

# HIGHLIGHT

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## Critical Review of the Molecular Topology of Semicrystalline Polymers: The Origin and Assessment of Intercrystalline Tie Molecules and Chain Entanglements

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**ABSTRACT:** Intercrystalline molecular connections in semicrystalline polymers have been the subject of numerous discussions and controversies. Nevertheless, there is one point of agreement: such intercrystalline tie molecules have a prime role in the mechanical and use properties of the materials, notably the resistance to slow crack growth. This article is a critical review of the mechanisms of generation of

the tie molecules during the stage of crystallization and of the experimental and theoretical assessment of their concentration. Polyethylene and related materials are mainly studied. The contribution of chain entanglements is also discussed in parallel with tie molecules. Particular attention is paid to Huang and Brown's statistical approach, which appears to be the most appropriate one for predictive purposes and has

aroused much interest from various authors. Attempts are made to provide solutions to the shortcomings of this model. ©2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 1729–1748, 2005

**Keywords:** chain entanglements; crystallization; mechanical properties; polyethylene (PE); semicrystalline polymers; slow crack growth; tie molecules

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## INTRODUCTION

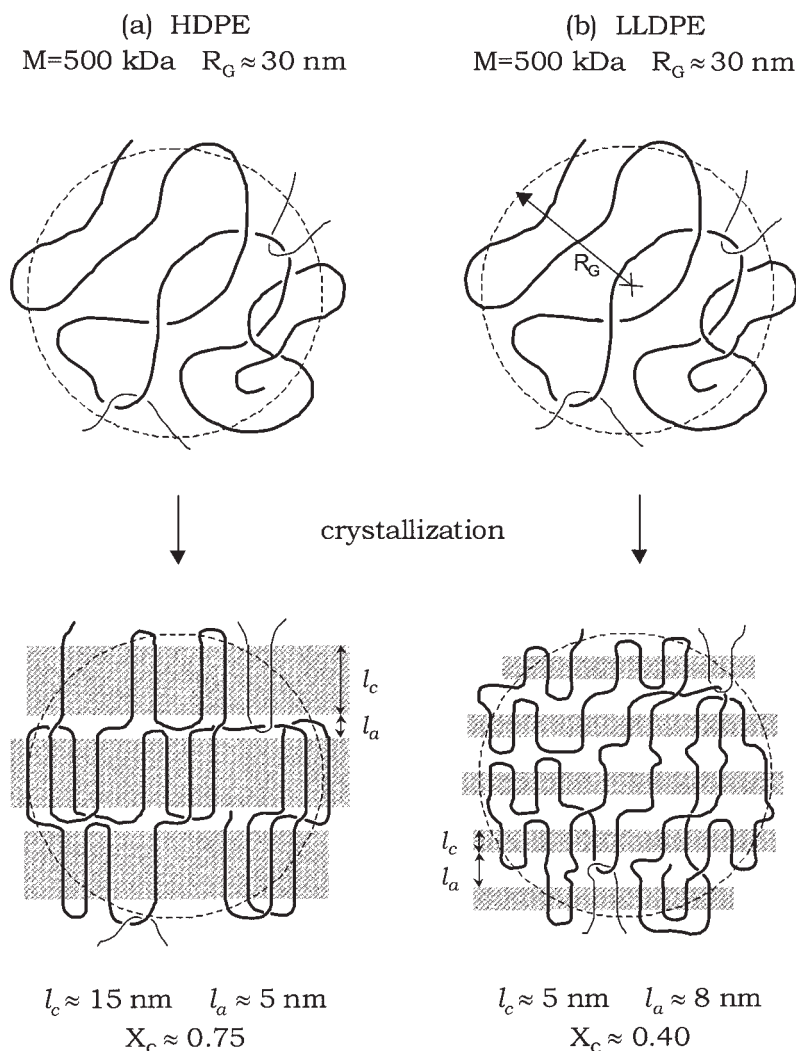
It is largely agreed that the mechanical properties of semicrystalline polymers are mainly governed by the presence of molecular connections between the crystallites, namely, chain entanglements and tie molecules (TMs). If those molecular connections composed of covalent bonds did not exist, the crystallites would be held together just by weak van der Waals or hydrogen interactions, and they would slip easily past one another or split away from one another under stress; this would result in macroscopic brittleness of the material. This is the typical behavior of mats of single crystals grown from dilute solutions, which display very poor mechanical properties because of a peculiar chain-folded topology devoid of intercrystalline molecular connections.

Besides their determining influence on the conventional short-term properties, such as the stiffness and strength, TMs have been recognized to have a tremendous influence on the long-term properties of semicrystalline polymers. Polyethylene (PE)-based materials are particularly sensitive to the phenomenon of slow crack growth, which leads to brittle failure at stress levels far below the yield point.<sup>1</sup> A number of authors have claimed that this phenomenon is evidence that the load applied onto semicrystalline materials is distributed over a small number of intercrystalline molecular connections that gradually lose their mechanical efficiency because of either chain scission, as evidenced by the generation of chain radicals, or chain disentanglement via cooperative diffusion through the crystalline component.

Direct experimental evidence of TMs by transmission electron microscopy has never been obtained because of the problem of imaging chemi-

cal species made of light atoms, such as carbon and hydrogen, although this technique is particularly well suited for studying objects with a typical size of just a few nanometers. However, several indirect pieces of evidence have been reported. The first convincing one is from Keith et al.,<sup>2-5</sup> who reported transmission electron micrographs of replicas of PE crystals showing fibrillar bridges between the individual crystals for samples crystallized from concentrated solutions in paraffin. Several tens of nanometers wide and hundreds of nanometers long, these fibrils consisted of crystalline bundles of TMs that developed at a solution concentration greater than a critical value. The critical concentration is the threshold for the overlapping and intertwining of the chain coils in the solution before crystallization. More recent studies of the crazing of semicrystalline polymers, by means of scanning electron microscopy and transmission electron microscopy with microtomic sample slices or thin-film surfaces,<sup>6-12</sup> have also demonstrated that molecular connections necessarily exist between the crystalline lamellae to enable their transformation into fibrils, on the scale of a few hundreds of nanometers, at the tip of a propagating crack.

Because of the tremendous importance ascribed to the intercrystalline molecular connections on the use properties of semicrystalline polymers, numerous experimental investigations have been carried out to elucidate the mechanism of their occurrence and to assess their concentration, with the aim of optimizing the benefit from their mechanical contribution. In the peculiar case of PE, intensive research has been focused for the last 20 years on understanding the role of the molecular architecture in the concentration of TMs, both in industry and in academia; the aspects of molecular architecture



**Figure 1.** Schematic molecular topology of semicrystalline polymers before and after crystallization: (a) HDPE and (b) LLDPE.

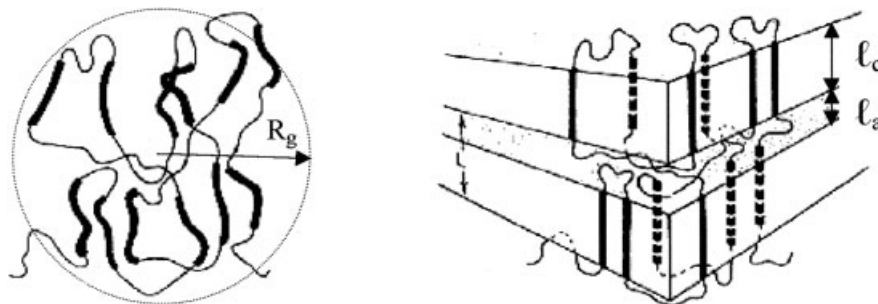
that have been specifically addressed are the molar weight distribution and the content and distribution. Theoretical approaches have also been attempted to both assess the TM concentration and predict the mechanical and use properties of the materials with respect to the molecular parameters.

The purpose of this article is to make a critical survey of these studies and propose some improvements of the deficiencies or shortcomings of the various approaches.

### ORIGIN OF THE INTERCRYSTALLINE MOLECULAR CONNECTIONS

There are two reasons for the presence of intercrystalline molecular connections in melt-crystallized semicrystalline polymers. The first is the existence of a critical molar weight above which chains become intertwined into a macromolecular network.<sup>13</sup> In the melt, the latter consists of transient entanglements that are essentially preserved throughout the crystallization process. In the solid state, these entanglements constitute topological defects that are excluded from the crystalline phase and thus build up molecular connections between the crystallites if the two intervening chains belong to two adjacent crystallites. The second reason is the scaling relationship between the random coil dimension in the molten material and the crystallite thickness in the solidified material.<sup>14</sup> On the one hand, under quiescent conditions, polymers crystallize from the melt in the form of chain-

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**Figure 2.** Fischer's solidification model for semicrystalline polymers. (From E. W. Fischer, *Pure Appl Chem*, 1978, 50, 1319, ©1978 International Union for Pure and Applied Chemistry, reproduced by permission.)

folded lamellae whose thickness does not exceed a few tens of nanometers: typical values range from about 20 nm for highly crystalline flexible-chain polymers such as PE, isotactic polypropylene (PP), and poly(oxymethylene) (POM) to about 4 nm for low-crystallinity ethylene/ $\alpha$ -olefin copolymers or rigid-chain polymers such as polyamide-6 (PA6) and poly(ethylene terephthalate). On the other hand, the size of a polymer chain in a random coil conformation in the melt obeys a scaling law of the following form:

$$R_g = aM^{1/2} \quad (1)$$

where  $R_g$  is the radius of gyration of the coil and  $M$  is the molar weight of the chain. For PE and related high-density copolymers,  $a$  is approximately 1.26 if  $R_g$  is given in nanometers and  $M$  is given in kilodaltons.<sup>15</sup> Figure 1 depicts the case of a PE chain for which  $M$  is 500 kDa and  $R_g$  in the melt is approximately 30 nm. Figure 1 also displays the chain conformation in the solid state for both high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) materials with average crystal thicknesses of about 15 and 5 nm, respectively. The figure shows that several crystalline lamellae can grow within the sphere of gyration of a chain as long as the chain molar weight is sufficiently high. This is the main process of building intercrystalline TMs, which cross the amorphous layer and provide mechanical bridging of the adjacent crystalline lamellae. This picture conforms to Fisher's solidification model<sup>14</sup> reported in Figure 2.

For the sake of further discussion, chain entanglements are also shown in Figure 1. Such topological features, which prevail in the melt because of chain overlap, are preserved in the

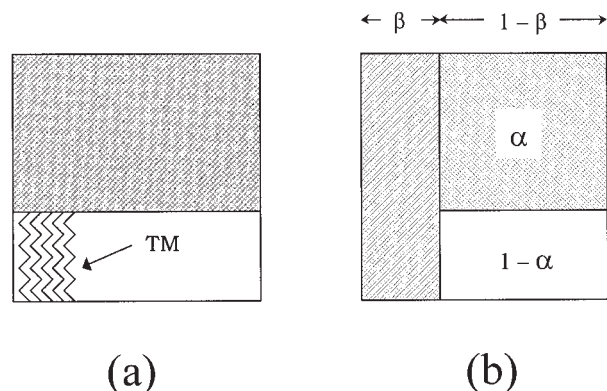
solid state and rejected in the amorphous layers at the issue of the crystallization of the material.

Although Fischer's picture of chain topology is very useful for understanding the mechanical behavior of semicrystalline polymers, the actual situation may be different, depending on the crystallization conditions. This point is discussed more explicitly in the next section.

It is well known that increasing the molar weight increases the probability of generating TMs and chain entanglements, as evidenced by the reduced drawability and the increase in both the strain hardening and tensile strength.<sup>16–20</sup> However, because of the concomitant drastic increase in the viscosity, technological applications are limited to materials with weight-average molar weights not exceeding a few hundreds of kilodaltons, regardless of the nature of the polymer under consideration.

In the case of polyolefins, copolymerization is known to be another means for increasing the TM concentration. Indeed, counits with bulky side groups are excluded from the crystal; this process disturbs the natural propensity of flexible-chain polymers to crystallize with regular chain folding. This results in an increase in random chain folding accompanied by a high rate of TMs.<sup>21,22</sup> The result is a significant improvement in the resistance to low-temperature impact,<sup>23</sup> to creep,<sup>24</sup> to slow crack growth,<sup>25–27</sup> and to tear and puncture.<sup>28</sup> However, copolymerization involves a reduction of the crystallinity index and a concomitant drop in the stiffness and yield stress.<sup>21</sup>

In recent years, PE developments have been oriented toward the synthesis of bimodal copolymers with preferred incorporation of the counits into the longer chains. The result has been an improvement in the long-term behavior, in com-



**Figure 3.** Peterlin's model<sup>38</sup> for  $E$  of semicrystalline polymer fibers: (a) phase association and (b) mechanical coupling (see the text for details).

parison with conventional unimodal copolymers of similar stiffness.<sup>29–33</sup> This successful outcome can be attributed to an increase in the TM concentration at an equivalent crystallinity.

### EXPERIMENTAL ASSESSMENT OF TMs AND ENTANGLEMENTS

The notions of TMs and chain entanglements are not always clear in the literature, and a number of studies do not make a distinction. The reason may be that the approach is not selective or that the authors confuse the two kinds of intercrystalline molecular connections.

#### Oriented Materials and Fibers

The question of quantifying the TM density in semicrystalline polymers was first tackled for drawn fibers with the aim of understanding the mechanism for improving the fiber strength and then optimizing the spinning and drawing process. Authors such as Peterlin<sup>34,35</sup> and Zurkov and Kuksenko<sup>36</sup> have studied the rupture of semicrystalline polymer fibers under static loading in the framework of thermally activated processes. The following equation is an example of this kind of approach and gives the lifetime to rupture ( $\tau_b$ ) of a chain sustaining a stress ( $\sigma$ ):

$$\tau_b = \tau_0 \exp[(U - \sigma\mu)/kT] \quad (2)$$

where  $U$  is the activation energy of the process,  $\mu$  is the stress sensitivity coefficient and has the dimensions of a volume,  $1/\tau_0$  is the fre-

quency of the thermal vibration of the atoms,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. The similarity between the activation energy for fiber rupture and that for the breaking of a covalent C—C bond (e.g., 40–70 kcal/mol for PA6 and HDPE) has been taken as evidence that fiber rupture is governed by the scission of chains that bridge the microfibrils constituting the basic structural element of drawn fibers. The fraction of broken chains ( $n/n_0$ ) can be computed as a function of time ( $\tau$ ) as follows:

$$n/n_0 = \exp(-\tau/\tau_b) \quad (3)$$

However,  $n/n_0$  computed with this theoretical approach is extremely low. The conclusion is that the damage before fiber rupture occurs in local defective regions of the fibrillar structure. Finally, this theoretical approach does not provide an estimation of the overall TM density, which is often considered the major parameter of polymer strength.

Peterlin<sup>37,38</sup> reported extensively on the improvement of stiffness of PE fibers upon drawing. His so-called fibrillar transition model is based on a mechanism of fragmentation of the original crystalline lamellae into crystal blocks, accompanied by an unfolding of the chains from the crystal blocks that become TMs. Assuming that stiffness results from the stretching of the TMs uniformly distributed through the fiber cross section, this author proposed several Takayanagi-like models based on series and parallel mechanical associations of the crystal phase, the amorphous regions, and the TMs. One of these models, shown in Figure 3, consists of a parallel mechanical coupling of soft and stiff components: the soft component (the right side of the model) consists of a series coupling of the crystal blocks connected with the isotropic amorphous chains, and the stiff one (the left side of the model) consists of a series coupling of the crystal blocks connected with taut TMs. Young's modulus of the fibers ( $E$ ) obeys the following equation:

$$E = E_c \left\{ \beta + [(1 - \beta)^2 E_a / E_c] / [1 - \alpha + (\alpha - \beta) E_a / E_c] \right\} \quad (4)$$

where  $\beta$  is the volume fraction of taut TMs in the amorphous layers;  $\alpha$  is the volume crystal index; and  $E_a$  and  $E_c$  are the moduli of the

isotropic amorphous phase and the crystalline phase parallel to the chain stems, respectively. The modulus of the taut TMs is assumed to be close to that of the crystalline phase. Ishikawa et al.<sup>39</sup> notably used a similar model to probe the relationship of the tacticity and molar weight with the TM concentration of drawn PP.

Vibrational spectroscopy has been used to investigate the orientation–property relationship of various kinds of PE films. Infrared has turned out to be useful for addressing comparatively the TM concentrations in PE drawn films because of the assumption that TMs contain oriented sequences of trans conformations, in contrast to any other chain segment in the amorphous phase, which contains a high rate of gauche conformations.<sup>40–43</sup> The problem of this elegant method is the rather low sensitivity for the conformational species under consideration. Raman spectroscopy also has proved to be an efficient means for probing the mechanically active chains that bear the main part of the load in a strained fiber, notably for oriented HDPE.<sup>44–47</sup> This technique gives valuable information on the stress distribution in the oriented materials and the stress level on the TMs. However, no quantitative data for the TM concentration have been reported.

Tarin and Thomas<sup>48</sup> considered the plastic drawing of a semicrystalline polymer with respect to the mechanism of chain unfolding after the lamellar fragmentation into blocks. These authors derived the following relation for the natural draw ratio ( $\lambda_n$ ):

$$\lambda_n = V_{uf}\lambda_{uf} + (1 - V_{uf})\lambda_{rot} \quad (5)$$

where  $V_{uf}$  is the volume fraction of unfolded crystals and  $\lambda_{uf}$  is the draw ratio associated with chain unfolding. The draw ratio associated with the rotation of the crystal blocks ( $\lambda_{rot}$ ) is assumed to be unity.  $V_{uf}$  is a key factor because of its direct connection with the TM surface density ( $\rho$ ). Besides, the latter is assumed to depend on the crystal growth rate ( $G$ ) via  $\rho = \rho_0 G$ , where  $\rho_0$  is a proportionality constant. Finally,  $\lambda_n$  is given as follows:

$$\lambda_n = 1 + (\tau/\delta - 1)[v_0/(v_0 + \sqrt{\rho_0 G \tau})]^2 \quad (6)$$

where  $v_0$  is a proportionality constant. The ability of this rather simple approach to account for the influence of crystallization kinetics on the occurrence of intercrystalline molecular links is

**Table 1.**  $f_T$  Values for HDPE from Low-Temperature Fracture Experiments according to Eq 6<sup>a</sup>

Parameters of Eq 6		$f_T^b$	
$\beta$	$C$	SC ( $\sigma_F = 0.101$ GPa)	Q ( $\sigma_F = 0.152$ MPa)
0.1	20	0.041	0.075
0.1	50	0.140	0.230
0.2	20	0.007	0.024
0.2	50	0.058	0.100

<sup>a</sup> The data were taken from ref. 50.

<sup>b</sup> SC = slowly cooled sample; Q = quenched sample.

one of its most attractive features. Unfortunately, no further attempt has been made to improve the model and try to compute TM density data from  $\lambda_n$  measurements.

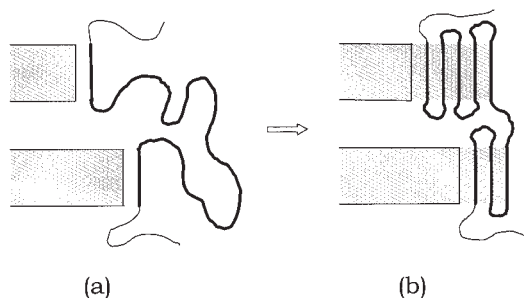
Hubert et al.<sup>49</sup> recently reported that  $\lambda_n$  is a parameter quite sensitive to the molecular architecture of HDPE for pipe applications and fairly well correlated with the long-term mechanical behavior of these materials. Because of the simple experimental access to  $\lambda_n$  and the rather good accuracy of the measurements, this approach deserves more attention.

### Isotropic Materials

Some approaches have been put forward for isotropic semicrystalline polymers. Brown and Ward<sup>50</sup> proposed to determine the TM density from the brittle strength at a low temperature; they assumed that rupture occurs in the mechanically weaker amorphous layers. The surface fraction of TMs ( $f_T$ ) in the cross section of an intercrystalline amorphous layer is given by the following relation:

$$f_T = (C\sigma_F - \beta E_{iso})/[\beta(E_T - E_{iso})] \quad (7)$$

where  $\sigma_F$  is the brittle failure stress,  $E_{iso}$  is Young's modulus of the van der Waals intermolecular interactions,  $E_T$  is the TM modulus,  $C$  is a stress concentration factor, and  $\beta$  is a proportionality constant. Because of the assumptions regarding the  $C$  and  $\beta$  parameters, the model is only worthwhile for comparison. It has been applied to HDPE,<sup>50,51</sup> LLDPE,<sup>23</sup> and POM<sup>52</sup> for probing the influence of either the cooling rate or the degree of undercooling in the case of isothermal crystallization. The



**Figure 4.** Molecular mechanism of crystallization of a flexible chain according to Krigbaum et al.<sup>57</sup> (a) the deposition of a chain segment onto two adjacent growing crystallites and (b) the crystallization of the chain segment via chain folding between the anchoring points.

data lie in the range of 1–25%, depending on the materials and the crystallization conditions. An example is shown in Table 1 for HDPE,<sup>50</sup> regardless of the choice of the adjustable parameters  $\alpha$  and  $\beta$ , changing the cooling rate from slow cooling to quenching increases the TM concentration in HDPE. This finding could be taken as evidence that long-range molecular rearrangements occur during the crystallization of HDPE; in that case, Fischer's solidification model would be irrelevant for HDPE and for POM as well.

By analogy with a treatment already proposed for glassy polymers, the mechanisms of the plastic flow of semicrystalline polymers can be viewed as a combination of a thermally activated contribution necessary to overcome the intermolecular forces in the stiff crystalline phase and a nonthermally activated contribution related to the stretching of the macromolecular network.<sup>22,53–56</sup> Equation 8 is an example of a constitutive equation that has been proposed for the drawing of semicrystalline polymers:<sup>55</sup>

$$\sigma = Y + G(\lambda^2 - 1/\lambda) \quad (8)$$

The first term of the second member of eq 8, which holds for the dependence of the yield stress ( $Y$ ) on the strain rate and temperature, may be expressed via an Eyring formalization. The second term holds for the stretching of the macromolecular network in the framework of the Gaussian-like rubber elasticity;  $G = nkT$  is the shear modulus and  $\lambda$  is the draw ratio. When applied to the analysis of the strain-hardening domain, this approach gives

access to quantitative data on the entanglement density of the macromolecular network via the number of mechanically active chains per unit of volume ( $n$ ). Several reports have demonstrated the usefulness of this model for comparing various PEs and related copolymers. However, some authors believe that the quantitative information concerns only entanglements,<sup>22,53,54</sup> whereas others assume that both entanglements and TMs are concerned.<sup>56</sup>

Krigbaum et al.<sup>57</sup> tried to account for the dependence of the modulus on the temperature of semicrystalline polymers with a molecular model based on the mechanism of crystallization. Every chain is assumed to start crystallizing at several loci along its length by depositing simultaneously short chain segments onto the growth surface of several crystallites. From that event, crystallization proceeds by chain folding until every chain portion between two consecutive anchoring points becomes a taut TM. This model is very close to Fischer's solidification model<sup>14</sup> and also agrees with the pictures of Figure 1. The basic parameter of the model ( $N$ ) is the contour length of the chain portion determined by two consecutive anchoring points of the chain, as sketched in Figure 4. Indeed, this parameter determines the probability of the occurrence of TMs: the higher  $N$  is, the lower the TM probability is. The tensile modulus ( $E$ ) obeys a relationship of the following form:

$$E = (\rho RT/M_0)F(\beta, \alpha, N) \quad (9)$$

where  $\rho RT/M_0$  is the rubberlike modulus and  $F(\beta, \alpha, N)$  is a rather complex function that takes into account the amorphous chain straining.  $\alpha$  is the crystal volume fraction, and  $\beta = \mathcal{L}^{-1}[1/N^{1/2}(1 - \alpha)]$  is a strain parameter that holds for the non-Gaussian rubber behavior of the taut TMs via the inverse Langevin function ( $\mathcal{L}^{-1}$ ).

From the determination of the parameter  $N$  by a fitting procedure of eq 9 with the experimental  $E(T)$  data, the model enables us to compute the number of regular chain folds between two consecutive TMs.<sup>22,39</sup> Table 2 reports data for a series of ethylene–butene copolymers that notably show a decrease in the number of regular folds between TMs ( $n$ ) with increasing cunit concentration.<sup>22</sup> It is tempting to convert these data into the TM surface fraction at the crystal–amorphous interface ( $F_s$ ) because the relationship is simply  $F_s = 1/n$ . This latter parameter is

**Table 2.** Number of Regular Folds ( $n$ ) as a Function of the Molar Cunit Concentration ( $\chi$ ) for Ethylene Copolymers<sup>a</sup>

$\chi$ (mol %)	$M_w$ (kDa) <sup>b</sup>	$X_c$ (wt %) <sup>c</sup>	$N^d$	$d_c$ (nm) <sup>e</sup>	$n^f$	$F_s$
—	135	75	350	20.5	16	0.06
0.6	157	66	170	17.5	8	0.12
1.1	178	62	110	14.5	6	0.17
2.5	136	53	25	11.5	1.5	0.40
5.0	140	43	6	8.5	1	~1

<sup>a</sup> The data were taken from ref. 22.

<sup>b</sup> Weight-average molecular weight.

<sup>c</sup> Weight-fraction crystallinity.

<sup>d</sup> Computed from  $n$  ( $F_s = 1/n$ ).

<sup>e</sup> Crystal thickness.

<sup>f</sup> See ref. 22 for the calculation of  $n$ .

equivalent to the  $f_T$  parameter of Brown and Ward defined in eq 7. The  $F_s$  data reported in the last column of Table 2 are of the same order of magnitude as the  $f_T$  data of Table 1. This agreement between the two models is really amazing because the two experimental approaches and the theoretical bases of the models are quite different. The main superiority of Krigbaum's model over Brown and Ward's model is that it does not involve any adjustable parameter. Nevertheless, the two approaches are able to account for the influence of crystallization kinetics. In the theoretical bases of Krigbaum's model, the  $N$  parameter notably accounts for the concurrence between nucleation and crystal growth: the greater the nucleation rate is, the lower  $N$  is. In conclusion, the value  $F_s \approx 1$  for the lower density copolymer (Table 2) is relevant to the fringed-micelle macroconformation, a chain topology that has been already claimed to be a characteristic of low-density copolymers with noncrystallizable cunits (see the discussion in refs. 21 and 22).

An experimental assessment of the TM density from nonmechanical tests was proposed by Fischer et al.<sup>58</sup> from small-angle neutron scattering. Just as in Krigbaum's model, the chains are assumed to crystallize into several chain-folded clusters belonging to adjacent lamellae, and the determination of the number of molecular clusters per chain allows a direct estimation of the number of TMs per chain. The approach has been applied to PE, PP, and poly(ethylene oxide).<sup>58</sup> The major problem of this method is that it requires the introduction of deuterated chains into the material before crystallization. Despite the promising capabilities of the method,

no further use of it has been reported, certainly because of experimental difficulties.

Small-angle X-ray scattering may also be used for probing the density of intercrystalline molecular connections, that is, TMs and entanglements. Indeed, experiments carried out on a semicrystalline polymer strained in the elastic domain, at a temperature above the glass transition of the amorphous phase, give access to the local compliance of the rubbery amorphous layers.<sup>59</sup> This approach does not provide practical data on the intercrystalline connection density, but it affords comparative information for polymers of the same kind. For instance, for PEs of various chemical architectures and equivalent crystallinity, a greater compliance of the amorphous phase reveals a lower density of TMs and entanglements.<sup>59</sup> This conclusion is likely to provide an explanation for the different long-term behaviors and creep resistances already reported for the same materials.<sup>49</sup>

## THEORETICAL ASSESSMENT OF TIE CHAINS AND ENTANGLEMENTS

Polymer crystallization has been the subject of numerous theoretical studies that are beyond the scope of this review. However, the most advanced of these approaches, developed by Hoffman and Miller (see their recent review in ref. 60), contains fundamental aspects of chain topology that deserve to be mentioned. Indeed, their approach, based on the experimental observation of three crystallization regimes for linear PE, predicts that isothermal crystallization at low undercooling involves a high fre-



quency of adjacent re-entry chain folding, whereas large undercooling promotes a high rate of nonadjacent re-entry accompanied by the generation of loose loops and TMs. In the second instance, chain folding is also suspected to involve a mechanism of reeling in the chains from the melt, with a concomitant disentanglement of the chains during crystallization.

The occurrence of chain folding with adjacent re-entry has been a matter of deep controversy (see ref. 61 and the discussion therein). Nonetheless, from the standpoint of mechanical properties, the main issue of the model is that the natural trend of flexible-chain molecules to crystallize by chain folding is strongly affected by the crystallization conditions, and the actual chain topology of semicrystalline polymers in the solid state will be, in many instances, different from Fischer's scheme (Fig. 2). The latter is most probable for crystallization at large undercooling or at high cooling rates. Unfortunately, Hoffman's model does not give access to the TM density or to the extent of chain disentanglement during crystallization.

Theoretical approaches specifically addressing the evaluation of the chain topology in the amorphous layers of semicrystalline polymers have been developed on the basis of the statistical mechanics of chain molecules. The general assumptions are that the crystallites are pre-existing entities and that the amorphous chains that exit from the crystal surface obey random-walk or Gambler's ruin statistics in the domain between two neighboring crystallites.<sup>62-73</sup> A number of these studies, which focused on the region close to the surface, concluded that about two-thirds of the chains re-enter the same crystal lamella at a site close to the site of exit, after a short run in the amorphous layer.<sup>62-67</sup> However, most of these studies did not consider the respective occurrence of loose loops or TMs in the remaining one-third of the amorphous chains. Some authors have specifically addressed the question of chain segments crossing the entire amorphous layer thickness ( $l_a$ ) and making TMs.<sup>62,66</sup> For instance, using a three-dimensional simple cubic lattice, Guttman et al.<sup>62</sup> predicted that the fractions of chain loops and intercrystalline molecular bridges ( $P_L$  and  $P_B$ , respectively) obey the following relations:

$$P_L = M/(M + 1) \quad \text{and} \quad P_B = 1/(M + 1) \quad (10)$$

where  $M$  is the thickness of the amorphous layer expressed as the number of statistical

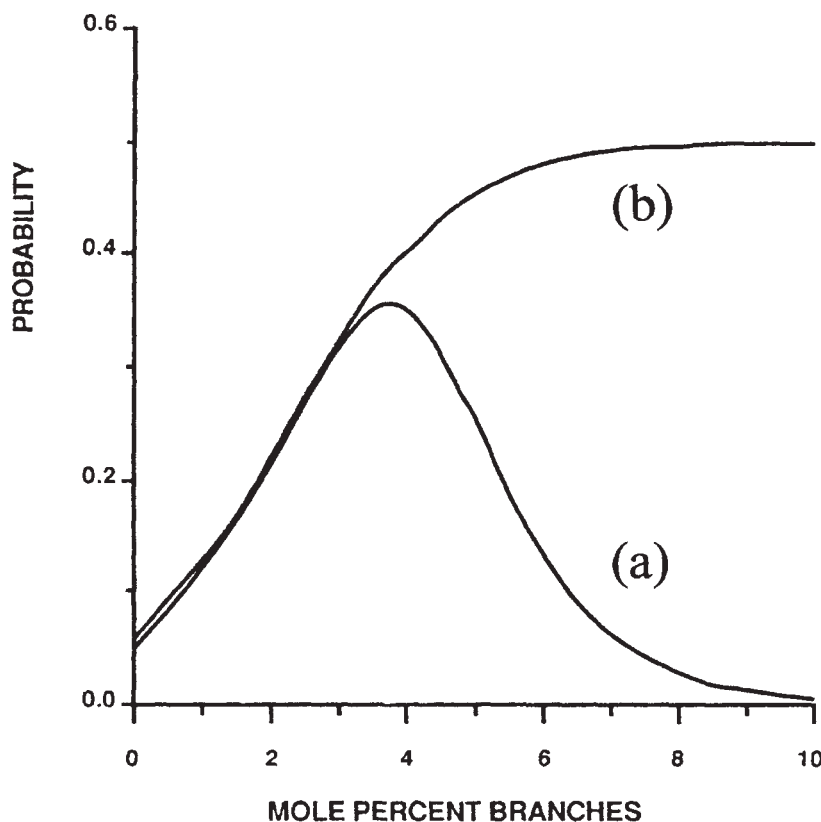
links. The model predicts that the ratio of bridges to loops decreases as  $1/M$  when  $l_a$  increases. The average lengths of loops ( $\langle L \rangle$ ) and bridges ( $\langle B \rangle$ ) are given by

$$\langle L \rangle = 2M + 2 \quad \text{and} \quad \langle B \rangle = (M + 1)^2 \quad (11)$$

Because  $M$  is much greater than unity, these relationships predict that bridges are much longer than loops, on average.

Although I do not deny the predictive capabilities of the models, neither the structure of the polymer chain nor the influence of the crystallization conditions is taken into consideration in the calculations. Therefore, the theoretical estimations are of little benefit for understanding the mechanical properties and long-term behavior of semicrystalline polymers with respect to the molecular architecture and processing.

The question of the influence of the molecular architecture on the probability of TM formation has been considered for ethylene copolymers. In all the endeavors, the counits are considered foreign elements that are rejected from the crystalline phase and thus disturb the chain statistics close to the crystal-amorphous interface. In a series of detailed studies, Mathur and coworkers<sup>68-70</sup> obtained contrasting results for the effect of counits. Using a two-dimensional square or a three-dimensional cubic lattice for describing the statistical pathway of the chain segments in the amorphous layer, these authors concluded that the introduction of counits entails either a decrease or a slight increase in the TM frequency, respectively. These conclusions, which depend on the model, are quite puzzling; besides, the issue of the two-dimensional model contradicts the common interpretation of the improvement of the mechanical properties of ethylene copolymers (see the introduction). Surprisingly, the authors concluded from their calculations that it was erroneous to ascribe the mechanical property improvement of ethylene copolymers to an increase in the TM concentration. In contrast, Lacher and coworkers<sup>71-73</sup> predicted a stringent increase of the TM probability from 0.05 to 0.5 as a result of an increase in the counit concentration from 0 to 8 mol %. The model considers the influence of the counits on the characteristic ratio  $C^\infty$  of the chains. Figure 5 shows the computed data.<sup>72</sup> The probability of the so-called links that correspond to entangled



**Figure 5.** Computed (a) TM and (b) entangled loop probabilities as a function of the cunit concentration in ethylene-butene copolymers. (From R. C. Lacher and J. L. Bryant, *Macromolecules*, 1988, 21, 1183, ©1988 American Chemical Society, reproduced by permission.)

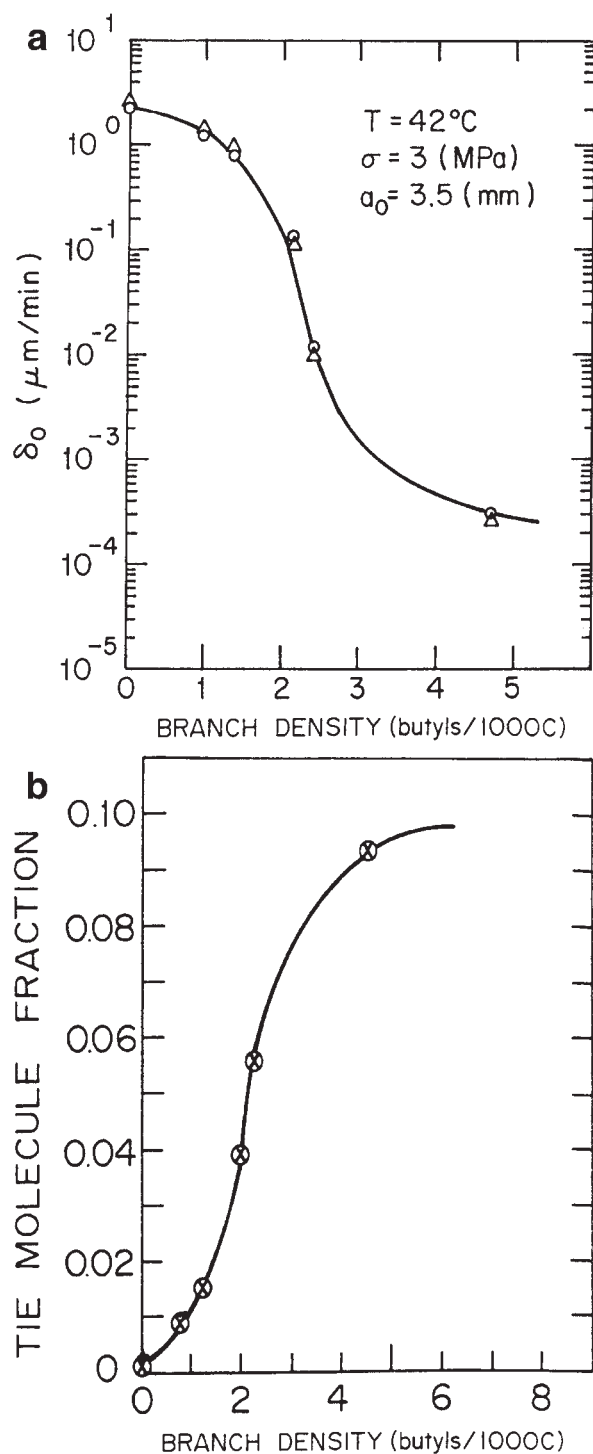
loose loops from opposite crystalline lamellae is also plotted in Figure 5.

Huang and Brown<sup>74,75</sup> proposed a quite different statistical approach specifically targeted at the assessment of TMs; they considered that the chain topology in a crystalline polymer is preserved during the crystallization stage. This assumption agrees with Fischer's solidification model (Fig. 2). In this instance, the probability for a chain in the melt to build up intercrystalline TMs during crystallization is given by the probability of finding chain segments long enough to span an amorphous layer and the two adjacent crystalline lamellae, that is, chain segments longer than  $L = 2l_c + l_a$ , where  $l_c$  is the crystal lamellar thickness. The approach requires the structural parameters  $l_c$  and  $l_a$  to be previously determined. The TM probability is then given by the following equation based on Gaussian statistics for the chain segments at the moment of crystallization:

$$p = \frac{1 \int_L^\infty r^2 \exp(-b^2 r^2) dr}{3 \int_0^\infty r^2 \exp(-b^2 r^2) dr} \quad (12)$$

where  $b^2$  is equal to  $3/2\langle r^2 \rangle$  and  $\langle r^2 \rangle$  is the mean-square value of the end-to-end distance of the entire chain in a random coil conformation. The value  $L$  for the lower limit of integration of the upper integral of eq 12 holds for the computation of the number of chain segments having an end-to-end distance greater than  $L$ . The 1/3 factor holds for the fact that only chain segments with their end-to-end vector normal to the crystalline lamellar surface can actually make TMs. This probability of occurrence of TMs concerns an isolated chain.

Equation 12 notably predicts an increase in the TM probability as  $l_c$  drops with decreasing crystallinity for ethylene copolymers.<sup>75</sup> Figure 1 provides a schematic view of this conclusion.

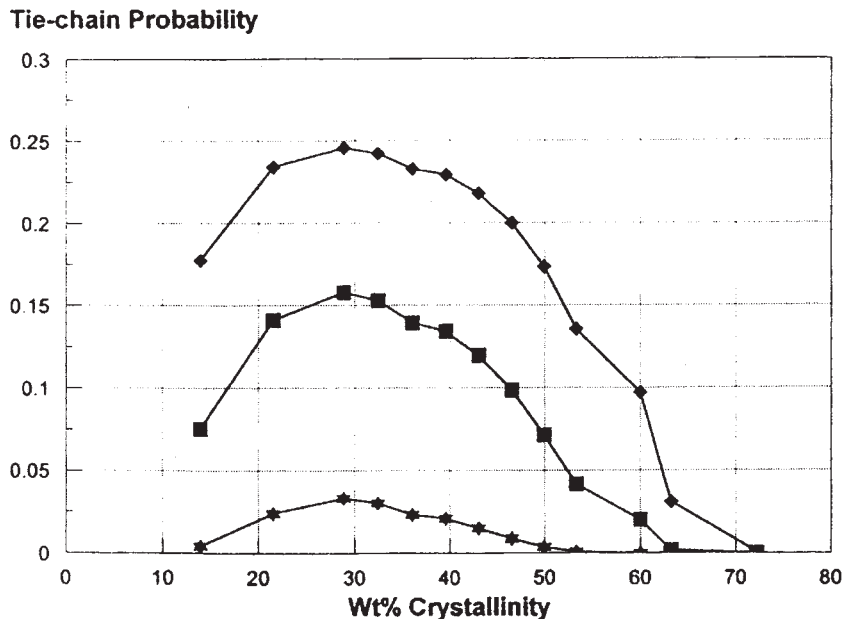


**Figure 6.** Slow crack growth behavior of ethylene copolymers: (a) the crack opening rate and (b) the predicted TM probability as a function of the branch content. (From Y.-L. Huang and N. Brown, *J Polym Sci Part B: Polym Phys* 1991, 29, 129, ©1991 John Wiley & Sons, Inc., reproduced by permission.)

The most remarkable aspect of this approach is that it provides a molecular explanation for the evolution of the mechanical properties of ethylene copolymers reported by Huang and Brown<sup>75</sup> and by many others.<sup>22-29</sup> More specifically, Figure 6 shows the very nice correlation found by Huang and Brown between the crack opening rate dependence on the short-branch content of ethylene copolymers and the predicted dependence of the TM density.<sup>75</sup> The TM probability data predicted by this model are significantly below the data from Lacher and Bryant<sup>72</sup> reported in Figure 5, at an equivalent branch content (for comparison, 5 butyl/1000 C  $\approx$  1 mol % hexene counts).

Using Huang and Brown's model, Hosoda and Uemura<sup>76</sup> and then Patel et al.<sup>56</sup> reported calculations of TM probability for a series of ethylene copolymers covering a wide range of crystallinities for various molar weights. An example of the theoretical results is shown in Figure 7; the computed data are based on a previous experimental determination of the structural parameter  $L$  for every copolymer. These data predict that, after an increase in the TM density with decreasing crystallinity, a decrease in the TM density should occur for crystal weight fractions below 30% because  $l_a$  increases more quickly than  $2l_c$  decreases. In addition, Patel et al. showed a significant disagreement between the data from Huang and Brown's model and the data from the rubber elasticity treatment of the strain hardening of the materials. This point emphasizes the role of chain entanglements, which are not taken into account in the former theoretical model but which actually contribute to the experimental measurement of the strain hardening.

Yeh and Runt<sup>77</sup> proposed to improve Huang and Brown's model by taking into consideration the chain entanglements in the amorphous layers, in parallel with TMs. The calculations are based on the probability of two entangled chains crystallizing into two different adjacent lamellae. It turns out that the probability of chain entanglement is much greater than that of conventional TMs, and so the latter can be neglected. Strebel and Moet<sup>78</sup> proposed a further improvement to Yeh and Runt's modifications, notably by considering the finite length of the chains and the influence on the TM probability of the chain segment inclination with respect to the lamellar surface. Unfortunately, these authors did not perform the probability calcula-



**Figure 7.** TM probability versus the density for homopolyethylene according to Huang and Brown's model: (\*)  $M = 20$  kDa, (■)  $M = 50$  kDa, and (◆)  $M = 99$  kDa. (From R. M. Patel et al., *J Appl Polym Sci*, 1996, 60, 749, ©1996 John Wiley & Sons, Inc., reproduced by permission.)

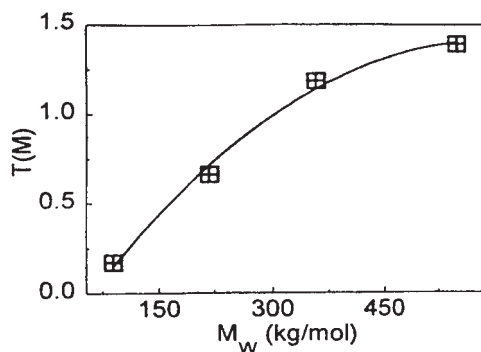
tions. Beerbaum and Grellmann<sup>79</sup> tried to use Yeh and Runt's theoretical approach to account for the dependence on the molar weight of the resistance to crack growth under impact of various kinds of PEs and parent copolymers. These authors notably showed a roughly linear dependence of the probability of entangled TMs on the molar weight of linear PE, as reported in Figure 8. The major criticism that can be made of this kind of analysis of isolated chains is that the quantity of matter under consideration increases linearly with the molar weight of the chain, and so the probability calculations are irrelevant for any mechanical property prediction. For instance, the data of Figure 8 show that the entangled TM probability per chain jumps by a factor of about 7, that is, from 0.2 to 1.4, when the molar weight increases by about 6 times, that is, from 90 to 550 kDa. A more relevant analysis would be a report of the data per unit of mass of material; in that instance, the TM probability would appear to be almost independent of the molar weight. The same criticism applies to Huang and Brown's study<sup>74</sup> of the slow crack growth of HDPE; indeed, the authors compared theoretical TM probability data for an isolated chain with experimental data of the TM surface fraction that refer to bulk intertwined chains. The phenomenon of chain overlapping,

which has a major influence on TM formation in the bulk, has never been taken into consideration. The computation of the probability of inter-crystalline connections per chain may be misleading if the reader does not keep in mind this phenomenon, which is further discussed in the next sections.

Lastly, Gedde and Jansson<sup>80</sup> put forward a calculation of the TM density mainly based on geometrical considerations of the polymer crystalline morphology, the only ingredient from statistical mechanics being the ratio of TMs to chain loops borrowed from Guttman et al.<sup>62</sup> As in the case of the Huang–Brown model, the authors predicted an increase in the TM concentration with increasing molar weight. However, they surprisingly also predicted a TM concentration increase with increasing crystal concentration above 50%: this is contrary to what is generally concluded from experiments and also predicted with Huang and Brown's model.<sup>56,75,76</sup>

## SHORTCOMINGS OF THE MODELS

The first models based on a statistical approach to the conformation of the amorphous chain segments consider the crystal lamellae from which the segments are making their way through the



**Figure 8.** Probability of entangled TMs versus the molar weight for homopolyethylene according to Yeh and Runt's approach. (From H. Beerbaum and W. Grellmann, *ESIS Publ* 2000, 27, 163, ©2000 European Survey of Information Society, reproduced by permission.)

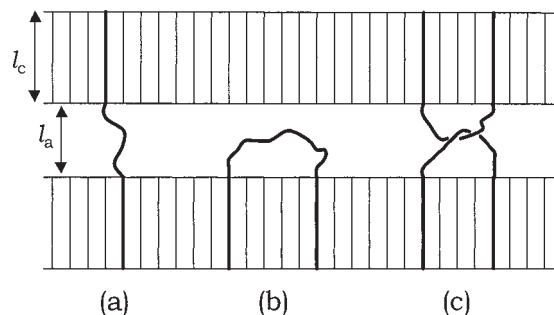
amorphous layer as pre-existing elements of the structure. The models ignore that the conformation of the chain segments confined in the amorphous layers can be strongly affected by the mechanisms of crystallization because every segment is anchored by its two ends before crystallization completion. This is sketched in Figure 8(a,b), which illustrates two situations of a chain segment of contour length  $2l_c + l_a$ : the two lateral moieties are anchored into crystalline lamellae via two stems of length  $l_c$ , and the remaining intermediate moiety of an end-to-end distance close to  $l_a$  is either a TM or a loose loop. The constrained intermediate moiety certainly no longer obeys the same statistics that are obeyed before crystallization. Also, for the trapped entanglements sketched in Figure 8(c), the chain conformation may hardly obey random-walk statistics.

In contrast to the previously mentioned theoretical models, Huang and Brown's approach and the derived models consider the chain topology as a result of crystallization. The probability of an isolated chain building up intercrystalline TMs within its own sphere of gyration, regardless of the occurrence of entanglements, is computed in the assumption that the random coil conformation in the melt is roughly preserved through crystallization: only local rearrangements of chain segments into parallel stems are allowed for the growth of the crystalline lamellae, according to Fischer's scheme (Fig. 2). Huang and Brown's model makes no hypothesis concerning the kind of statistics that amorphous chain segments obey after crystallization; it just makes a calculation of the TM potentiality

before crystallization. An implicit assumption of the model is that molecular rearrangements do not involve TM loss during crystallization.

The main point of criticism of this latter model is that no analytical expression has been provided for the volume fraction or the surface fraction of TMs that can be compared with experimental  $f_T$  data obtained with the Brown-Ward brittle failure method. As a matter of fact, because the stiffness and strength of the material are determined by the stress distribution through the cross section of the material, the relevant parameter is the surface density of TMs normal to the main stress. The situations depicted in Figure 1 show that if the TM probability per chain is actually much larger with a LLDPE chain in comparison with a HDPE chain, the situation is not so obvious regarding the TM cross-section density in an amorphous layer.

Second, as sketched in Figure 9, the TM probability of Huang and Brown's model necessarily includes chain segments that re-enter the same lamella after a run of a distance close to or greater than  $l_a$  in the amorphous phase, namely, the nonadjacent re-entry loose loops. Such topological elements of the amorphous phase, which do not contribute to TMs, are not taken into account in the  $1/3$  prefactor of eq 12. However, such folding loops may trap the entanglements that already exist in the molten material [Fig. 9(c)], and in that case, they may constitute entangled TMs of the kind considered by Yeh and Runt.<sup>77</sup> This phenomenon is not explicitly mentioned by Huang and Brown, and the rate of entanglement of the loose loops is not known. If



**Figure 9.** Sketch of three situations after crystallization for amorphous chain segments with a total contour length equal to or greater than  $2l_c + l_a$  in the melt: (a) TMs, (2) loose loops, and (3) entangled loose loops.

this statement is true, the modifications introduced by Yeh and Runt and by Strebel and Moet<sup>78</sup> are irrelevant.

The third point concerns the fact that a majority of authors wonder about the evaluation of the molecular interconnections only from the standpoint of TMs, the chain entanglements being neglected as active elements for the stress transfer between crystallites. As shown in Figure 9(c), an entanglement can transfer stress between neighboring crystallites just as two close TMs can. Surprisingly, in the extension of Huang and Brown's model proposed by Yeh and Runt,<sup>77</sup> the authors came to the conclusion that chain entanglements are much more numerous than TMs, and so they neglected the latter. This is a major problem for both the physical meaning and the mechanical relevance of TMs as viewed in Huang and Brown's model.

The fourth point of criticism is the question of chain overlapping. In a given volume of a bulk material, several chains are intertwined, and so the concentration of intercrystalline molecular connections in the reference volume element is proportionally increased. So far, no attempt has been made to account for this phenomenon in the evaluation of the TM concentration, all calculations being made per chain.

The fifth point of criticism is that all theoretical approaches always assume that chains in the melt are under equilibrium conditions, and so this equilibrium state is basically preserved throughout crystallization. This is the situation depicted in Figures 1 and 2. However, there have been a number of experimental findings that strongly suggest that the crystallization of linear flexible-chain polymers at low undercooling involves large-scale chain rearrangements that result in a significant modification of the chain topology in the solid state.<sup>48,50,51,79,80</sup> These rearrangements notably involve a reduction of the TM and chain entanglement concentration, as predicted by Hoffman's crystallization model (see the previous section). As a matter of fact, the reduction of the low-temperature fracture resistance of high-crystallinity PE after crystallization by slow cooling or high-temperature isothermal treatment has been ascribed by several authors to reduced TM and chain entanglement concentrations, in comparison with those of the quenched material.<sup>48,50,80,81</sup> PP<sup>82</sup> and POM<sup>52,83</sup> also are highly sensitive to crystallization kinetics: increasing the isothermal crystallization temperature reduces intercrystal-

line molecular connections, as evidenced by the drop in the mechanical performances. In such instances, the estimation of the TM probability with Huang and Brown's model may lead to erroneous conclusions. In contrast, regarding copolymers, the cointer exclusion from the crystalline phase has been shown to disturb the mechanism of regular chain folding, which allows a crystallization process close to the solidification model.<sup>21,22</sup> In that case, the final entanglement density in the solid copolymers should be close to that of the melt; Huang and Brown's model conforms to this topological situation.

The observation by Gedde and Jansson<sup>80</sup> that high-molar-weight PE materials are not sensitive to crystallization conditions provides support for the previous comment about chain disentanglement during crystallization. Indeed, under the assumption that chain reeling is an actual phenomenon, chain reptation theory predicts that the time necessary for undoing a point of entanglement between two chains in the melt should increase as the cubic power of the distance from the chain end,<sup>84</sup> and so long chains are expected to be much less sensitive to disentanglement than short chains.

A sixth and final point is that only linear chains have been considered in the theoretical approaches. Long-chain branching (LCB) in PE is well known to bring modifications to the chain topology in the solid state and, therefore, to the mechanical properties, in comparison with PE with linear chains of equivalent  $R_g$  in the melt. There are two reasons. First, chain diffusion in the melt is strongly reduced by LCB, as evidenced by the strain hardening of the elongational viscosity,<sup>85,86</sup> and this is likely to prevent disentanglement during crystallization. However, increasing LCB reduces the coil overlapping in the melt and thus promotes intrachain entanglements, which are mechanically less efficient than interchain entanglements in the solid state.<sup>87</sup> Second, the reduced chain mobility due to LCB improves the crystallization kinetics of PE<sup>88</sup> and thus reduces the time allowed for the local rearrangement of the chain stems during the crystallite growth. As a matter of fact, the relaxation time in the melt of chains with LCB is shifted to very high values in comparison with linear chains of equivalent molar weight.<sup>89</sup> This immobilization of the chains is favorable to the nucleation step of the crystallization process. This effect is similar to quenching crystallization, which has been previously mentioned to

improve the TM concentration, in comparison with slow crystallization.

For all these reasons, it would be worthwhile to propose a more adequate calculation of the density of mechanically active molecular species of the amorphous phase that bridge neighboring crystallites.

## ENDEAVOR TO IMPROVE HUANG AND BROWN'S MODEL

Huang and Brown's model has proved to be one of the most attractive models for predicting the TM probability because of the assumption of a chain topology similar to the largely accepted solidification model of Fischer. As a matter of fact, a successful comparison of the experimental data for the mechanical properties has been made with theoretical calculations from the model. The model yet suffers from a few shortcomings, and we now propose some improvements to give direct access to a mechanically accessible quantity analogous to the  $f_T$  parameter of Brown and Ward (eq 6).

### Chain Overlapping

In a given volume of the material, several chains are deeply intertwined, and so the actual density of TMs in the bulk material is  $R$  times greater than the TM density per chain,  $R$  being the chain overlapping ratio. This  $R$  factor can be approached from a comparison of the actual density ( $\rho$ ) of the materials and the apparent density ( $\rho_{\text{app}}$ ) of an isolated chain.

A number of poly( $\alpha$ -olefin)s with short lateral groups, including isotactic and atactic PP and isotactic polybutene, as well as ethylene/ $\alpha$ -olefin copolymers of low counit contents, obey the unique scaling law between  $R_g$  of the coils in the melt and the molar weight; it has the form of eq 1 with a constant  $a$  value of  $1.26 \pm 0.2$ .<sup>15</sup> A departure from this law has been observed for ethylene/ $\alpha$ -olefin copolymers with a high counit content, for which the crystallinity drops drastically.<sup>90</sup> However, using eq 1 with the aforementioned constant enables us to estimate  $\rho_{\text{app}}$  of an isolated chain in a random coil conformation of any ethylene copolymer:<sup>87</sup>

$$\rho_{\text{app}} = M/N_A V_{\text{coil}} = 3M/4\pi N_A R_g^3 \quad (13)$$

where  $M$  is the molar weight of the chain,  $V_{\text{coil}}$  is the gyration volume of the chain coil, and  $N_A$

is Avogadro's number. For the sake of illustration,  $\rho_{\text{app}}$  of an isolated ethylene copolymer chain drops from 0.10 to 0.02 g/cm<sup>3</sup> when the molar weight increases from 5 to 100 kDa. For a melt density of PE-like materials of approximately 0.85 g/cm<sup>3</sup>,<sup>91</sup> the data indicate that the actual density of chain segments in a given volume is 8.5 or 42 times greater than the segment density due to a single chain. The same figures applies to the TM probability for a bulk material in comparison with the TM probability for a single chain.

### Cross-Section TM Density

Starting from Huang and Brown's model, we can express the TM probability in an isolated chain ( $p$ ) as the ratio of the accumulated weight of TMs to the total molar weight ( $M$ ) of the chain:

$$p = n_{\text{TM}} M_{\text{TM}}/M \quad (14)$$

where  $M_{\text{TM}}$  is the average molar weight of a single TM and  $n_{\text{TM}}$  is the average number of TMs per chain. The question of the average molar weight of TMs, that is, their average contour length, is not a trivial one. People dealing with chain topology from the standpoint of crystallization often assume random-chain statistics (see the Theoretical Assessment of Tie Chains and Entanglements section). In contrast, people dealing with chain topology from a mechanical standpoint rather assume a stretched chain conformation for the TMs. This is notably the case for Peterlin's and Krigbaum's approaches to the elastic modulus. It is also the assumption implicitly made by Brown and Ward for their approach to low-temperature rupture. The major reason for this assumption is that slack TMs are likely not to contribute to both the stiffness and the strength of the material. Therefore, in this work, the TM conformation is assumed to be close to chain-extended, according to the sketch of Figure 9(a). The TM contour length is not much different from  $l_a$ . Then, the molar weight of a single TM roughly obeys the following:

$$M_{\text{TM}} = M_0 l_a / l_0 \quad (15)$$

where  $l_0 = 0.25 \text{ nm}$ <sup>92</sup> and  $M_0 = 28 \text{ Da}$  are the length and molar weight of the PE monomer unit, respectively.

**Table 3.** Physical Characteristics of Ethylene–Hexene Copolymers<sup>a</sup>

$\chi$ (mol %) <sup>b</sup>	$\rho$ (g/cm <sup>3</sup> )	$W_c$ (%) <sup>c</sup>	$V_c$ (%) <sup>d</sup>	$l_c$ (nm)	$l_a$ (nm)	$p \times 10^3$	$F_s^e$
—	0.968	71	68.7	33	13	1.6	0.005
0.16	0.959	64	61.4	27	15	9.2	0.022
0.24	0.950	61	58.0	24	15	15.4	0.033
0.40	0.947	59	55.9	23	16	38.3	0.080
0.46	0.942	58	54.6	21	15	54.7	0.110
0.92	0.938	52	48.8	17	16	92.7	0.160

<sup>a</sup> The data were taken from ref. 75.

<sup>b</sup> Molar count concentration.

<sup>c</sup> Crystal weight fraction.

<sup>d</sup>  $V_c = (\rho/\rho_c) W_c$ , where  $\rho_c$  is 1.00 g/cm<sup>3</sup> according to ref. 91.

<sup>e</sup> Computed with eq 17.

Then, the density of TMs per unit of volume ( $\delta_v$ ) of the amorphous phase in the crystallized material, for an isolated chain, can be expressed as follows:

$$\delta_v = n_{TM}/(1 - V_c)V_{coil} \quad (16)$$

where  $V_{coil}$  is the volume of the sphere pervaded by a chain of molar weight  $M$  and  $R_g$  in a random coil conformation and  $V_c$  is the crystal volume fraction of the solid material.

As a more reliable parameter for mechanical properties, we can derive the density of TMs per unit of surface ( $\delta_s$ ) of the crystal–amorphous interface for an isolated chain in the crystallized material:

$$\delta_s = \delta_v \times l_a \quad (17)$$

It is now easy to convert the TM density per unit of surface into a TM area fraction per chain via

$$f_s = \delta_s \times S_0 \quad (18)$$

where  $s_0 = 0.18 \text{ nm}^2$  is the cross section area of a single stem emerging from the crystal surface, as determined from the basal plane area of the PE orthorhombic unit cell.<sup>92</sup>

Finally, taking into consideration the fact that the actual material consists of intertwined chains, we can obtain the overall area fraction of TMs at the crystal–amorphous interface as follows:

$$F_s = f_s \times R \quad (19)$$

where  $R$  is given by  $\rho/\rho_{app}$  (the ratio of the actual density of the material to the apparent density of an isolated chain coil, as given in eq 13).

Therefore, the final equation for the TM area fraction is

$$F_s = p\rho N_A l_0 s_0 / M_0 (1 - V_c) \quad (20)$$

For the sake of illustration, the TM surface fraction has been computed for a series of ethylene copolymers already studied by Huang and Brown.<sup>75</sup> All the necessary parameters for the calculation are reported in Table 3. The TM probability for an isolated chain increases from  $p \approx 0.002$  for the high-density homopolymer up to  $p \approx 0.093$  for the copolymer of lower density. In parallel, the TM surface fraction increases from  $F_s \approx 0.005$  to  $F_s \approx 0.160$ . These data are fairly close to the values of the  $f_T$  parameter computed with the Brown–Ward experimental approach (see the data in Table 1).

If chain overlapping is not taken into consideration, the calculations give  $F_s$  values about 50 times lower than the figures of Table 3. In addition, as already underlined, these  $F_s$  figures include both the actual TMs that bridge neighboring crystalline lamellae and the loose loops that connect chain stems from the same lamella and are likely to form entanglements with loose loops from the opposite lamella. Because TMs and entangled loops both contribute to the stress transfer between crystalline lamellae, this remark may be an explanation for the good agreement between the theoretical  $F_s$  data and the experimental  $f_T$  data.

Regarding the influence of the chain length, Huang and Brown<sup>74</sup> computed the TM probability per chain ( $p$ ) for linear homopolyethylene as a function of the molar mass. The  $p$  data reported in Table 4 are significantly higher than



**Table 4.** Physical Characteristics of Ethylene Homopolymers of Various Molar Weights<sup>a</sup>

$M_w$ (kDa) <sup>b</sup>	$\rho$ (g/cm <sup>3</sup> )	$W_c$ (%) <sup>c</sup>	$V_c$ (%) <sup>d</sup>	$l_c$ (nm) <sup>e</sup>	$l_a$ (nm) <sup>c</sup>	$p \times 10^3$	$F_s^f$
174	0.970	70	68	18.3	8.7	50	0.145
539	0.964	66	64	17.2	9.8	140	0.360
786	0.961	63	61	16.3	10.7	195	0.460
1001	0.958	61	58	15.8	11.2	235	0.510

<sup>a</sup> The data were taken from ref. 74.

<sup>b</sup> Weight-average molecular weight.

<sup>c</sup> Crystal weight fraction.

<sup>d</sup>  $V_c = (\rho/\rho_c) W_c$ , where  $\rho_c$  is 1.00 g/cm<sup>3</sup> according to ref. 91.

<sup>e</sup> Huang and Brown<sup>74</sup> assumed  $L_p = l_c + l_a = 27$  nm;  $l_c$  and  $l_a$  were then computed from the equations  $l_c = V_c \times L_p$  and  $l_a = L_p - l_c$ .

<sup>f</sup> Computed with eq 17.

the corresponding figure for the homopolymer in Table 3 because of the assumption of a rather low value of 27 nm for the long period for all the materials under consideration. The  $F_s$  data of Table 4 display a steady increase with increasing molar weight, and this corroborates the common statement that the improvement of the mechanical properties with increasing molar weight results from a concomitant increase of the TM concentration. However, this increase is less pronounced than that of the  $p$  data. A similar conclusion could be made from the analysis of the data reported by other authors who checked the predicting capabilities of Huang and Brown's model.<sup>56,76,79</sup>

### Chain Entanglements

The second point of criticism discussed in the Shortcomings of the Models section emphasizes that Huang and Brown's model for evaluating the TM probability includes loose loops at the surface of the crystalline lamellae that are able to make entanglements with their counterparts of the opposite lamellae. Therefore, the  $F_s$  data computed from eq 20 also include loose loops and their eventual entanglements. Notwithstanding this problem, the entanglement contribution to intercrystalline molecular connections can be evaluated separately from that of TMs. Yeh and Runt<sup>77</sup> formerly proposed a theoretical approach to chain entanglements for an isolated chain derived from Huang and Brown's model for TMs. The model takes into account the distance between entanglements in the melt but considers selectively the entanglements from chains that are likely to be buried in different

crystalline lamellae, that is, entanglements that will actually give rise to intercrystalline bridges. Unfortunately, as for Huang and Brown's model, the probability calculations only concern an isolated chain. Also, no account was made of chain overlapping and intertwining, and this is necessary for a comparison with experimental data for bulk materials. More precisely, no attempt was made to compute the surface fraction of entanglements in the cross section of the amorphous layer.

Regardless of the reasons that all entanglements or only the ones pertaining to chains buried in different lamellae should be taken into consideration, the surface fraction of entanglements can be determined by analogy with the previous approach to TMs. The molar weight between entanglements ( $M_e$ ) can be defined as follows:

$$M_e = M/n_e \quad (21)$$

where  $n_e$  is the average number of entanglements per chain. Because two chains are required to form an entanglement but every entanglement gives rise to two equivalent TMs, the number of TMs equivalent to the entanglements, for a single chain, is

$$n_{TM,e} = n_e = M/M_e \quad (22)$$

The equivalent TM surface fraction due to chain entanglements ( $F_{s,e}$ ) is given by a combination of eqs 16–19 with eqs 13 and 22. The following relationship, analogous to eq 20, is then obtained:

$$F_{s,e} = \rho N_A l_a s_0 / M_e (1 - V_c) \quad (23)$$

If all entanglements are preserved during crystallization,  $F_{s,e}$  should directly depend neither on the molar weight nor on the count concentration. However,  $F_{s,e}$  should indirectly depend on these parameters via the density ( $\rho$ ) and, most of all, via  $l_a$ .

Comparing eqs 20 and 23 provides a means of evaluating the respective contributions of TMs and entanglements. The ratio of the surface fraction of TMs to that of entanglements is

$$F_s/F_{s,e} = pl_0M_e/l_aM_0 \quad (24)$$

If all entanglements are preserved throughout the crystallization process, the  $M_e$  value in the solid materials should be the same as the characteristic figure of molten PE (i.e.,  $M_e = 2$  kDa), regardless of the molar weight and crystallinity. Then, considering that  $l_a$  can span the range 5–20 nm for PE materials covering the crystallinity range 0.75–0.30, and taking  $p \approx 0.001$  for HDPE and  $p \approx 0.3$  for LLDPE,<sup>75</sup> we can obtain the following:

$$\begin{aligned} F_s/F_{s,e} &\approx 0.4 \text{ for LLDPE} \\ F_s/F_{s,e} &\approx 0.007 \text{ for HDPE} \end{aligned}$$

These figures indicate that intercrystalline molecular connections due to entangled chains are more numerous than those due to conventional TMs for both HDPE and LLDPE, the departure being rather high for HDPE and quite moderate for LLDPE. This corroborates Yeh and Runt's<sup>77</sup> statement that conventional TMs can be neglected with respect to entangled TMs for HDPE. However, this is not the case for LLDPE. Moreover, if only entanglements pertaining to chains that are buried in opposing lamellae were taken into consideration, the  $F_s/F_{s,e}$  ratio for LLDPE might be greater than unity.

## CONCLUSIONS

The question of the experimental or theoretical determination of TMs is far from being resolved. For highly oriented fibers, it is rather logical to consider taut TMs for modeling the stiffness and strength. For plastically drawn specimens, it is also likely that most of the TMs are actually taut. The problem is yet more complex regarding the long-term behavior of isotropic materials. Indeed, slow crack growth proceeds via crazing in an unforeseeable locus because of stress

concentration on microscopic structural defects or inclusions of foreign materials. Therefore, the properties of the polymer matrix that rule the long-term behavior are no longer those of the isotropic material but are those of the drawn one, that is, a material whose lamellar microstructure has been transformed into a fibrillar one, after the fragmentation of the crystalline lamellae and the unfolding of a great number of folded chains. This is the reason that some authors have studied the properties of drawn samples to understand the long-term behavior. Crucial questions then arise: should all TMs be taken into consideration, or only the taut ones, and should all entanglements have to be considered, or only the ones involving chains buried in different crystalline lamellae?

Copolymerization definitively is a means of increasing the concentration of intercrystalline TMs. It is quite obvious, from experiments, that the reduction of the crystal thickness resulting from the segregation of the counts out of the crystal in ethylene copolymers is a favorable factor for increasing the TM concentration. An increase in the chain length also results in an increase in the TM concentration because of the reduction of chains ends. In recent years, the synthesis of copolymers with a bimodal distribution of chain lengths has turned out to be a successful route for increasing the TM concentration, in parallel to both a high crystal content and a high stiffness, because of the capability of this method for incorporating selectively the counts in the longer chains (see the discussion in ref. 33). This route is still an open field for progress in the way to a very long lifetime PE.

Several experimental approaches reported in the literature provide access to a quantitative assessment of the TM concentration. The advantage of the experimental approaches is that they are able to account for the influence of the thermomechanical treatment of the material and the crystallization conditions on the TM concentration.

Regarding theoretical approaches proposed for quantifying the TM density, Huang and Brown's model is the only one that can account for the crystallization conditions through the crystal thickness, in addition to the effect of the counts and chain length. There is still a question about the meaning of TMs in this model: does the TM calculation include entangled tie chains or not? As a corollary, one may have doubts about the relevance of the attempts to introduce a spe-

cific computation of the entangled tie chains in addition to conventional TMs.

Some improvements are proposed in this article to allow a direct comparison of theoretical data of the TM surface fraction with data obtained from experimental approaches. Despite the solutions that have been put forward for the shortcomings of the theoretical models, a serious shortcoming remains regarding the inability to account for large-scale molecular rearrangements, such as chain reeling and chain disentanglement, that may occur during crystallization at low undercooling, notably for short chains.

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## REFERENCES AND NOTES

- Kausch, H.-H. *Polymer Fracture*; Springer-Verlag: Berlin, 1978.
- Keith, H. D.; Paden, F. J., Jr.; Vadimsky, R. G. *J Polym Sci Part A-2: Polym Phys* 1966, 4, 267–281.
- Keith, H. D.; Paden, F. J., Jr.; Vadimsky, R. G. *J Appl Phys* 1966, 37, 4027–4034.
- Keith, H. D.; Paden, F. J., Jr.; Vadimsky, R. G. *J Appl Phys* 1971, 42, 4585–4592.
- Keith, H. D.; Paden, F. J., Jr.; Vadimsky, R. G. *J Polym Sci Polym Phys Ed* 1980, 18, 2307–2309.
- Friedrich, K. *Adv Polym Sci* 1983, 52, 225–273.
- Battacharya, S. K.; Brown, N. *J Mater Sci* 1984, 19, 2519–2532.
- Lustiger, A.; Corneliussen, R. D. *J Mater Sci* 1987, 22, 2470–2476.
- Narisawa, Z.; Ishikawa, M. *Adv Polym Sci* 1990, 91, 354–391.
- Plummer, C. J. G.; Kausch, H.-H. *Macromol Chem Phys* 1996, 197, 2047–2063.
- Shah, A.; Stepanov, E. V.; Capaccio, G.; Hiltner, A.; Baer, E. *J Polym Sci Part B: Polym Phys* 1998, 36, 2355–2369.
- Kausch, H.-H.; Gensler, R.; Grein, C.; Plummer, C. J. G.; Scaramuzzino, P. *J Macromol Sci Phys* 1999, 38, 803–815.
- Porter, R. S.; Johnson, J. F. *Chem Rev* 1966, 66, 1–27.
- Fischer, E. W. *Pure Appl Chem* 1978, 50, 1319–1341.
- Darras, O.; Séguéla, R. *Colloid Polym Sci* 1995, 273, 753–765.
- Vincent, P. I. *Encycl Polym Sci Technol* 1967, 7, 292–361.
- Meinel, G.; Peterlin, A. *Eur Polym J* 1971, 7, 657–670.
- Capaccio, G.; Ward, I. M. *Polymer* 1975, 16, 239–243.
- Smith, P.; Lemstra, P.; Pijpers, J. P. L. *J Polym Sci Polym Phys Ed* 1982, 20, 2229–2241.
- Bastiaansen, C. W. M. *J Polym Sci Part B: Polym Phys* 1990, 28, 1475–1482.
- Séguéla, R.; Rietsch, F. *Polymer* 1986, 27, 703–708.
- Séguéla, R.; Rietsch, F. *J Mater Sci* 1988, 23, 415–421.
- Liu, T. M.; Baker, W. E. *Polym Eng Sci* 1992, 32, 944–955.
- Ward, I. M.; Wilding, M. A. *J Polym Sci Polym Phys Ed* 1984, 22, 561–575.
- Hannon, M. J. *J Appl Polym Sci* 1974, 18, 3761–3767.
- Lustiger, A.; Markam, R. L. *Polymer* 1983, 24, 1647–1654.
- Saeda, S.; Suzaka, Y. *Polym Adv Technol* 1994, 6, 593–601.
- Schurzky, K. G. *J Plast Film Sheeting* 1985, 1, 142–151.
- Brown, N.; Lu, X.; Huang, Y.; Harrison, I. P.; Ishikawa, N. *Plast Rubber Compos Process Appl* 1992, 17, 255–258.
- Berthold, J.; Böhm, L.; Enderle, H.-F.; Göbel, P.; Lüker, H.; Lecht, R.; Schulte, U. *Plast Rubber Compos Process Appl* 1996, 25, 368–372.
- Clutton, E. Q.; Rose, L. J.; Capaccio, G. *Plast Rubber Compos Process Appl* 1998, 27, 478–482.
- Soares, J. B. P.; Abbott, R. F.; Kim, J. D. *J Polym Sci Part B: Polym Phys* 2000, 38, 1267–1275.
- Hubert, L.; David, L.; Séguéla, R.; Vigier, G.; Degoulet, C.; Germain, Y. *Polymer* 2001, 42, 8425–8434.
- Peterlin, A. *J Macromol Sci Phys* 1973, 7, 705–727.
- Peterlin, A. *Int J Fract* 1975, 11, 761–780.
- Zurkov, S. N.; Kuksenko, V. S. *Int J Fract* 1975, 11, 629–639.
- Peterlin, A. *J Appl Phys* 1977, 48, 4099–4108.
- Peterlin, A. In *The Strength and Stiffness of Polymers*; Zachariades, A. E.; Porter, R. S., Eds.; Marcel Dekker: New York, 1983; Chapter 3.
- Ishikawa, M.; Ushui, K.; Kondo, Y.; Hatada, K.; Gima, S. *Polymer* 1996, 37, 5375–5379.
- Glenz, W.; Peterlin, A. *J Polym Sci Part A-2: Polym Phys* 1971, 9, 1191–1217.
- McRae, M. A.; Maddams, W. F. *Makromol Chem* 1976, 177, 473–484.
- Hosoda, S. *Makromol Chem* 1984, 185, 787–795.
- Lustiger, A.; Ishikawa, N. *J Polym Sci Part B: Polym Phys* 1991, 29, 1047–1055.
- Prasad, K.; Grubb, D. T. *J Polym Sci Part B: Polym Phys* 1989, 27, 381–403.
- Wong, W. F.; Young, R. J. *J Mater Sci* 1994, 29, 520–526.
- Meier, R. J.; Vansweefelt, H. *Polymer* 1995, 36, 3825–3829.

47. Lagaron, J. M.; Dixon, N. M.; Gerrard, D. I.; Reed, W.; Kip, B. J. *Macromolecules* 1998, 31, 5845–5852.
48. Tarin, P. M.; Thomas, E. L. *Polym Eng Sci* 1979, 19, 1017–1022.
49. Hubert, L.; David, L.; Séguéla, R.; Vigier, G.; Corfias-Zuccalli, C.; Germain, Y. *J Appl Polym Sci* 2002, 84, 2308–2317.
50. Brown, N.; Ward, I. M. *J Mater Sci* 1983, 18, 1405–1420.
51. Runt, J.; Jacq, M. *J Mater Sci* 1989, 24, 1421–1428.
52. Runt, J.; Gallagher, K. P. *J Mater Sci* 1991, 26, 792–798.
53. G'Sell, C.; Jonas, J. J. *J Mater Sci* 1981, 16, 1956–1974.
54. Mills, P. J.; Hay, J. N.; Haward, R. N. *J Mater Sci* 1985, 20, 501–507.
55. Haward, R. N. *J Polym Sci Part B: Polym Phys* 1995, 33, 1481–1494.
56. Patel, R. M.; Sehanobish, K.; Jain, P.; Chum, S. P.; Knight, G. W. *J Appl Polym Sci* 1996, 60, 749–758.
57. Krigbaum, W. R.; Roe, R.-J.; Smith, K. J. *Polymer* 1964, 5, 533–542.
58. Fischer, E. W.; Hahn, K.; Kugler, J.; Struth, U.; Born, R.; Stamm, M. *J Polym Sci Polym Phys Ed* 1984, 22, 1491–1513.
59. Hubert, L.; David, L.; Séguéla, R.; Vigier, G. *Polym Int* 2004, 53, 582–585.
60. Hoffman, J. D.; Miller, R. L. *Polymer* 1997, 38, 3151–3212.
61. Organization of macromolecules in the condensed phase; Faraday Discuss Chem Soc Vol. 68; The Royal Society of Chemistry: London, 1979.
62. Guttman, C. M.; Di Marzio, E. A.; Hoffman, J. D. *Polymer* 1981, 22, 1466–1479.
63. Yoon, D. Y.; Flory, P. J.; Dill, K. A. *Macromolecules* 1984, 17, 862–868.
64. Yoon, D. Y.; Flory, P. J. *Macromolecules* 1984, 17, 868–871.
65. Mansfield, M. L. *Macromolecules* 1986, 19, 851–854.
66. Mansfield, M. L. *Macromolecules* 1988, 21, 126–130.
67. Termonia, Y. *Macromolecules* 1995, 28, 7667–7670.
68. Mathur, S. C.; Mattice, W. L. *Macromolecules* 1987, 20, 2165–2167.
69. Mathur, S. C.; Mattice, W. L. *Macromolecules* 1988, 21, 1354–1360.
70. Mathur, S. C.; Rodriguez, K.; Mattice, W. L. *Macromolecules* 1989, 22, 2781–2785.
71. Lacher, R. C.; Bryant, J. L.; Howard, L. N.; Summers, D. W. *Macromolecules* 1986, 19, 2639–2643.
72. Lacher, R. C.; Bryant, J. L. *Macromolecules* 1988, 21, 1183–1184.
73. Lacher, R. C. *Macromolecules* 1987, 20, 3054–3059.
74. Huang, Y.-L.; Brown, N. *J Mater Sci* 1988, 23, 3648–3655.
75. Huang, Y.-L.; Brown, N. *J Polym Sci Part B: Polym Phys* 1991, 29, 129–137.
76. Hosoda, S.; Uemura, A. *Polym J* 1992, 24, 939–949.
77. Yeh, J. T.; Runt, J. *J Polym Sci Part B: Polym Phys* 1991, 29, 371–388.
78. Strebel, J.; Moet, A. *J Polym Sci Part B: Polym Phys* 1995, 33, 1969–1984.
79. Beerbaum, H.; Grellmann, W. *ESIS Publ* 2000, 27, 163–174.
80. Gedde, U. W.; Jansson, J. F. *Polymer* 1985, 26, 1469–1476.
81. Lu, X.; Qian, R.; Brown, N. *Polymer* 1995, 36, 4239–4244.
82. Greco, R.; Coppola, F. *Plast Rubber Process Appl* 1986, 6, 35–41.
83. Plummer, C. J. G.; Menu, P.; Cudré-Mauroux, N.; Kausch, H. H. *J Appl Polym Sci* 1995, 55, 489–500.
84. de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter 8.
85. Kwack, T. H.; Han, C. D. *J Appl Polym Sci* 1983, 28, 3419–3433.
86. Schlund, B.; Utracki, L. A. *Polym Eng Sci* 1987, 27, 380–386.
87. Guichon, O.; Séguéla, R.; David, L.; Vigier, G. *J Polym Sci Part B: Polym Phys* 2003, 41, 327–340.
88. Prasad, A.; Shroff, R.; Rane, S.; Beaucage, G. *Polymer* 2001, 42, 3101–3113.
89. Shroff, R.; Prasad, A.; Lee, C. *J Polym Sci Part B: Polym Phys* 1996, 34, 2317–2333.
90. Carella, J. M.; Graessley, W. W.; Lohse, D. J.; Fetters, L. J. *Macromolecules* 1984, 17, 2775–2786.
91. Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1973; Vol. 1, Chapter 8.
92. Bunn, C. W. *Trans Faraday Soc* 1939, 35, 482–491.