JOURNAL OF MATERIALS SCIENCE **36** (2001) 1879–1884

Inter-relationships between tie-molecule concentrations, molecular characteristics and mechanical properties in metallocene catalysed medium density polyethylenes

J. J. JANIMAK*, G. C. STEVENS
Polymer Research Centre, School of Physics and Chemistry, University of Surrey Guildford, Surrey, GU2 7XH

Classical tie-molecule concentrations in a series of metallocene catalysed medium density polyethylenes have been computed and comparisons made with literature data on non-metallocene catalysed systems over a comparable density range. It is shown that a complex inter-relationship exists between the concentration of classical tie-molecules and molecular weight, lamellar thickness and crystallinity and the X-ray long period where the latter is influenced by the concentration of short chain branches. Tie-molecule concentration levels increase steeply beyond a short chain branch (SCB) content of approximately 4 butyls/1000 C atoms with a maximum value for a metallocene sample containing 9.7 butyls/1000 C atoms. Relative tie-molecule concentrations corrected for volume crystallinity decrease sharply with increasing X-ray long period and decreasing short chain branch content. Comparisons among the different catalyst systems revealed that a chromium catalysed polyethylene with 6.8 butyls/1000C atoms had a similar tie-molecule concentration to a metallocene catalysed polyethylene with 11.5 butyls/1000C atoms. Tear and impact strength data showed a continuous increase with increasing short chain branching, varying slightly with catalysts type but differing significantly at the highest concentration levels of short chain branching. These mechanical property – SCB content correlations are closely related to those between classical tie-molecule concentrations and the degree of short chain branching.

1. Introduction

Crystalline domains within semicrystalline polymers influence such low strain rate properties as modulus, yield stress, slow crack growth and environmental stress cracking [1–13]. High strain rate properties like impact, tear and fast fracture resistance are viewed as being controlled largely by the amorphous regions [14, 15]. However, both low and high strain rate properties are influenced by tie-molecules that traverse the amorphous interface between adjacent lamellae.

Tie-molecules can exist in a variety of different forms, with some more permanent and having different relaxation characteristics under imposed strain. Fig. 1 shows two tie-molecules, one marked in bold the other (dashed line) not, connecting three lamellar crystals. In this 2-D picture of the lamellae and interlamellar sharing of molecules, the simplest tie-molecule is a single chain traversing the amorphous phase from one lamella to another. This "classical" tie-molecule is able to transfer stress effectively from one lamella to the next when strained. Calculating the probability of formation of this type of tie-molecule and its influence on properties is the subject of this paper. Other forms of topological tie-molecules arising from entanglements can also exist where the interaction level can range from being strong, in the case of adjacent re-entry to weak in the case of simple physical entanglements of emergent chains from lamellae into the amorphous entanglement network. For brevity, these types are not considered here.

In chromium catalysed ethylene copolymers, the influence of random short chain branching leads to a marked decrease in lamellar thickness and a sizeable increase in tie-molecule concentration. This observation first reported by Huang *et al.* [16] was explained in terms of branch size and concentration, which influences lamellar thickness and subsequent lamellar thickening processes immediately following the initial stages of chain folding. The presence of branches inhibits the motion of tie-molecules through the amorphous and crystal phases by branch pinning to the surfaces of lamellar crystals. It was suggested that probably the optimum condition for tie-molecule formation in the case of branched chains is when the

---

[*] *Present Address:* Lilly Clinical Operations SA, Parc Scientifique de Louvain-la-Neuve, Rue Granbonpré 11, 1348 Mont-Saint-Guibert, Belgium.

0022–2461

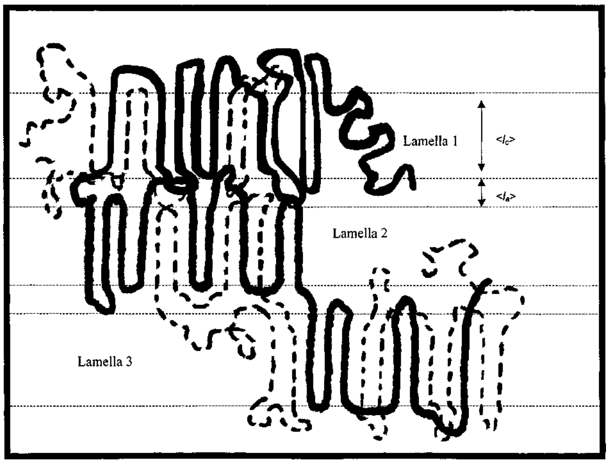

Figure 1 Schematic representation of an individual chain shared between several different lamellar crystals. A collection of various molecular arrangements in neighbouring lamellae are drawn connected by tie-molecules.

spacing between branches is about equal to the thickness of the lamella. This would favour branches being rejected periodically onto the fold surfaces of lamellae. By examining metallocene catalysed medium density polyethylenes (mMDPEs) the possibility of regular inter-branch sequences offers different rejection possibilities to that in heterogeneously branched systems. In this case, the exploration of different chain conformations and folding intervals presumed to occur for the latter because of mixed branch free sequences is denied in the case of regularly branched materials [17].

Mechanically, evaluating the nature and potential concentrations of tie-molecules usually involves the use of complementary techniques, including theoretical methods, but until now the main thrust has been experimental. Usually the measurement of a physical property is required in parallel with molecular information derived from calculation [18]. Properties like brittle fracture toughness and electron spin resonance measurements of free radicals associated with broken tie-molecules have been used to assess tie-molecule concentrations [8]. Inevitably, fracture, crazing and slow crack growth measurements are used to infer information on tie-molecules [19, 20]. In the case of craze strength, tie-molecule concentrations have been evaluated from the modulus of oriented samples (during necking) with the aid of a simple Takayanagi model [21]. Spectroscopic techniques like Raman and infrared dichroism after deformation of chlorinated films can be used to extract more detailed information on tie-molecules [22, 23]. Post yield true stress-strain data and an interpretational approach based on rubber elasticity theory can also provide an estimate of the concentration of static and dynamic tie-molecules in a semicrystalline network [9]. Post yield experiments assume that tie-molecules and entangled chains in the amorphous phase behave like a rubbery network. Additionally, in the drawing and strain hardening region of the stress-strain curve beyond the yield point, tie-molecules are steadily pulled out from fragmented lamellae and become part of the oriented amorphous state. This description however excludes formation of voids in the necked region, which cannot easily be accounted for in terms of tie-molecule characteristics alone.

In this paper, we have attempted to theoretically predict the concentration of classical tie-molecules in a series of branched mMDPEs using only chain dimensions as first proposed by Huang and Brown, denoted hereafter as (H&B) [16] and the lamellar microstructure based on crystal melting points and small angle X-ray determined long period spacing. These tie-molecule concentrations were then compared with published data on heterogeneous catalysed branched polyethylenes. Refinements to the H&B calculation were also investigated following developments by Patel *et al.* [24]. In this modification of the H&B model, the associated effects of volume fraction crystallinity are incorporated into the tie-molecule calculations, leading to a more precise evaluation of the classical tie-molecule fraction. Finally, standard experimental dart impact and tear strength measurements on 40 μm thick films were correlated against tie-molecule concentrations as a function of the degree of short chain branching.

2. Materials and equipment

Our medium density polyethylenes with known branch content, molecular weight and polydispersity were kindly provided by Fina Research (Belgium) through the Fina-Surrey Scholar research programme. Details of as received materials and their molecular characteristics are listed in Table I. Molecular weights were determined using Gel Permeation Chromatography (GPC) following standard procedures for polyolefins.

2.1. Specimen preparation for mechanical testing

The Elmendorf tear strength in 40 μm thick films was evaluated in the machine direction, because the ratio of tear strength parallel and perpendicular to the machine direction biased the most polydisperse polymers. The Elmendorf tear strength tester determines the force required to propagate a tear catastrophically across a pre-split film specimen. These measurements conformed to ASTM standard D1922. The dart impact test evaluates the resistance to impact failure of polyethylene film. In this experiment, a dart is dropped onto a tightly clamped film specimen from a height of 660 mm. A series of 10 specimens were used for each sample where each sample was subjected to increasingly heavier weights. Impact strength (measured in grams) is defined as being at the 50% failure rate for each set. These impact measurements complied with ASTM standard D1709. In each of these different experiments, 40 μm thick film specimens were prepared and tested at Fina Research (Belgium).

3. Results and discussion

Calculating the relative density of classical tie-molecules was first derived by Huang and Brown [16]. The basic approach requires that the root-mean-square

TABLE I Molecular and melting characteristics of as received material. Short chain branch content was assessed using C^{13} NMR

Surrey Reference		Polymer A	Polymer B	Polymer C	Polymer D	Polymer E	Polymer F
Catalyst Type	Units	Cr	Met	Met	Met	Met	Met
Density	kg/m^3	934	922	927	931	943	924
M_n	kDa	17	25.8	37.9	28	49	22.3
M_w	kDa	223	172	83	107	123	118
M_w/M_n		13.2	6.7	2.2	3.8	2.6	6.3
SCB(/1000C)$^{(a)}$		6.8	9.7	4.3	5.4	0.4	11.5
T_m	°C	123.3	116.1	123.5	122.4	131.3	118
$\Delta H_m{}^{(b)}$	J/g	128.4	123.9	139	143	176	126
$\omega^{c\,(c)}$	%	44	42	47	49	60	43
$\nu^{e\,(d)}$	%	39	37	41	44	54	38
$2l_c + l_a{}^{(e)}$	(nm)	50.4	37.3	48.4	44.2	72.2	39.6
$L_p{}^{(f)}$	(nm)	21.7	16.1	20.1	20.0	29.5	15.5

Cr = Chromium.

Met = Metallocene.

(a) = 1-hexene comonomer.

(b) = 100% crystallinity (293 J/g).

(c) = Weight fraction crystallinity (DSC measurements).

(d) = Volume fraction crystallinity [$\nu^c = (\omega^c \cdot \rho)/\rho_e$].

(e) = The lamellar thickness was calculated from the Thomson-Gibbs equation as follows: $T_m = T_m^\circ\,(1 - 2\sigma_e/\Delta H_f l_c)$, where the parameters used $T_m^\circ = 141.5°\text{C}$, $\sigma_e = 93\ \text{mJ/m}^3$ and $\Delta H_f = 293$ J/g. The amorphous layer thickness was calculated using $l_a = \rho_c l_c(1 - \omega^e)/\rho_a\omega^c$ where $\rho_c = 1000\ \text{kg/m}^3$ and $\rho_a = 852\ \text{kg/m}^3$.

(f) = Long Period estimated from SAXS using Bragg Maximum [17], $L_p = l_c + l_a$.

end-to-end distance, $\langle r_0\rangle$ of a polymer chain in the isotropic melt phase be equal to or greater than the mean distance between adjoining crystallites. Based on reptation arguments, $\langle r_0\rangle$ should be at least approximately the same size as the lamellar long spacing for a tie-molecule to form. If this is the case, formation of a tie-molecule is statistically unlikely with $\langle r_0\rangle$ values less than this critical value. In other words, formation of a tie-molecule does not necessarily lead to complete disentanglement or extension of a polymer chain in the molten state. This event is viewed as unlikely because that part of the polymer chain not involved in crystallization (forming a lamellar crystal) becomes confined to the amorphous region.

The equation which gives the probability of forming a tie-molecule assumes also that the end-to-end distance of a random coil in the melt is greater than $(2l_c + l_a)$, and thus the probability of tie-molecule formation for a given molecular weight is simply:

$$P(M_w) = \frac{1}{3}\frac{\int\limits_{2l_c+l_a}^{\infty} r^2 \exp(-b^2r^2)\,dr}{\int\limits_{0}^{\infty} r^2 \exp(-b^2r^2)\,dr} \qquad (1)$$

where r = end-to-end distance of a random coil, $b^2 = 3/2\langle r\rangle^2$ and l_c = crystal thickness (uncorrected for chain inclination) and l_a the thickness of the amorphous layer. The factor 1/3 was introduced into the model because the *a* and *b*-axis dimensions of a lamella are approximately 100 times larger than the long period (generally along the *c*-axis). In calculating l_c we used the Gibbs-Thomson equation as applied by H&B for folded lamellar crystals $\{l_c(\text{nm}) = 0.624 \times 414.7/(414.7 - T_m(\text{K}))\}$ [16]. The weight fraction crystallinity and peak melting temperatures were also obtained from calorimetry. Using the approach of a two-phase model, we were able to estimate l_a. Tie-molecule calculations using the lower integration limit of $2l_c + l_a$ (based on calorimetric measurements) were compared with experimentally determined L_p (X-ray long period). Our polymers exhibit a range of polydispersites. However, since there is a distribution of molecular weights and a distribution of long periods, the above equation can easily be modified to consider these variables. This is the subject of another paper that focuses attention exclusively on metallocene catalysed high density polyethylenes (mHDPEs) [25]. Here we have simply used the weight average molecular weight, the average of $2l_c + l_a$ and L_p values. The X-ray long period is taken as corresponding to the first Bragg maximum in the small angle X-ray scattering patterns, which will be reported in a separate paper [17].

Fig. 2 shows estimated tie-molecule concentrations for each of our mMDPEs that are compared with results from H&B on a heterogeneous series of 1-hexene ethylene copolymers. Our data set also includes a chromium catalysed medium density polyethylene, identified here as polymer A. The H&B data are shown represented by filled circles and our mMDPE data by the open circles. Both sets of data show an increase in tie-molecule fraction, starting from zero and rising to 9% for the H&B data and to 18% for our data. In the case of the H&B data, the rise in tie-molecule concentration is relatively linear with short chain branching. This condition is only observed beyond approximately 4 butyls/1000 C atoms in the metallocene catalysed polymers. Interestingly, both sets of data exhibit a familiar pattern up to polymer A (shown labelled) where there exists reasonable overlap in the short chain branch content. A straight line (dashed) is drawn connecting the H&B data that includes polymer A. The tie-molecule fraction would appear to reach a maximum at polymer B for a short chain branch content of approximately 9.7 butyls/1000 C atoms. Similarly, for molecular weights above 10^5, the concentration of tie-molecules increases quite steeply but there is a reduction for polymer F

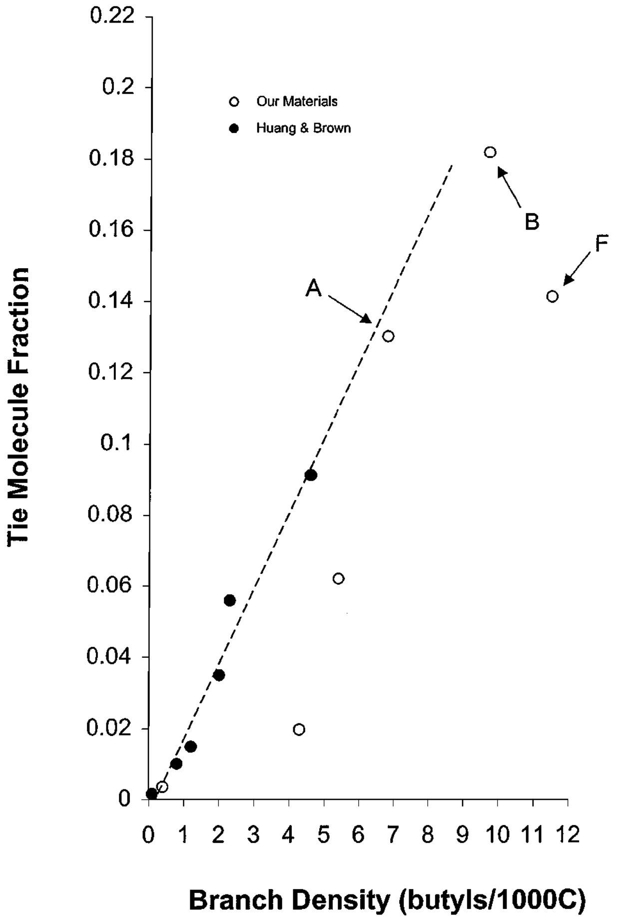

Figure 2 Calculated tie-molecule concentrations between data from Huang & Brown (heterogeneous system) with our metallocene medium density polymers. The comparison is represented as a function of short chain branching.

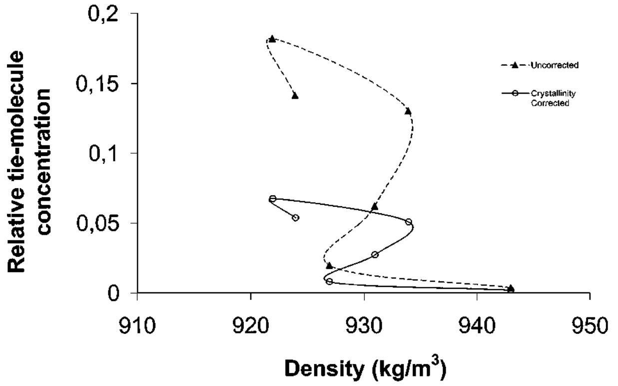

Figure 3 Plots of the relative tie-molecule fractions as a function of density for short chain branching corrected and uncorrected for volume fraction crystallinity.

which has the highest branch content and the lowest L_p value.

Fig. 3 shows the dependence on density of the volume fraction crystallinity corrected tie-molecule concentration. Relative to the equilibrium polymer melt, Patel *et al.* were the first to introduce volume fraction crystallinity into the H&B model because of the indirect association to short chain branch content and the corresponding link with tie-molecule concentration [24]. Their results showed that a maximum in the relative tie-molecule concentration existed for all heterogeneously branched 1-alkene polyethylene copolymers. This maximum shifted to higher crystallinities with increasing molecular weight and density. Nitta *et al.* used a similar approach to good effect in estimating tie-molecule concentrations in heterogeneous ethylene-propylene copolymers and polypropylene homopolymers [4].

Our results are in close alignment with the study of Patel *et al.*, similar to their work we found no simple correlation of density and tie-molecule concentration. We found a pronounced maximum in the relative tie-molecule fraction versus density curve. The maximum in our data in Fig. 3 occurred close to a density of 920 kg/m^3. The profiles of these curves in many ways reflect the broad SCB compositional range. Interestingly, the difference between volume fraction crystallinity corrected tie-molecule concentration and uncorrected tie-molecule concentration is more significant at higher comonomer loadings, indicating the importance of crystallinity particularly at the high end of the short chain branch concentration. This observation reinforces the importance of the underlying polymer morphology in determining the tie-molecule concentration because similar crystallinities and densities can easily obscure wide variations in supermolecular structure [17].

Nitta *et al.* also estimated tie-molecule probabilities as a function of lamellar thickness and discovered that it decreased monotonically with lamellar size. The probability of tie-molecule formation approached zero when the size of the interlamellar region (amorphous phase) exceeded five times the X-ray long period (where $L_p = l_c + l_a$) [4]. In estimating the extent to which tie-molecules of mMDPE extend across stacks of contiguous lamellae, we have calculated the probability of tie-molecule formation as a function of long period for the weight average molecular weight. In Fig. 4 we compare tie-molecule concentrations with the number of long period repeats (n) and the number required for tie-molecule concentrations to decay to zero. The starting point for each simulation is the SAXS long period for each polymer. These values are different for each polymer because the experimentally observed long period is very sensitive to the degree of short chain

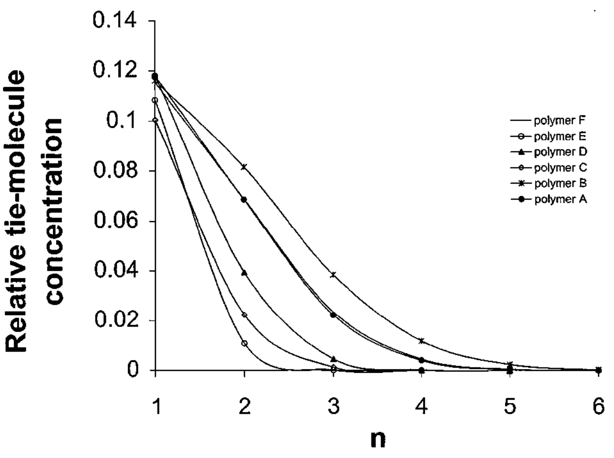

Figure 4 Plot of the relative tie-molecule fractions corrected for volume fraction crystallinity against the number (n) of selected long periods based on SAXS data.

branching, crystallization behaviour and morphology. While all our polymers show a similar behaviour, polymer E having the largest long period within this set of materials decayed the fastest. Polymer B on the other hand having by far the broadest molecular weight distribution and a comparatively small long period decayed the slowest. Polymers A, C, D and F, followed the same trend but were intermediate in character. Comparing our results with published data by Nitta *et al.* we found that when the projected long period approaches 60 nm (3 times 20 nm) for the lowest molecular weight polymer (polymer C), or 100 nm (approximately 6 times 16 nm) for the highest molecular weight polymer (polymer B), the tie-molecule probability decayed to zero. These sizes fall within the approximate range of 4 to 5 times the interlamellar spacing, which corresponds closely to the observed results of Nitta *et al.* [4]. In fact, we believe this length scale is probably representative of a large number of semicrystalline polymers and it reveals a particular limitation of classical tie-molecules to extend significantly beyond 5 to 6 times the interlamellar spacing.

Modifications to the above approach by Yeh and Runt [15] suggest that the critical tie-molecule length should be approximately twice the X-ray long period, L_p. The reason for this is that the diameter of gyration (rather than the radius of gyration) of a random coil in the melt must be larger than twice the long period in order for it to possess *true tie-molecule* forming properties. In other words, a molecule will not crystallize as a tie-molecule if the diameter of gyration is less than twice the long period. Yeh and Runt have shown that from knowing the relationship between radius of gyration and mean square end-to-end distance that the lower limit for the formation of tie-molecules should be 2.45 L_p. One salient observation of their work when applied to folded lamellar crystals with large lateral dimensions, in contrast to models based on fringed micelles, is the invalid application of the Gibbs-Thomson equation[†] in calculating, l_c and l_a.

The resistance of polyethylene film material to tearing and impact is of particular importance to many packaging applications. Illustrated in Fig. 5 is mechanical property data for tear and dart impact strength on biaxially oriented 40 μm thick films. The data set is taken from films oriented along the machine direction. The tear and dart impact strength is shown plotted as a function of short chain branch content. Both sets of results show a continuous rise with comonomer concentration, however, for polymer A, a discontinuity is observed which is repeated for polymer F, this time in the dart impact measurement. In fact, the dart impact strength that rises to a maximum at polymer B (labelled) exhibits the same profile as that of the calculated tie-molecule concentration observed in Fig. 2. This interesting observation is not observed completely in the tear strength behaviour. Tearing relative to dart impact is a low strain deformation process where entanglement types of tie-molecules can also actively contribute to the behaviour. The dart impact test on the other hand is sensitive to the response from classical tie-molecules, which explains the apparent discrepancy with short chain branching at larger tie-molecule concentrations.

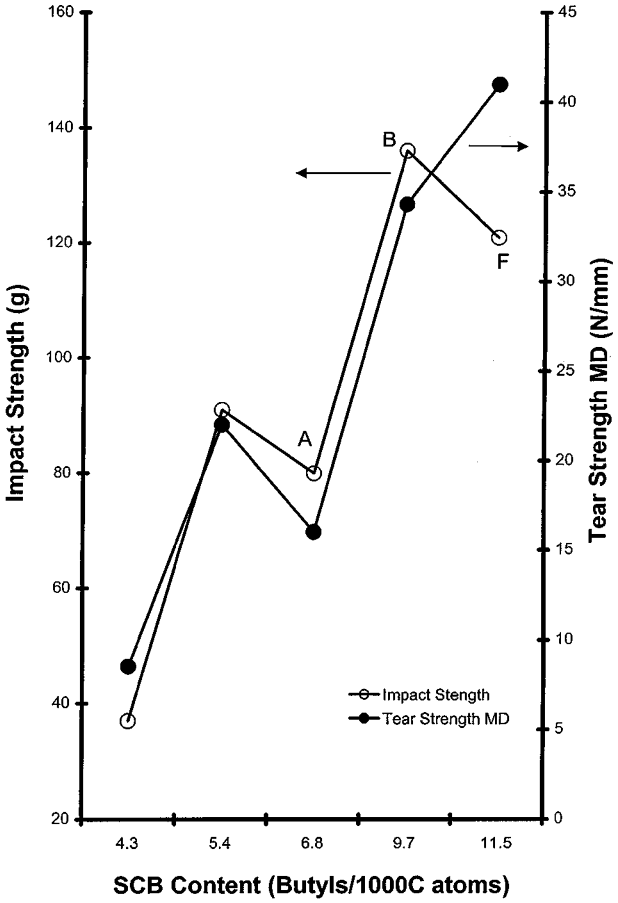

Figure 5 Plot of tear and dart impact strength on 40 μm thick films versus short chain branch content.

4. Summary

Tie-molecule modelling in metallocene catalysed medium density polyethylenes (mMDPEs) and its relevance to mechanical properties has been demonstrated. It is shown that a complex interrelationship exists between the concentration of classical tie-molecules and molecular weight, lamellar thickness and crystallinity and the X-ray long period where the latter is influenced by the concentration of short chain branches. Short chain branching primarily affects the crystallization behaviour, lamellar thickness and supermolecular structure [17]. High molecular weights combined with high short chain branching and smaller crystal thicknesses leads to sizeable increases in the predicted classical tie-molecule concentration. These values were also lower than reported literature data on heterogeneous catalysed systems at equivalent density, indicating clearly the consequence of regular versus irregular branching on the lamellar size and spatial distribution. Tear and impact strength data showed a continuous increase with short chain branching, varying slightly with catalysts type but differing significantly at the highest concentration levels of short chain branching. These correlations are closely related to those between classical tie-molecule concentration and the degree of short chain branching.

[†] Gibbs-Thomson equation used to evalute l_c from melting data requires folded lamellar crystals.

Acknowledgements

This research was sponsored by Fina Research, Feluy (Belgium) as part of the Surrey Scholar Scheme. The authors wish to thank Mary Vickers at Cambridge in particular for the provision of X-ray long periods used in our calculations, and, one of us (JJJ) wishes to thank also for the advice and guidance offered by Dr. J. Michel from Fina Research, Feluy (Belgium).

References

1. P. INGRAM, H. KIHO and A. PETERLIN, *J. Polym. Sci. Part C*: **16** (1967) 1857.
2. A. PETERLIN, *J. Mater. Sci.* **6** (1971) 490.
3. A. LUSTIGER and N. ISHIKAWA, *J. Polym. Sci. Polym. Phys. Ed.* **29** (1991) 1047.
4. K. H. NITTA and M. TAKAYANGI, *J. Polym. Sci. Part B: Polym. Phys.* **37** (1999) 357.
5. A. N. GENT and J. JEONG, *Polymer Engineering and Science* **26** (1986) 285.
6. A. N. GENT and S. MADDEN, *J. Polym. Sci. Part B: Polym. Phys.* **27** (1989) 1529.
7. J. SCHELLENBERG and G. FIENHOLD, *Polymer Engineering and Science* **38** (1998) 1413.
8. N. BROWN and I. M. WARD, *J. Mater. Sci.* **18** (1983) 1405.
9. J. T. YEH, J. H. CHEN and H. S. HONG, *J. Appl. Polym. Sci.* **54** (1994) 2171.
10. N. BROWN and Y. L. HUANG, *J. Mater. Sci.* **23** (1988) 3648.
11. L. J. ROSE, A. D. CHANNELL, C. J. FRYE and G. CAPACCIO, *J. Appl. Polym. Sci.* **54** (1994) 2119.
12. T. TRÄNKNER, M. HEDENQVIST and U. W. GEDDE, *Polymer Engineering and Science* **36** (1996) 2069.
13. *Idem., ibid.* **37** (1997) 346 .
14. A. LUSTIGER, C. N. MARZINSKY and R. R. MUELLER, *J. Polym. Sci. Part B:* **36** (1998) 2047.
15. J. T. YEH and J. RUNT, *J. Polym. Sci. Part B: Polym. Phys.* **29** (1991) 371.
16. Y. L. HUANG and N. BROWN, *J. Mater. Sci.* **23** (1988) 3648.
17. J. J. JANIMAK, M. E. VICKERS and G. C. STEVENS, *Macromolecules*, Submitted.
18. N. BROWN, X. LU, Y-L. HUANG and R. QIAN, *Makromol. Chem., Macromol. Symp.* **41** (1991) 55.
19. M. ISHIKAWA, K. USHUI, Y. KONDO, K. HATADA and S. GIMA, *Polymer* **37** (1996) 5375.
20. Y. ZHOU, X. LU and N. BROWN, *ibid.* **34** (1993) 2520.
21. M. TAKAYANGI, I. IMADA and T. KAJIYAMA, *J. Polym. Sci. C.* **15** (1966) 263.
22. E. A. EGOROV, A. E. TSHMEL and V. V. ZHIZHENKOV, *Polymer Communications* **39** (1998) 497.
23. A. LUSTIGER and R. L. MARKHAM, *Polymer* **24** (1983) 1647.
24. R. M. PATEL, K. SEHANOBISH, P. JAIN, S. P. CHUM and G. W. KNIGHT, *J. Appl. Polym. Sci.* **60** (1996) 749.
25. J. J. JANIMAK and G. C. STEVENS, in advanced preparation.

Received 21 April
and accepted 29 August 2000