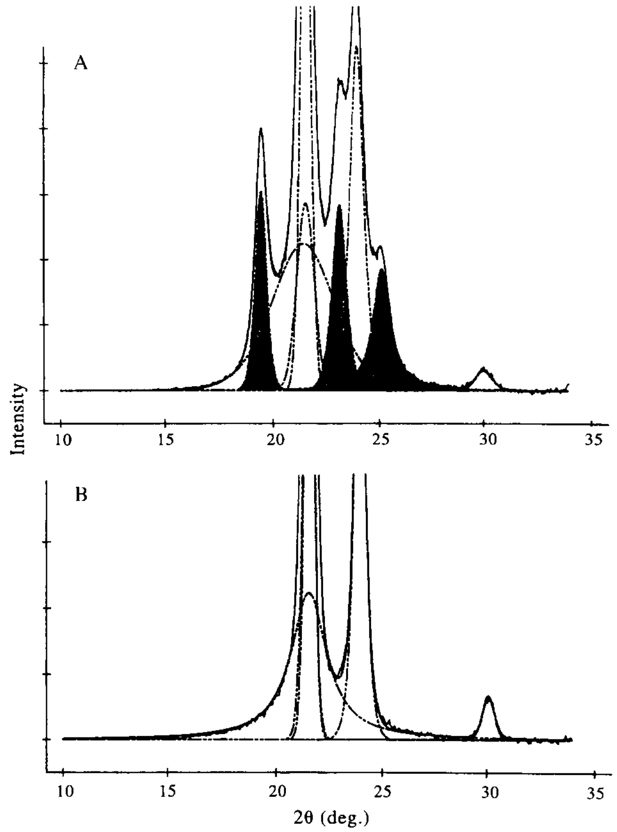

Figure 3 (A) The WAXS pattern of a battered polyethylene. The reflections due to the monoclinic phase are shaded. Monoclinic component, 24.8%; orthorhombic, 46.1%; total crystallinity, 70.9%. The ^{13}C n.m.r. spectrum for this sample is shown in *Figure 2*. (B) The WAXS diffraction pattern for this sample after annealing for 30 min at 115°C. Orthorhombic component, 71.4%. The ^{13}C n.m.r. spectrum is shown in *Figure 2*

Table 3A Comparison of diffraction data for battered PE samples following terminal anneal with standard PE patterns

2θ (Cu K_α) values for crystalline peaks: relative intensities in parentheses
Sample A: Maine #31 hot drawn rod[21]; annealed 72 h at 60°C
Sample B: Maine/Symplastic hot extruded rod; annealed 20 h at 62°C
The WAXS pattern of this polymer is shown in *Figure 4*

Sample	$(1\,1\,0)_o$	$(2\,0\,0)_o$	$(2\,1\,0)_o$	$(0\,0\,1)_m$	$(2\,0\,0)_m$	$(2\,0\,1)_m$	% Mono	% Xtal
A	21.55°	23.95°	30.09°	19.52° (62)	23.29° (100)	25.05° (62)	3.1%	78.7%
B	21.50°	23.94°	30.06°	19.47° (24)	23.16° (64)	25.03° (100)	9.0%	68.5%
PE Std	21.50°	23.90°	30.01°	19.45° (100)	23.17° (73)	25.11° (46)		

Table 3B Examples of polyethylene powders showing a WAXS reflection at *ca.* 19.5° 2θ

2θ (Cu K_α) values for crystalline peaks: relative intensities in parentheses
Dalla Lana polymers[25]: Cr/silica catalyst
Sample A 6.39 g PE/g catalyst, reaction time 75 min
Sample B 77.13 g PE/g catalyst, reaction time 210 min, *Figures 6 and 7*

Sample	$(1\,1\,0)_o$	$(2\,0\,0)_o$	$(2\,1\,0)_o$	$(0\,0\,1)_m$	$(2\,0\,0)_m$	$(2\,0\,1)_m$	% Mono	% Xtal
A	21.46°	23.94°	30.08°	19.50° (100)	23.23° (69)	– (0)	5.7%	46.4%
B	21.51°	23.97°	29.93°	19.56° (100)	23.24° (37)	– (0)	8.5%	46.0%
PE std	21.50°	23.90°	30.01°	19.45° (100)	23.17° (73)	25.11° (46)		

Table 3C Comparison of WAXS pattern for PE copolymers with standard patterns

2θ (Cu K_α) values for crystalline peaks: relative intensities in parentheses
Sample A Copolymer, 1-octadecene, 5.5 mol%; transmission
Sample B Copolymer, 1-octadecene, 7.7 mol%; transmission
Sample C Copolymer, 1-butene, catalytic reactor product, 65 m with 2 wt% Cr/silica catalyst (Dalla Lana[25]) 1.5 mm capillary (*Figures 8* and *9*)

Sample	2θ	2θ	2θ	Xtallinity
A	19.65° (40)	21.15° (100)	23.21° (43)	46.1%
B	19.66° (80)	21.21° (100)	23.03° (55)	41.4%
C	19.53° (43)	21.34° (100)	23.69° (54)	36.5%
PE standard	19.45° (mono)	21.50° (ortho)	23.90° (ortho)	

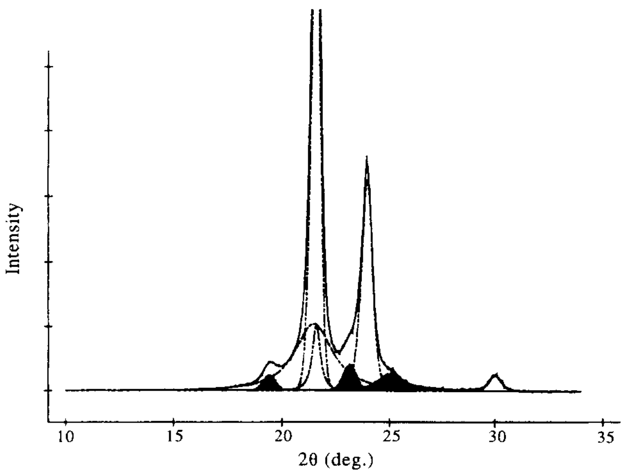

Figure 4 The WAXS pattern of a polyethylene sample containing a reduced quantity of the monoclinic phase. The monoclinic pattern is shaded. Corresponds to Sample B, *Table 3A*. The ^{13}C n.m.r. spectrum for this sample is shown in *Figure 5*

reactor products—that is, polymer samples not subjected to stress except at the molecular level—provided by Prof. Dalla Lana[25]. The powder data are given in *Table 3B*, and illustrated in *Figure 6*; the n.m.r. spectrum of one of the powders is shown in *Figure 7*. The WAXS identification of the reflections in these samples is less certain than that accorded the battered samples because the amorphous content is much larger and the crystallites less well developed. On the other hand, there can be no preferred orientation, and differences in relative intensities cannot be attributed to that effect. The observation is that the third monoclinic reflection is not in evidence, and the interplanar spacings of the first two differ significantly from the standards. The n.m.r. evidence is more ambiguous, since, in *Figure 7* for example, if the shoulder to the left of the orthorhombic signal is due to the monoclinic configuration, the concentration would have to be much greater than that indicated by the powder pattern, or implied by WAXS analysis.

The second example of ambiguous results involves an

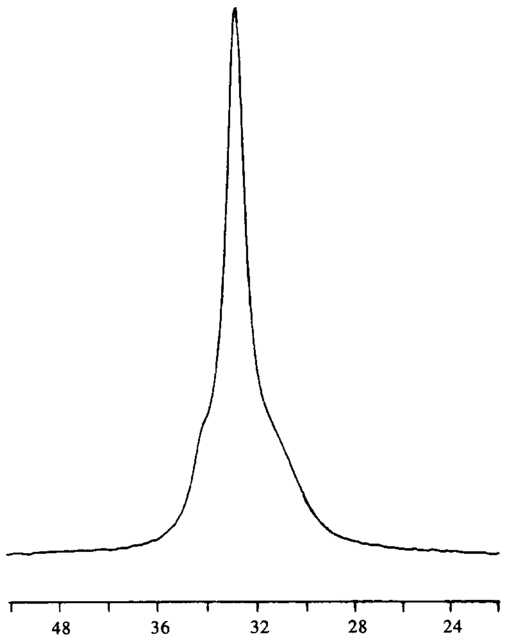

Figure 5 The ^{13}C n.m.r. spectrum of a sample containing 9.0% of the monoclinic phase. The WAXS pattern is given in *Figure 4*

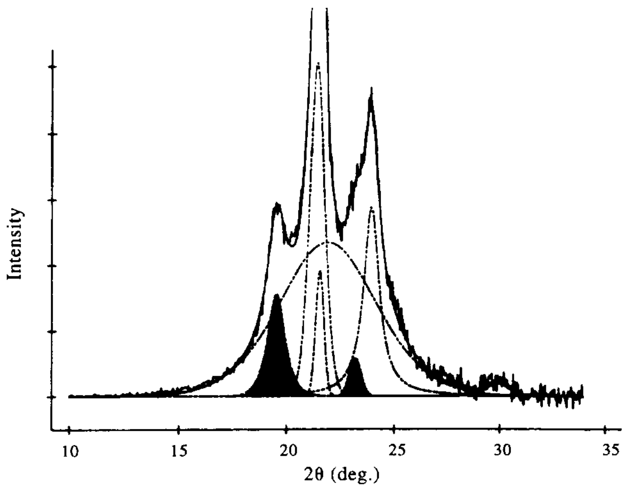

Figure 6 The WAXS pattern of a catalytic reactor powder. Corrected for capillary scattering. Corresponds to Sample B in *Table 3B*

extension of this discussion to a consideration of polyethylene copolymers, which often give a diffraction pattern similar to that shown in *Figure 8*, for which it is not unreasonable to suppose that the first reflection, at *ca.* 19.5° 2θ, is the monoclinic (0 0 1) reflection, while the second and third are the orthorhombic (1 1 0) and (2 0 0) reflections. The failure to recognize any other reflections could be attributed to the poor overall quality of the pattern.

The patterns of the three copolymers described in *Table 3C* are all of this general form. WAXS analyses show that the interplanar spacings for the ordering that is present, such as it is, differ significantly from those of the monoclinic and orthorhombic polyethylene structures. The n.m.r. spectrum (*Figure 9*) is not helpful. In the strictest crystallographic sense, the structure of the crystalline phase in these copolymers is unknown.

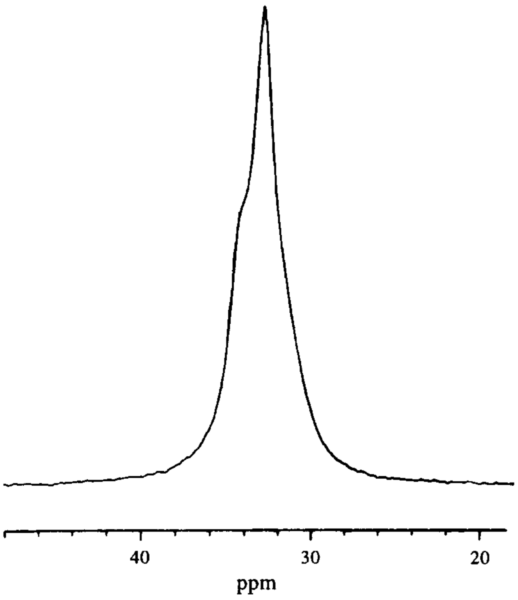

Figure 7 The ^{13}C n.m.r. spectrum of a catalytic reactor powder. The WAXS pattern is shown in *Figure 6*. The main signal is at 32.9 ppm, and the down field shoulder at *ca.* 34.3 ppm

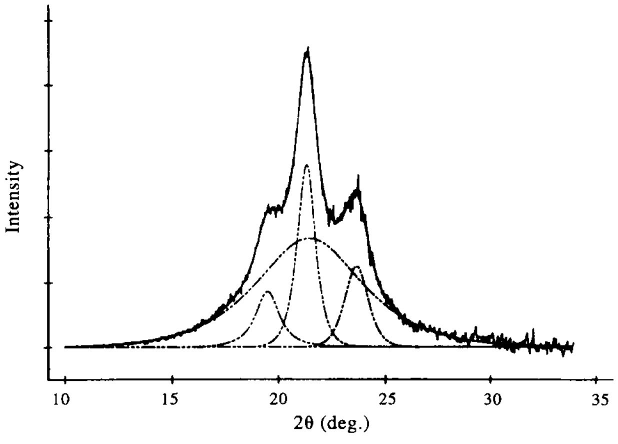

Figure 8 The WAXS pattern of a catalytic reactor copolymer. This corresponds to Sample C in *Table 3C*. The ^{13}C n.m.r. spectrum is shown in *Figure 9*

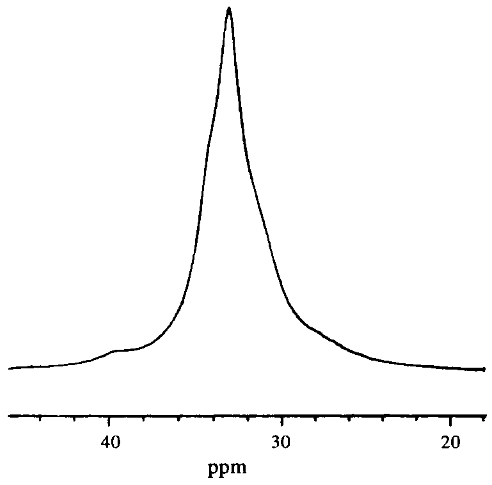

Figure 9 The ^{13}C n.m.r. spectrum of a polyethylene copolymer. The WAXS pattern for this sample is shown in *Figure 8*

SUMMARY

If the first three monoclinic reflections can be identified by WAXS analysis in the diffraction pattern of a polyethylene and the interplanar spacings are correct; and/or if the n.m.r. spectrum includes a distinct signal 1.4 ppm down field from the signal due to the orthorhombic modification, then the presence of the monoclinic form can be claimed with confidence. (If the diffraction sample is anisotropic, intensities may be other than expected.) Otherwise the suggestion that the monoclinic phase is present can only be tentative. If the crystallinity of the sample is low and the widths of the reflections or spectral lines broad, the question of the presence of any recognizable crystalline structure, including orthorhombic, is moot.

ACKNOWLEDGEMENT

We are indebted to Ms S. Blake for the n.m.r. spectra used in this study.

REFERENCES

1 Teare, P. W. and Holmes, D. R. *J. Polym. Sci.* 1957, **24**, 496
2 Turner-Jones, A. *J. Polym. Sci.* 1962, **62**, S53
3 Pierce, R. H. Jr., Tordella, J. P. and Bryant, W. M. D. *J. Am. Chem. Soc.* 1952, **74**, 282
4 Geniewski, C. and Moore, R. S. *Macromolecules* 1969, **2**, 385
5 Allan, P. S., Crellin, E. B. and Bevis, M. *Phil. Mag.* 1973, **27**, 127
6 Painter, P. C., Runt, J., Coleman, M. M. and Harrison, I. R. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1255
7 Gerrits, N. S. J. A. and Young, R. J. *J. Polym. Sci., Polym. Phys. Edn.* 1991, **29**, 825
8 Seto, T., Hara, T. and Tanaka, K. *Japan J. Appl. Phys.* 1968, **7**, 31
9 Mayaji, H., Asahi, T. and Miyamoto, Y. *J. Polym. Sci., Polym. Phys. Edn.* 1987, **25**, 159
10 Takahashi, Y., Ishida, T. and Furusaka, M. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 2267
11 Pollock, S. S., Robinson, W. H., Chiang, R. and Flory, P. J. *J. Appl. Phys.* 1962, **33**, 237
12 Fatou, J. G., Baker, C. H. and Mandelkern, L. *Polymer* 1965, **6**, 243
13 Fatou, J. G. and Mandelkern, L. *J. Phys. Chem.* 1965, **69**, 417
14 Jarrett, W. L., Mathias, L. J. and Porter, R. S. *Macromolecules* 1990, **23**, 5164
15 Ottani, S., Wagner, B. E. and Porter, R. S. *Polym. Commun.* 1990, **31**, 370
16 Ottani, S., Ferracini, E., Ferrero, A. Malta, V. and Porter, R. S. *Macromolecules* 1995, **28**, 2411
17 Benn, R., Fink, G., Herrmann, W. and Muller, T. *Makromol. Chem., Rapid Commun.* 1992, **13**, 321
18 Kitamaru, R., Horii, F., Zhu, Q., Bassett, D. C. and Olley, R. D. *Polymer* 1994, **35**, 1171
19 Bunn, C. W. *Trans. Faraday Soc.* 1939, **35**, 482
20 VanderHart, D. L. and Khoury, F. *Polymer* 1984, **25**, 1589
21 Frank Maine Consulting Ltd., 71 Sherwood Dr., Guelph, ON N1E 6E6, Canada
22 Burke, P. E., Weatherly, G. L. and Woodhams, R. T. *Polym. Eng. Sci.* 1987, **27**, 518
23 Kojima, M. and Magill, J. H. *Makromol. Chem. Rapid Commun.* 1991, **12**, 505
24 Russell, K. E., Hunter, B. K. and Heyding, R. D. *Eur. Polym. J.* 1993, **29**, 211
25 Dalla Lana, I. G., Szymura, J. A. and Zelinski, P. A. *Stud. Surf. Sci. Catal.* 1993, **75**, 2329