Two-dimensional ^{13}C n.m.r. studies of the morphology and orientational order in gel-spun ultrahigh molecular weight polyethylene fibres

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In this communication we demonstrate the feasibility of determining the orientational distribution functions of various morphological components in ultrahigh molecular weight polyethylene fibres by two-dimensional rotor-synchronized ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (n.m.r.) techniques. For comparative purposes we have also included a drawn polyethylene fibre of normal molecular weight. The results showed that these fibres contain two crystalline components, designated C_1 and C_2, and an amorphous (non-crystalline) component, A. Order parameters and orientational distribution functions of these components can be obtained through analysis of the two-dimensional ^{13}C n.m.r. spectra.

(**Keywords: polyethylene; morphology; ^{13}C n.m.r.; orientational order; fibre**)

Introduction

Formation of high mechanical performance fibres from ultrahigh molecular weight linear polyethylene (UHMWPE) represents an important technical advance in the quest for realizing maximum mechanical performance from organic polymers, especially those with considerable intrinsic flexibility[1–20]. The morphology of these fibres is, without doubt, dominated by previously unattained degrees of chain extension and orientation in such polymers. There is general agreement that the hierarchy of organization from fibre to the polyethylene (PE) chain in UHMWPE fibres consists of macrofibres constituted by microfibrils (~15 nm in diameter) of extended chains[20]. The interfibrillar regions are believed to be extended domains of non-crystalline material and/or microvoids. There is some disagreement regarding the structure of the microfibrils themselves, with proposals ranging from perfectly crystalline fibrils (except for chain ends) to the classical synthetic fibre structure, namely alternating crystalline and non-crystalline domains in the fibril. Recent studies in our laboratories in this regard, with extensive thermorheological and X-ray scattering data, imply that the microfibrils in UHMWPE fibres consist of an alternating sequence of crystals of high and relatively lower degrees of perfection, with a low concentration of amorphous material dispersed in the interfibrillar domains[21]. In this communication we describe preliminary results from studies with one- and two-dimensional nuclear magnetic resonance (n.m.r.) techniques to determine the nature and extent of various morphological components quantitatively, and also the orientational order in these components.

Experimental

The experiments were carried out with three PE fibres (*Table 1*), designated as PE-I (Allied Spectra 900), PE-II (Allied Spectra 1000) and PE-D. PE-II and PE-I are both UHMWPE fibres ($M_W > 10^6$, draw ratio >40), with strength of 32 and 25 cN/dtex*, elongation of 3.8 and 6%, and modulus of 1940 and 750 cN/dtex, respectively. PE-D is a normal molecular weight melt-spun fibre that has been subsequently drawn ($M_W = 10\,200$, draw ratio = 3.0).

N.m.r. experiments were performed on a custom-built spectrometer operating at 75.5 MHz (^{13}C)[22]. A Doty magic angle probe (Doty Scientific, SC) with 7 mm rotors was employed to obtain the cross-polarization/magic angle spinning (CP/MAS) ^{13}C spectra. Experimental conditions: 1 ms CP, 4 s (PE-I and PE-D) or 90 s (PE-II) recycle delay. Spectra of 50 kHz width were taken with 4 k points resolution and zero-filled to 8 k. Spectra were taken at room temperature (22°C). The relative populations of different morphological components were obtained by computer line shape simulation of the observed spectra. The intensities of these components must be corrected to compensate for the presence of difference in CP efficiency and proton $T_{1\rho}$. This is accomplished by simulating the relative intensities of these components for spectra obtained with contact times ranging from 50 μs to 80 ms. The absolute intensities of these components were obtained by extrapolating to zero second contact time, as described previously[22]. Sample spinning speed was controlled by a custom-built microprocessor controlled spinning rate controller to within ± 1 Hz[23]. The two-dimensional rotor synchronized magic angle spectra (ROSMAS) were obtained with the pulse sequence proposed by Harbison *et al.*[24]. Samples for these experiments were prepared by carefully winding the fibres on a flat-spool with a precision mechanical advancing mechanism. Six layers of the fibres were glued together and allowed to dry overnight before cutting into 4 × 12 mm rectangular pieces. Six pieces of these rectangles were glued together and placed in a 7 mm MAS spinner. The fibre axis was tilted by 51° from the

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* dtex is a measure of linear density of fibres and corresponds to the mass in grams of 10 000 m of fibres

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Table 1 Relative fraction and line width of the morphological components

Sample	C_1[a]	$\Delta\nu_{1/2}$ (Hz)[b]	C_2[a]	$\Delta\nu_{1/2}$ (Hz)[b]	A[a]	$\Delta\nu_{1/2}$ (Hz)[b]
PE-II	0.15	33	0.85	35	0.00	–
PE-I	0.06	35	0.76	35	0.18	120
PE-D	0.06	59	0.68	40	0.26	120

[a] Relative fraction (± 0.02)
[b] Line width ± 5 Hz
Separation between C_1 and C_2 = 105 Hz (1.5 ppm) and between C_2 and A = 135 Hz (1.8 ppm)

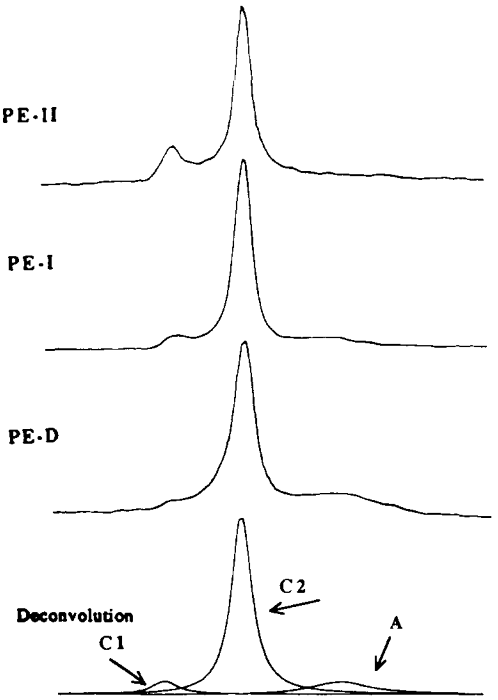

Figure 1 ^{13}C CP/MAS n.m.r. spectra of three unoriented PE samples obtained at room temperature. The computer simulation displays the components employed; the three components C_1, C_2 and A are indicated by arrows

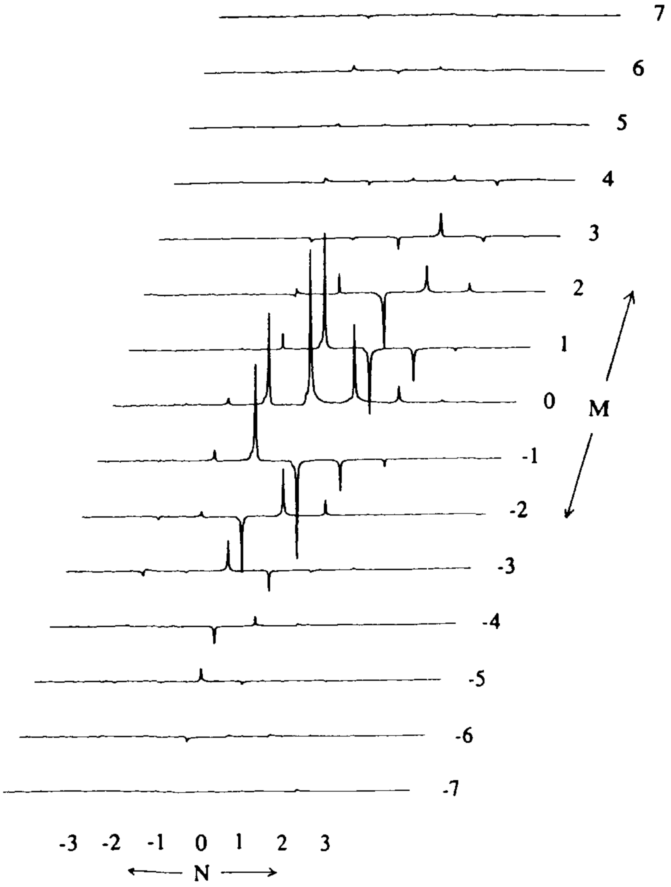

Figure 2 Two-dimensional rotor synchronized ^{13}C CP/MAS spectra of the PE-II sample. The presence of high order is evident from the intensities present in the high-order spectra in the *M*-dimension. Similar spectra were also obtained with other samples, except that the intensities decrease faster in the *M*-dimension, especially for the PE-D sample

rotor axis. The empty space was filled with fine talcum powder. The spinning speed was set to 1000 ± 1 Hz for the two-dimensional ROSMAS experiments.

Results and discussion

Figure 1 shows a set of ^{13}C CP/MAS spectra of PE-I, PE-II and PE-D. Each of these spectra consists of three components (labelled C_1, C_2 and A). Similar results were also observed by Jarrett *et al.* in a series of high molecular weight PE reactor powders synthesized under slurry and gas phase reaction conditions using Ziegler-Natta catalysis[25]. The relative intensity and line width of each component can be deduced from spectral simulation. The results, after appropriate correction for CP and relaxation effects as described in the Experimental section, are given in *Table 1*. The accuracy in per cent population obtained from simulation is estimated to be $\pm 2\%$. The line widths are $\Delta\nu_{1/2} = 35 \pm 5$ Hz for C_1 and C_2 and 120 ± 10 Hz for component A. These data show that PE-II contains the highest population of C_1 (15%) and the PE sample contains the highest amount of component A (29%). There is also a substantial fraction of component A present in the PE-I sample (18%) but not in the PE-II sample.

Figure 2 shows one set of the two-dimensional ROSMAS spectra of the PE-II sample. The sidebands in the *N*-dimension are the normal MAS sidebands, modulated by orientational order of the fibres. Thus, the $M = 0$ spectrum is exactly the same as the normal one-dimensional CP/MAS spectrum. Each of these spectra was deconvoluted to obtain the intensities of various morphological components for all *M*-slices. The intensity variation of a given component in the *M*-dimension is employed to determine the orientational distribution functions of that component using a modified procedure[26] similar to that employed by Harbison *et al.*[24]. The presence of strong intensity in the spectra with

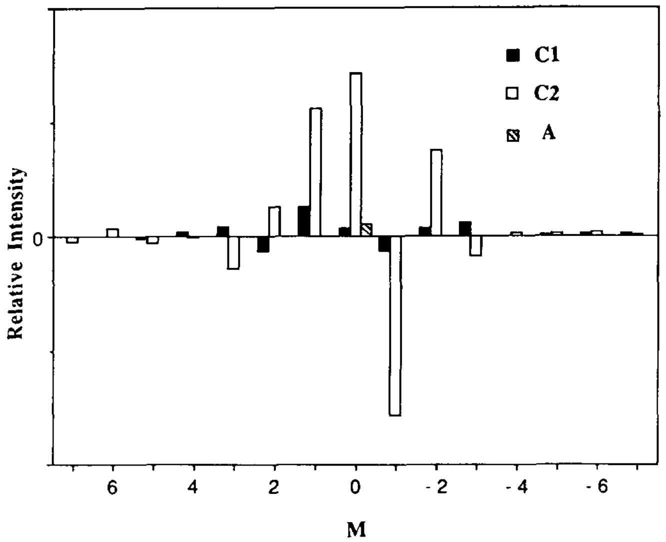

Figure 3 Intensity variation of various morphological components in the M-dimension in the two-dimensional ROSMAS spectra of the PE-II sample

high M values represents high orientational order. *Figure 3* shows the intensity variation in the M-dimension of the three components of the $N = 0$ slice for PE-II sample. Substantial intensities can still be seen at $M = \pm 7$ for both C_1 and C_2 components. However, no intensity of the A component is detectable even in the $M = \pm 1$ spectra. This is a clear indication that the A component corresponds to an unoriented amorphous region of the fibres. The presence of high-order intensities for the C_1 and C_2 components suggests that both of these components are likely to be from oriented crystalline regions. This is consistent with the observed narrow line width of 35 Hz for both components and supports the assignments of Jarrett *et al.*[25]. For PE-I and PE-D samples, similar plots show that both C_2 and C_1 are ordered (results not shown), but the intensities of these components decrease faster than in the PE-II sample, suggesting that the long range order in the fibrils of PE-I and PE-D samples is lower than that of PE-II. A more detailed quantitative description of the orientation distributions, together with an analysis of the effect of processing on the morphology and orientational distribution function of these fibres, is currently in progress.

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References

1 Cifferri, A. and Ward, I. M. 'Ultrahigh Modulus Polymers', Applied Science, London, 1979, p. 1
2 Wu, W. and Black, B. *Polym. Eng. Sci.* 1979, **19**, 1163
3 Southern, J. H. and Porter, R. S. *J. Appl. Polym. Sci.* 1970, **14**, 2305
4 Zachariades, A. E. and Kanamoto, T. *Polym. Eng. Sci.* 1986, **26**, 658
5 Rotzinger, B. P., Chanzy, H. D. and Smith, P. *Polymer* 1989, **30**, 1814
6 Pennings, A. J. in 'Crystal Growth, Proc. Int. Conf. on Crystal Growth' (Ed. H. S. Peiser), Pergamon Press, New York, 1967, p. 389
7 Pennings, A. J., Schouteten, C. J. H. and Kiel, A. M. *J. Polym. Sci. (C)* 1972, **38**, 167
8 Barham, P. J. and Keller, A. *J. Mater. Sci.* 1985, **20**, 2281
9 Barham, P. J. *Polymer* 1982, **23**, 1112
10 Hoogsteen, W., Van den Hooft, R. J., Postema, A. R., ten Brinke, G. and Pennings, A. J. *J. Mater. Sci.* 1988, **23**, 3459
11 Hoogsteen, W., Kormelink, H., Eshuis, G., ten Brinke, G. and Pennings, A. J. *J. Mater. Sci.* 1988, **23**, 3467
12 Smooks, J. and Pennings, A. J. *J. Mater. Sci.* 1984, **19**, 31
13 Smith, P., Lemstra, P. J., Kalb, B. and Pennings, A. J. *Polym. Bull.* 1979, **1**, 733
14 Smooks, J. and Pennings, A. J. *J. Appl. Polym. Sci.* 1982, **27**, 2209
15 Torfs, J. C. M. and Pennings, A. J. *J. Appl. Polym. Sci.* 1987, **26**, 303
16 Frank, F. C., Keller, A. and Mackley, N. R. *Polymer* 1971, **12**, 467
17 Narh, K. A., Barham, P. J. and Keller, A. *Macromolecules* 1982, **15**, 464
18 Pennings, A. J. *J. Cryst. Growth* 1980, **48**, 574
19 Hoogsteen, W., ten Brinke, G. and Pennings, A. J. *Colloid Polym. Sci.* 1988, **266**, 1003
20 Van Hutten, P. E., Koning, C. E. and Pennings, A. J. *J. Mater. Sci.* 1985, **20**, 1556
21 Saraf, A., Desai, P. and Abhiraman, A. S. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1991, **47**, 67
22 Tzou, D. L., Desai, P., Abhiraman, A. S. and Huang, T.-h. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 49
23 Maier, T. D. and Huang, T.-h. *J. Magn. Reson.* 1991, **91**, 165
24 Harbison, G. S., Vogt, V.-D. and Spiess, H. W. *J. Chem. Phys.* 1987, **86**, 1206
25 Jarrett, W. L., Porter, R. S. and Mathias, L. J. *Polym. Prepr.* 1990, **31**, 647
26 Tzou, D. L. *PhD Thesis* Georgia Institute of Technology, 1991