Correspondence to the Editor

Comments on paper 'Distribution of chain defects and microstructure of melt crystallized polyethylene'. (F. J. Baltá Calleja, J. C. González Ortega and J. Martinez de Salazar *Polymer* 1978, 19, 1094–1099)

In a recent paper, Baltá Calleja *et al.*[1] described a combined wide-angle and small-angle X-ray diffraction study of a series of polyethylenes, mostly of the low density type with a wide range of defect concentrations, that had been crystallized from the melt. They interpreted their results quantitatively in terms of a model which assumes inclusion of defects within the lattice by means of the generation of 2 *gl* chain kinks and concluded that the fraction of defects incorporated the lattice does not exceed 20% of the total number of defects in any of the samples investigated. In drawing this conclusion they did emphasize that it might only apply to their series of samples, crystallized from the melt, and not necessarily to isothermally crystallized branched materials. In this Letter we present evidence which suggests that even with melt crystallized polymers their conclusions may not be valid for polyethylenes with methyl and ethyl branches.

In their work Baltá Calleja *et al.* used the structural parameter total defect concentration, obtained by summing the branch content and the unsaturation, including chain ends. They worked with samples which had previously[2] been used for a series of structural studies and which, with a few exceptions, contained between one and seven branches per hundred carbon atoms. Although the branch levels were quoted in terms of methyl groups in the earlier work[2] they now[1] state that they are butyl or longer branches and, bearing in mind the overall level of the branching, this would be expected from the work of Cudby and Bunn[3]. We should like to point out that the distribution of branches between the crystalline and amorphous phases is dependent on branch length and, therefore, to work in terms of total defect concentration without taking into account the nature of the branches will lead to invalid conclusions in some cases.

The results of Baltá Calleja *et al.* show that the expansion of the polyethylene unit cell in the *a*-direction is not necessarily a measure of the degree of incorporation of branches into the lattice. Nevertheless, unit cell dimension measurements are capable of providing useful information if they are made on a particular sample with various thermal histories over a range of temperatures. Preedy[4] has shown that with polyethylenes having methyl or ethyl branches at levels up to 1.4 per 100 C, that had been annealed at 115°C following crystallization from the melt, the increase in the *a*-dimension is identical for the two types of branches and is proportional to their concentrations. With polymers having butyl branches at these rather low levels the branches are rejected into the amorphous phase and the *a*-dimension, 7.42 Å, is identical with that obtained for unbranched polyethylene. In subsequent measurements we have found that it is possible to force butyl branches into the crystalline lattice by vigorous quenching (–80°C) from the melt; a polymer with 0.47 butyl branches per 100 C then had an *a*-value of 7.485 Å. When such quenched samples are annealed the butyl branches revert to amorphous regions and the *a*-values fall to 7.42 Å.

The more recent work of Preedy and Wheeler[5], in which the *a*-dimensions of a series of polyethylenes having various types and levels of branching were measured over a range of temperatures from ambient to the molten state, has provided additional evidence for the substantial incorporation of methyl and ethyl branches into the lattice. The change in the *a*-dimension as a function of temperature is separable into three regions. In the first, extending from ambient to about 115°C, the *a*-dimension increases linearly with temperature, as is also the case with linear polyethylene, and the effect is attributable to small rotations of the planar zig–zag chain backbone. In the approximate range 115° to 140°C the *a*-dimension increase is much less marked and there is a clear plateau; this is the result of a melting and recrystallization process during which the branches are rejected from the lattice. Finally, for the limited temperature range above 140°C examined the *a*-dimension increases rapidly and this behaviour has been tentatively associated with the presence of some residual crystalline material having the hexagonal unit cell. These deductions were substantiated by parallel measurements of crystallinity and crystallite size. Although polymers with butyl branches behave similarly to those with methyl and ethyl branches over the first temperature range the second region is substantially absent with butyl branched polymers and no significant plateau is observed. This is a consequence of the fact that no butyl branches are present in the lattice at ambient temperature so that at higher temperatures melting and recrystallization and the rejection of branches does not occur.

These results indicate clearly that at the branching levels covered by the generic term high density polyethylene methyl and ethyl branches are substantially accommodated in the lattice, although the measurement of *a*-values does not give quantitative levels of accommodation. In this connection it may be pertinent to question the basic assumption used by Baltá Calleja *et al.*[1] in deriving values for the proportion of defects accommodated in crystalline regions, namely that the average volume occupied by a defect can be assumed to be equal to the average volume of a CH_2 unit in a crystal. Is this assumption equally valid for branches as different in size as methyl and butyl groups and, therefore, would calculations based on the results of Preedy[4] for polymers containing methyl and ethyl branches be directly comparable with those of Baltá Calleja *et al.*[1] ?

Hence it is necessary to specify not only the level of defect structures but also their type in attempting to correlate their presence with the polymer microstructure. This point has also not been appreciated in the recent work of Miyaji and Asai[6], who measured changes in the unit cell *a*- and *b*-dimensions of drawn polyethylene specimens as a function of time and temperature of annealing. The polymer studied, Sumitomo L705, was stated to have about 3 methyl branches per 100C. However, a polymer with this level of branching that is not explicitly stated to be an ethylene/propylene copolymer is clearly a low density material and will contain ethyl, butyl and longer branches. It will show a complex annealing behaviour, in agreement with the reported observations that at temperatures below about 70°C plots of the *a*-dimension against the logarithm of annealing time are linear, whereas at higher temperatures they pass through a maximum at about ten minutes annealing time. It would obviously be valuable to have measurements of the type described by Baltá Calleja *et al.* and by Miyaji and Asai for polyethylenes containing known levels of methyl, ethyl or butyl branches.

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