Degree of branch inclusion into the lamellar crystal for various ethylene/α-olefin copolymers

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Various copolymers of ethylene with α-olefins, i.e. propylene, but-1-ene, hex-1-ene, oct-1-ene, dodec-1-ene and 4-methylpent-1-ene, were degraded oxidatively with fuming nitric acid (FNA). For all copolymers, the fraction of residue after FNA treatment was in close agreement with the degree of crystallinity before treatment. The X-ray diffraction pattern of the treated sample did not show any amorphous peak. These results indicate that selective removal of the amorphous region occurs by FNA treatment. The ^{13}C nuclear magnetic resonance (n.m.r.) spectrum and size exclusion chromatogram of the degraded sample suggested that the main component of the residue was dicarboxylic acid, with a molecular weight dependent on the lamellar crystal thickness. Inclusion of short-chain branches into the crystalline core was also proved directly via the ^{13}C n.m.r. spectrum. The probability of branch inclusion determined from the n.m.r. spectrum is in the order methyl > ethyl > n-butyl = n-hexyl = n-decyl > isobutyl, which seems to depend on the bulkiness of the branch. The difference in the probabilities of branch inclusion between n-butyl and isobutyl could be explained from the viewpoint of the mobility of the branch when the methylene sequences containing the branches crystallize from the molten state.

(Keywords: ethylene copolymers; oxidative degradation; branch inclusion; ^{13}C nuclear magnetic resonance)

INTRODUCTION

More than 10 years has passed since linear low-density polyethylene (LLDPE) was commercially developed, and it has gained a steadfast position as the third commercial polyethylene through its superior properties. The authors have investigated both the molecular structure and crystalline structure of LLDPE using various techniques[1-6]. A unique distribution of chemical composition[6-14] and a wide variety of crystalline morphologies[3,4,15-17] have been revealed for LLDPE by us and other authors. Meanwhile, the mechanical and optical properties of LLDPE are well known to be strongly affected by the kind of α-olefin used as comonomer, even if the chemical composition distributions are in the same range in the samples[9,18]. Thus it is significant to investigate the effect of the kind of short-chain branch on the crystalline structure. From this point of view, the location of the branch in the solid state, which is still a subject of controversy for polyethylenes, was studied here for a wide variety of ethylene/α-olefin copolymers.

X-ray diffraction (x.r.d.) has been used most frequently for the analysis of the crystalline structure of polyethylene, and the inclusion of branches into the crystal has been discussed on the basis of crystal lattice expansion with increase in the content of branches[19-23]. Assuming that accommodation of branches within the crystalline lattice results in a 2 gl kink defect, it is suggested[22] that the amount of branches in the crystalline phase can be estimated. However, as several authors have indicated[24-27], the lamellar crystal thickness itself largely affects the unit-cell dimensions: the thinner the lamellae, the more the unit cell is expanded. Therefore, it seems reasonable to consider that the x.r.d. method does not necessarily evaluate only the branches included in the crystal but rather the overall effect of the branch on crystalline morphologies.

On the other hand, recent advanced techniques in solid-state n.m.r. have provided new insight into this subject. The location of the branch in ethylene/α-olefin copolymers has been estimated from the spin–lattice relaxation time (T_1) and the cross-polarization/magic-angle spinning (c.p./m.a.s.) n.m.r. spectrum for solid samples as reported by McFaddin *et al.*[28,29], Pérez *et al.*[30-32] and Laupretre *et al.*[33]. Their results suggest that a considerable amount of methyl branches (21–27%) can be accommodated in the crystalline core independently of the thermal history of the sample, and a lower amount of ethyl branches (6–20%) are present in the ordered region (crystalline and interface regions). However, we must recognize that quantitative discrimination by this method has a substantial limitation, which is due to the small differences in both the chemical shift and the relaxation time between the branch in the crystalline phase and that in the amorphous phase. So, a more straightforward method is necessary to determine the degree of branching included into the perfect crystalline phase.

Degradation of polyethylene by ozone[34] or fuming nitric acid (FNA)[35-44] is well known to remove the amorphous phase selectively. By using this method, followed by i.r. spectroscopy, several authors[41-43] have tried to determine the amount of branches included within the crystal. But the accuracy was lowered by the appearance of interference peaks and the increase in the baseline of the i.r. spectrum after degradation. Holdsworth

et al.[38] measured the amount of radioactive ^{14}C in the residue left after degradation, and reported that 25% of methyl branches and 5% of ethyl branches were accommodated within the crystal for solution-crystallized copolymers.

In this paper, FNA treatment followed by high-resolution n.m.r. measurements in solution were applied to determine the degree of branching in the crystalline phase for a wide variety of ethylene/α-olefin copolymers in which the length of short-chain branches and their content vary.

EXPERIMENTAL

Materials

The copolymer samples of ethylene with α-olefin were synthesized in our laboratory with a vanadium catalyst system in n-hexane at 40°C. The comonomers used in this work are propylene, but-1-ene, hex-1-ene, oct-1-ene, dodec-1-ene and 4-methylpent-1-ene. Some of the characteristic data for the copolymers are shown in *Table 1*.

Characterization

The molecular weight and molecular-weight distribution of the copolymer samples and of the FNA-treated samples were measured in trichlorobenzene at 135°C using a Toyosoda HLC 811 equipped with a refractometer. The melting curves of about 5 mg of the sample were measured with a Perkin–Elmer DSC 2 differential scanning calorimeter. The system was calibrated with an indium standard (m.p. = 156.6°C, enthalpy of fusion = 28.4 J g^{−1}). X-ray crystallinity in weight fraction (X_c) was measured according to Aggarwal's method[45] with a Rigaku RAD RB X-ray diffractometer. Small-angle X-ray scattering (SAXS) was also measured to determine the long period (L) of the sample. The thickness of the lamellar crystalline core (l_c) was calculated from the following relationship by assuming a two-phase model for polyethylene in the solid state[46]:

$$l_c = 0.85 X_c L/(1 - 0.15 X_c) \quad (1)$$

where L is the long period determined by SAXS, and the densities of crystalline and amorphous phases of polyethylene were taken to be 1.00 and 0.85 g cm^{−3}, respectively[47].

Fuming nitric acid (FNA) treatment

The sample was compression-moulded at 150°C into a sheet of $30 \times 10 \times 0.3$ mm[3] and quenched in a water-cooled press. After dipping in FNA at 50°C for a definite period, the sample specimen was washed in pure water for 3 h at room temperature and in acetone for 6 h at the boiling temperature of acetone, and then dried *in vacuo* for 24 h.

N.m.r. measurements

[13]C n.m.r. spectra were obtained on a Bruker AM400 spectrometer operating at 100.6 MHz at 120°C. Sample solutions for n.m.r. measurements were prepared in benzene-d_6 with concentration maintained at 10% by weight. A small amount of tetramethylsilane was used as a chemical-shift reference. The conditions for measurement were as follows: pulse interval, 8 s; acquisition time, 0.56 s; pulse width, 4.8 μs (90°); spectral width, 29 kHz; number of data points per spectrum, 33 000.

RESULTS AND DISCUSSION

Structure of the residue after FNA degradation

The samples used in this study are shown in *Table 1*. Two groups of samples having crystallinity >60% and <50% were studied for each kind of copolymer. The molecular-weight distribution (MWD) of the samples was fairly narrow $(M_w/M_n = 2$–3), and only one sharp peak was observed in the d.s.c. endotherm of each sample, indicating a narrow distribution of chemical composition. Thus it is considered that the effect of the MWD and the chemical composition distribution on the crystalline structure are very small for the samples used here.

The weight loss during immersion in FNA increased with time within a first step (0–150 h) and reached a plateau followed by a very slow increase (second step) under the conditions used in this study, as shown in *Figure 1*. *Figure 2* shows the relationship between the weight of the residue after treatment for 150 h and the crystallinity of the original sample. Data for samples not shown in *Table 1* are also included to survey a wider range of crystallinity. A good correspondence can be seen among them, which suggests selective removal of the amorphous phase by FNA. This is also supported by X-ray diffraction of the FNA-etched sample. The broad

Table 1 Samples of ethylene/α-olefin copolymer

Sample	Comonomer	Branches (per 1000 C)	M_w ($\times 10^4$)	M_n ($\times 10^4$)	M_w/M_n	X-ray crystallinity (%)	T_m (°C)	ΔH_m (J g^{−1})
P-1	Propylene	17.6	11.2	3.3	3.4	64.1	112.4	120
P-2		38.0	8.4	3.5	2.4	23.4	–	–
B-1	But-1-ene	11.5	13.6	6.4	2.1	64.7	113.5	110
B-2		21.5	9.7	4.5	2.2	51.8	–	–
H-1	Hex-1-ene	12.9	10.9	3.3	3.1	63.8	114.4	113
H-2		21.8	13.6	5.6	2.3	44.4	–	–
M-1	4-Methylpent-1-ene	7.2	7.9	2.7	2.9	61.1	117.8	127
M-2		18.5	5.4	2.2	2.5	49.9	–	–
O-1	Oct-1-ene	9.8	8.8	3.8	2.3	63.5	117.7	118
O-2		25.0	8.1	3.3	2.7	31.7	75.1	48
D-1	Dodec-1-ene	10.3	8.9	3.3	2.7	60.6	113.3	115
D-2		22.1	8.3	3.8	2.2	27.7	74.8	35

letting the c axis length be 2.54 Å:

$$l_c = 1.27(M_n/14 - 1) \tag{2}$$

The results are consistent with those calculated from the crystallinity and the long period of the original sample (equation (1)), as shown in *Table 2*.

All the etched samples had a bimodal MWD, as shown in *Figure 4*. The molecular weight of the higher (second) peak is just twice that of the main peak, suggesting that some of the folded parts of the chain at the lamellar surface remain without undergoing decomposition by FNA treatment[37].

A typical n.m.r. spectrum of an etched sample of ethylene/but-1-ene copolymer and possible assignments are shown in *Figure 5* and *Table 3*, respectively. Besides the large peak assigned to the methylene sequences at 30 ppm, a number of peaks due to carboxyl groups and ethyl branches are observed. The other small peaks are
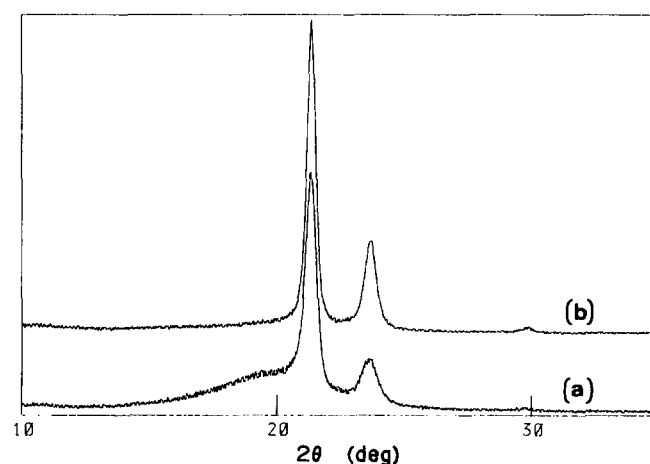
Figure 1 Percentage weight loss of ethylene/but-1-ene copolymer (B-2) as a function of degradation time in fuming nitric acid (FNA)
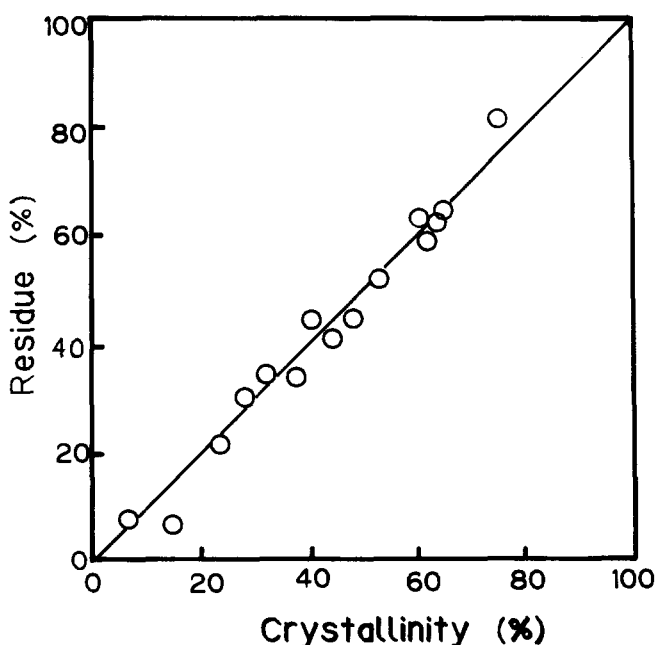
Figure 2 Relationship between the residue after FNA treatment and the crystallinity of the original copolymer samples

Figure 3 X-ray diffraction pattern of ethylene/but-1-ene copolymer (B-2): (a) original, (b) after FNA treatment

diffraction peak due to the amorphous phase, the maximum intensity of which is located at diffraction angle $2\theta = 19.5°$, completely disappeared for the etched sample, as shown in *Figure 3*. This result also indicates that the sample was degraded selectively in the amorphous regions, leaving fragmental crystalline debris.

A typical size exclusion chromatogram (s.e.c.) of the etched sample is shown in *Figure 4* and molecular-weight data for various samples are shown in *Table 2*. Since the etched samples are considered to correspond to the crystalline core of the lamellae, judging from the results described above, calculation of the crystalline core length was tried according to equation (2), using number-average molecular weight (M_n) of the etched sample and
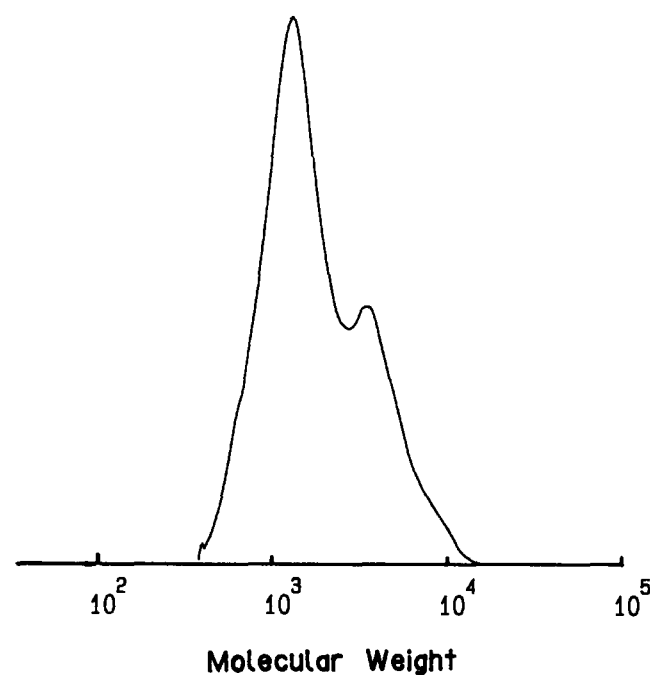
Figure 4 A typical size exclusion chromatogram of ethylene/but-1-ene copolymer (B-1) degraded in FNA for 150 h at 50°C

Table 2 Characterization of the residue after FNA treatment for ethylene/α-olefin copolymers

Sample	M_w	M_n	M_w/M_n	$l_c{}^a$ (Å)	$l_c{}^b$ (Å)	B_c (per 1000 C)	B_a (per 1000 C)	B_c/B_a
P-1	3060	1920	1.59	173	173	8.2	34.3	0.24
B-1	2110	1350	1.56	121	124	2.8	25.9	0.11
H-1	2460	1340	1.81	120	122	1.8	32.4	0.06
M-1	2470	1540	1.60	138	120	0.71	17.3	0.04
O-1	2300	1330	1.73	120	140	1.5	24.2	0.06
D-1	2640	1520	1.74	137	126	1.3	24.1	0.05

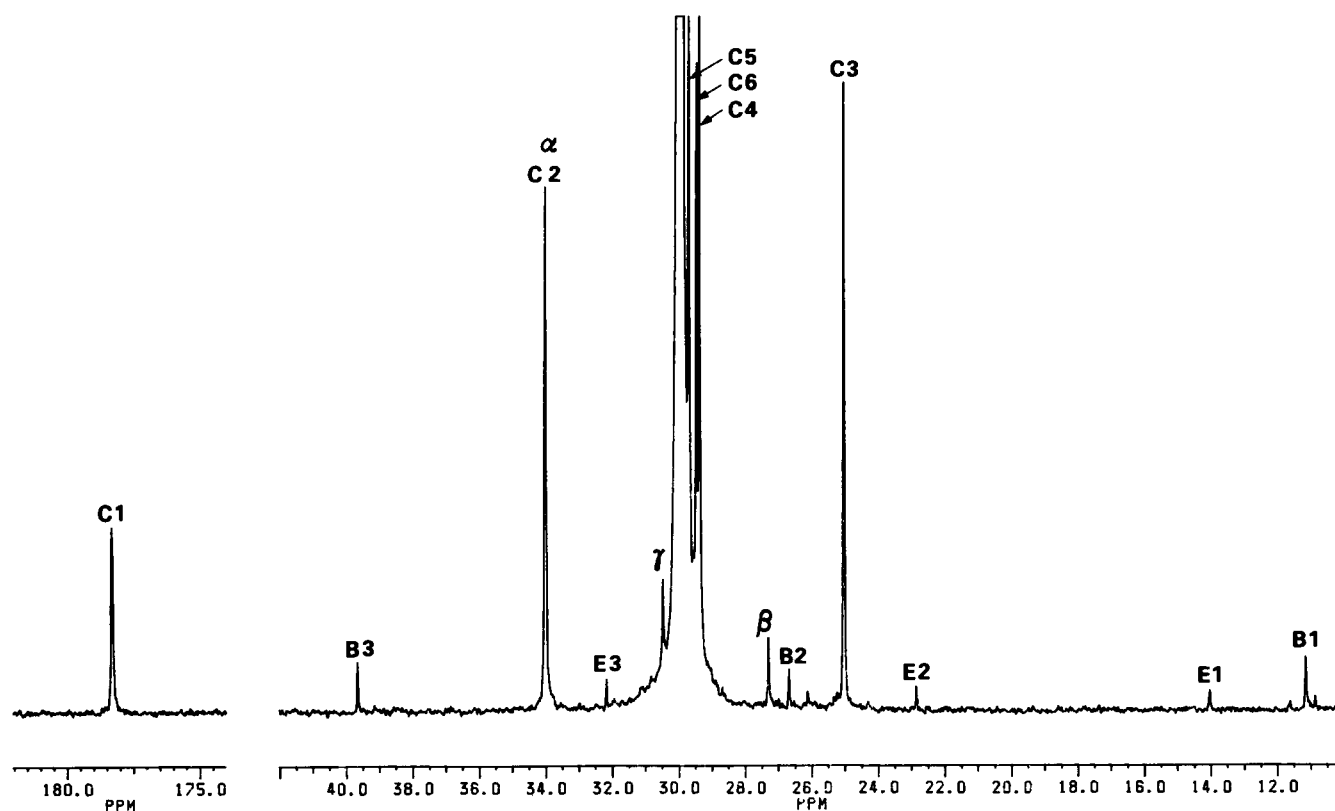*^{a} Thickness of crystalline core determined from long period and X-ray crystallinity*
^{b} Thickness of crystalline core calculated from M_n, letting c axis be 2.54 Å

Figure 5 A typical ^{13}C n.m.r. spectrum of ethylene/but-1-ene copolymer (B-1) after FNA degradation: assignments are described in *Table 3*

Table 3 Chemical-shift assignment in ^{13}C n.m.r. spectrum of FNA-treated ethylene/but-1-ene copolymer

Chemical shift (ppm)		Assignment^a
11.13	CH$_3$	B(1)
14.02	CH$_3$	E(1)
22.84	CH$_2$	E(2)
25.02	CH$_2$	C(3)
26.67	CH$_2$	B(2)
27.29	CH$_2$	β
29.35	CH$_2$	C(4)
29.44	CH$_2$	C(6)
29.67	CH$_2$	C(5)
29.97	CH	δ^+
30.46	CH$_2$	γ
32.15	CH$_2$	E(3)
33.99	CH$_2$	α, C(2)
39.65	CH	B(3)
177.71	C=O	C(1)

^{a} Symbols in assignments are based on the following structure
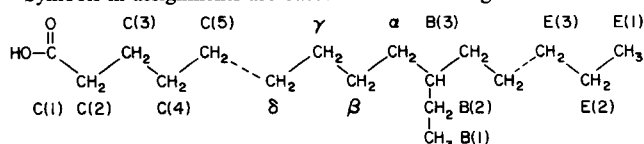
considered to be due to the carbons of the alkyl end-groups. Since several authors[35,41] have indicated the existence of NO$_2$ groups in FNA-etched polyethylenes on the basis of i.r. spectral measurements, the ^{1}H and ^{13}C n.m.r. spectra of two kinds of model compounds, i.e. (a) 12-nitrododecanoic acid and (b) stearic acid (both commercial reagents produced by Aldrich Chemical Co. Ltd), were measured to confirm the peak assignments. *Table 4* shows ^{13}C and ^{1}H chemical shifts of methylenes and methyl groups attached to the end-groups of each compound. The chemical shifts for methylenes near the COOH end and near the alkyl end methyl group were consistent with those in the spectra of etched samples. However, peaks assigned to methylenes neighbouring NO$_2$ groups, which have peaks at 75 ppm (^{13}C) and 3.7 ppm (^{1}H), were not observed at all in the n.m.r. spectra of the etched samples, indicating that almost all the NO$_2$ groups, even if generated by FNA treatment, were oxidized and converted into COOH groups under the conditions in this work, i.e. rather long contact with FNA compared with those reported previously[35,41] (8 h at 70°C). From these results, 97% of the end-groups of

Table 4 ^{13}C and ^{1}H n.m.r. chemical shifts of model compounds

12-Nitrododecanoic acid				Stearic acid			
$HOOC-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NO_2$				$HOOC-CH_2-CH_2-CH_2-CH_2-(CH_2)_9-CH_2-CH_2-CH_2-CH_3$			
1 2 3 4 5 6 7 8 9 10 11				1 2 3 4 5-13 14 15 16 17			
Atom	^{13}C (ppm)	Atom	^{1}H (ppm)	Atom	^{13}C (ppm)	Atom	^{1}H (ppm)
1	34.33	1	2.14	1	34.26	1	2.11
2	25.00	2	1.53	2	25.10	2	1.53
3	29.31			3	29.45	3, 4	1.21
4, 7	29.59	3-8	1.20	4	29.59		
5, 6	29.45			5-13	30.13	5-16	1.34
8	29.02			14	29.75		
9	27.48	9	1.03	15	32.34		
10	26.40	10	1.55	16	23.02		
11	75.52	11	3.70	17	14.11	17	0.91

the etched sample (B-1) were found to be carboxyl and the remainder methyl.

It is generally considered from the initiation mechanism of the polymerization reaction (insertion of monomer into alkyl–metal bond) that one end-group of polyethylene polymerized with a Ziegler–Natta catalyst is alkyl. Since the other end-group is vinyl, vinylidene or alkyl, depending on the type of termination reaction, the number of alkyl groups per polymer molecule varies between one and two. Thus, the concentration of methyl end-groups per 1000 carbons can be estimated from M_n of the original sample. The measured concentration of methyl end-groups for the etched sample (0.6/1000 C) seems to be appreciably higher if the methyl end of the original polymer remains chemically unchanged by FNA treatment (0.2/1000 C in the case for one end to be methyl, 0.4/1000 C for both ends to be methyl). Therefore, a considerable amount of methyl end-groups seem to be newly produced during treatment, though the mechanism is ambiguous at present.

Degree of branch inclusion into crystal

The existence of peaks assigned to ethyl branches in the ^{13}C n.m.r. spectrum of the residue after FNA treatment (*Figure 5*) obviously indicates the inclusion of ethyl groups into the crystalline core. Peaks due to other kinds of branches were also observed in ^{13}C n.m.r. spectra of other copolymer samples. So, the amount of branches included in the crystalline phase was measured by n.m.r. spectra for various copolymers, and the results are shown in *Table 2* and *Figure 6*, where the degree of branching in the amorphous phase was calculated from:

$$B_t = B_c X_c + B_a(1 - X_c) \tag{3}$$

where B_t stands for the total degree of branching of the original sample, and B_c and B_a the degree of branching in the crystalline phase and in the amorphous phase, respectively. The low level of branch content in the FNA-etched sample (B_c) in comparison with that in the amorphous phase (B_a) indicates that the majority of the alkyl branches are excluded into the amorphous phase when they crystallize. It was proved again by this experiment that a considerable amount of methyl branches can be included into the crystalline phase, as already reported by several authors and described above. The ratio of the probability that the branches are observed in the crystal
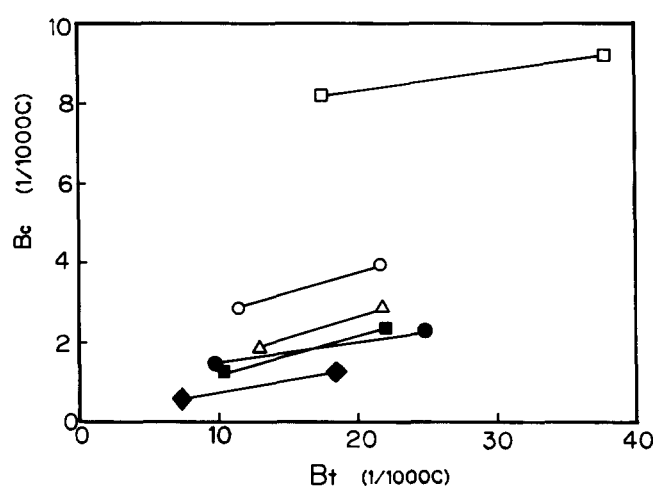

Figure 6 Degree of branching in crystal (B_c) *versus* total degree of branching (B_t) for various ethylene/α-olefin copolymers: comonomers are ($\square$) propylene, ($\bigcirc$) but-1-ene, ($\triangle$) hex-1-ene, ($\bullet$) oct-1-ene, ($\blacksquare$) dodec-1-ene and ($\blacklozenge$) 4-methylpent-1-ene

to that in the amorphous phase (B_c/B_a) is in the following order: methyl $(0.22) \gg$ ethyl $(0.10) >$ n-butyl $(0.07) =$ n-hexyl $(0.06) =$ n-decyl $(0.06) >$ isobutyl (0.04). Here, the number in parentheses denotes the average value of B_c/B_a for two samples of different crystallinity. This order seems to correspond to the order of bulkiness of the alkyl branches. We have estimated from a statistical treatment using the crystallinity–degree of branching relationship that the probability of including ethyl branches into the crystalline phase is twice as large as that of a bulkier branch like isobutyl[6]. The result obtained in this work is in good agreement with this estimation.

Furthermore, it is interesting that the inclusion of a branched chain such as isobutyl into the crystal takes place to a lesser extent than the inclusion of a normal unbranched chain of the same excluded volume.

In our paper on the infra-red dichroism of various ethylene/α-olefin copolymers[1], normal alkyl branches longer than n-propyl were found to orient such that the methyl group in the alkyl branch was parallel to the main chain when the sample was stretched. It is considered that flexible branches could likewise change their conformations by rotating around the C–C bond to decrease the mutual interaction energy with other main chains

when, during the crystallization process, polyethylene molecules with alkyl branches are located on the growing edge of the crystal and other polymer chains approach their branches. In other words, methylene sequences containing a less flexible branch would not be able to avoid the increase of repulsive energy generated between the alkyl branch and other main chains, resulting in the exclusion of the branches from the crystalline phase.

Thus, energy levels for the various conformations caused by the rotation of C–C bonds in the branch were calculated for n-butyl and isobutyl branches, using a commercial computer-aided chemistry system 'ACACS' (Sumitomo Chemical Co. Ltd). In the calculations, mutual interactions between the main chain and an alkyl group branched from it and the interactions generated within the alkyl branch were taken into consideration.
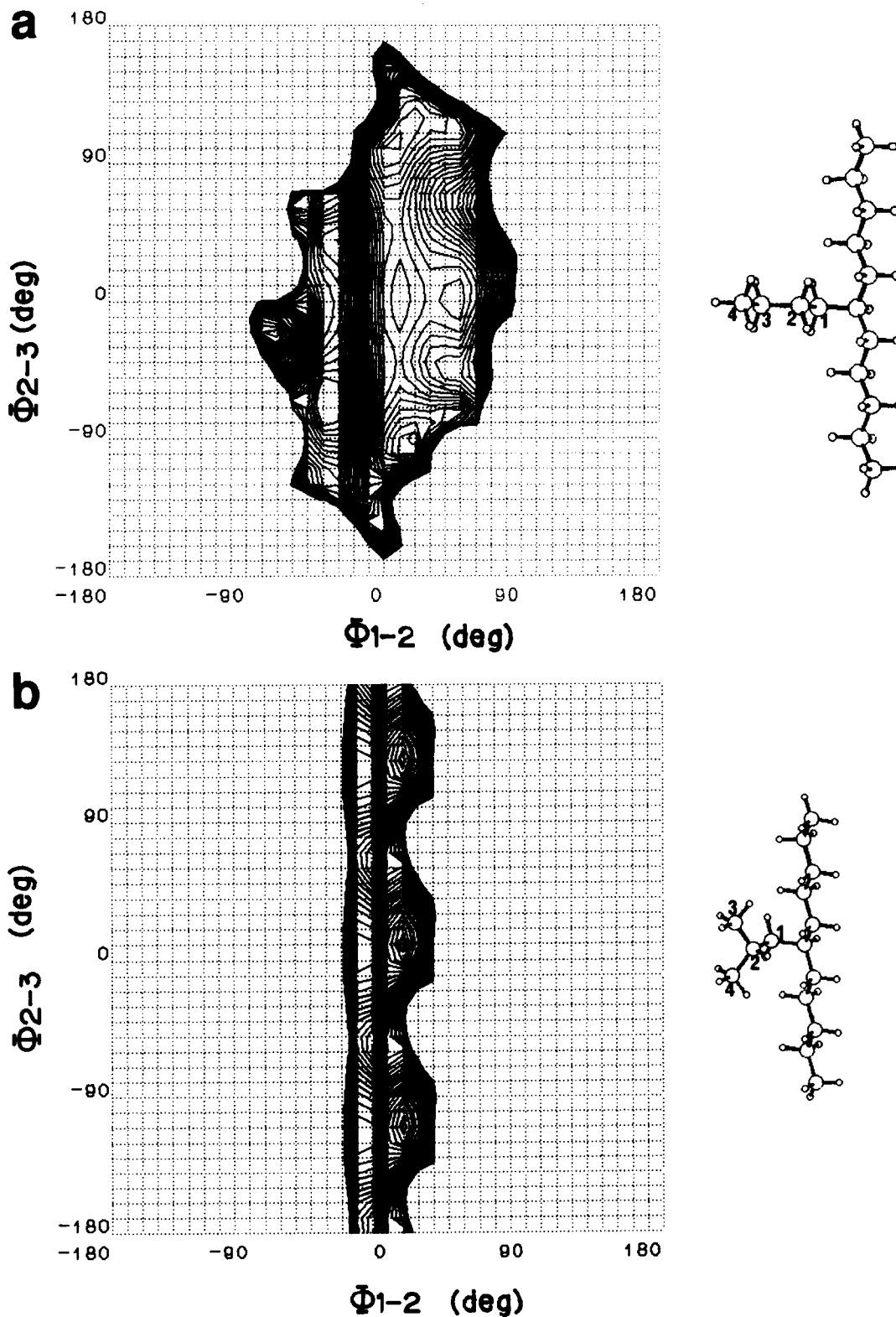

Figure 7 'ACACS' energy calculation for various conformations caused by the independent rotations of C(1)–C(2) (Φ_{1-2}) and C(2)–C(3) (Φ_{2-3}) bonds for copolymers of ethylene with (a) but-1-ene and (b) 4-methylpent-1-ene: the figures show the area where the branch could move without imposing serious obstruction on each atom

The n-butyl branch in an all-*trans* conformation in the plane perpendicular to the main-chain axis was taken as a standard state, as shown in *Figure 7a*. As for an isobutyl branch, the standard conformation is shown in *Figure 7b*, in which C(1) and C(2) are located in the plane perpendicular to the main-chain axis and methyl groups are situated symmetrically on both sides of this plane. *Figures 7a* and *7b* illustrate the areas where the branch could move without imposing serious obstructions on each atom under the independent rotations of C(1)–C(2) and C(2)–C(3) bonds. We can easily understand from these figures that the isobutyl branch is restricted in possible conformations much more than n-butyl. Although it is difficult to make any strict conclusions because of the lack of calculations for the mutual interaction energy between the alkyl branch and other polymer main chains in various conformations and locations in the crystal lattice, it is supposed that the results in *Figure 7* indicate the relative difficulty of branch inclusion in terms of the flexibility of the branch.

ACKNOWLEDGEMENTS

REFERENCES

1 Hosoda, S. and Furuta, M. *Makromol. Chem., Rapid Commun.* 1981, 2, 577
2 Hosoda, S. *Makromol. Chem.* 1984, 185, 787
3 Hosoda, S., Kojima, K. and Furuta, M. *Makromol. Chem.* 1986, 187, 1501
4 Furuta, M., Hosoda, S. and Kojima, K. *J. Appl. Polym. Sci.* 1987, 33, 401
5 Hosoda, S. and Gotoh, Y. *Polym. J.* 1988, 20, 17
6 Hosoda, S. *Polym. J.* 1988, 20, 383
7 Mirabella, F. M., Jr and Ford, E. A. *J. Polym. Sci., Polym. Phys. Edn.* 1987, 25, 777
8 Cady, L. D. *Plastic Eng.* 1987, 43, 25
9 Cady, L. D. Broadening Horiz. Linear Low Technol. 1985, p. 107
10 Wild, L., Ryle, T. R., Knobeloch, D. C. and Peat, I. R. *J. Polym. Sci., Polym. Phys. Edn.* 1982, 20, 441
11 Fujimoto, K., Ogawara, K. and Emura, N. *Toyosoda-kenkyuu Houkoku* 1984, 28, 89
12 Burfield, D. R. *Makromol. Chem.* 1985, 186, 2657
13 Mathot, V. B. F. 'POLYCON '84', Chameleon Press, London, 1984, p. 1
14 Mathot, V. B. F., Schoffeleers, H. M., Brands, A. M. G. and Pijpers, M. F. J. in 'Morphology of Polymers', Walter de Gruyter & Co., Berlin, FRG, 1986, p. 363
15 Furuta, M. and Kojima, K. *J. Macromol. Sci.-Phys. (B)* 1986, 25, 349
16 Mirabella, F. M., Jr, Westphal, S. P., Fernando, P. L., Ford, E. A. and Williams, J. G. *J. Polym. Sci.* 1988, 26, 1995
17 Deblieck, R. A. C. and Mathot, V. B. F. *J. Mater. Sci. Lett.* 1988, 7, 1276
18 Payer, W., Wicke, W. and Cornils, B. *Angew. Makromol. Chem.* 1981, 94, 49
19 Swan, P. R. *J. Polym. Sci.* 1962, 56, 409
20 Baker, C. H. and Mandelkern, L. *Polymer* 1966, 9, 71
21 Shirayama, K., Kita, S. and Watabe, H. *Makromol. Chem.* 1972, 151, 97
22 Baltá Calleja, F. J., González Ortega, J. C. and Martinez Salazar, J. *Polymer* 1978, 19, 1094
23 Sánchez Cuesta, M., Martinez Salazar, J. and Baltá Calleja, F. J. *Polym. Bull.* 1987, 17, 23
24 Cutler, D. J., Hendra, P. J., Cudby, M. E. A. and Willis, H. A. *Polymer* 1977, 18, 1005
25 Landes, B. G. and Harrison, I. R. *Polymer* 1987, 28, 911
26 Davis, G. T., Eby, R. K. and Colson, J. P. *J. Appl. Phys.* 1970, 41, 4316
27 Kitamaru, R. and Mandelkern, L. *J. Appl. Polym. Sci. (A-2)* 1970, 8, 2079
28 McFaddin, D. C., Russell, K. E. and Kelusky, E. C. *Polym. Commun.* 1986, 27, 204
29 McFaddin, D. C., Russell, K. E. and Kelusky, E. C. *Polym. Commun.* 1988, 29, 258
30 VanderHart, D. L. and Pérez, E. *Macromolecules* 1986, 19, 1902
31 Pérez, E., VanderHart, D. L., Crist Jr., B. and Howard, P. R. *Macromolecules* 1987, 20, 78
32 Pérez, E. and VanderHart, D. L. *J. Polym. Sci., Polym. Phys. Edn.* 1987, 25, 1637
33 Laupretre, F., Monnerie, L., Barthelemy, L., Varion, J. P., Sauzeau, A. and Roussel, D. *Polym. Bull.* 1986, 15, 159
34 Patel, G. N., Keller, A. and Martuscelli, E. *J. Polym. Sci., Polym. Phys. Edn.* 1975, 13, 2281
35 Palmer, R. P. and Cobbold, A. J. *Makromol. Chem.* 1964, 74, 174
36 Blundell, D. J., Keller, A. and Connor, T. M. *J. Polym. Sci. (A-2)* 1967, 5, 991
37 Holdsworth, P. J., Keller, A., Ward, I. M. and Williams, T. *Makromol. Chem.* 1969, 125, 70
38 Holdsworth, P. J. and Keller, A. *Makromol. Chem.* 1969, 125, 82
39 Holdsworth, P. J. and Keller, A. *Makromol. Chem.* 1969, 125, 94
40 Sadler, M., Williams, T., Keller, A. and Ward, I. M. *J. Polym. Sci. (A-2)* 1969, 7, 1819
41 Shida, M., Ficker, H. K. and Stone, I. C. *Polym. Lett.* 1966, 4, 347
42 Cagiao, M. E., Rueda, D. R. and Baltá Calleja, F. J. *Polym. Bull.* 1980, 3, 305
43 Cagiao, M. E. and Baltá Calleja, F. J. *J. Macromol. Sci.-Phys. (B)* 1982, 21, 519
44 Maeda, Y. and Kanetsuna, H. *Polym. J.* 1981, 13, 357
45 Aggarwal, S. L. and Tilley, G. P. *J. Polym. Sci.* 1955, 18, 17
46 Borart, R. and Hosemann, R. *Kolloid Z.* 1962, 186, 16
47 Dollbopf, W., Grossmann, H. P. and Leute, U. *Colloid Polym. Sci.* 1981, 259, 267