Thermodynamically-controlled crystal orientation in stressed polymers: 2. Effect of free energy of the amorphous chains surrounding an intramolecular crystal in a crosslinked system

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Partial crystallization of a polymer chain in a crosslinked system affects *inter alia* the configurational entropy of such a chain. The change in free energy is orientation-dependent and can contribute to the distribution of crystal orientations. Using a simple tetrahedron model of the polymer network, the change in configurational free energy due to the partial crystallization of polymer chains has been derived and its effect on the distribution of crystal orientations analysed. Model numerical calculations have been performed for uniaxially stretched polyethylene, and compared with the effects of strain energy on crystals embedded in an uncrosslinked matrix and flow potential.

INTRODUCTION

In the first paper of this series[1], it was shown that crystal orientation in a stressed polymer can be controlled by the orientation-dependent free energy of the system $F(\underset{\sim}{\theta})$. A natural contribution to $F(\underset{\sim}{\theta})$ is the strain energy of an anisotropically elastic crystal in a non-spherical stress field, $F_{cr}(\underset{\sim}{\theta})$. This effect has been derived and analysed in the previous paper[1]. In a crosslinked system, where crystals appear as sections of chains spanning network junctions (crosslinks), the free energy of the amorphous phase is also orientation-dependent, $F_{am} = F_{am}(\underset{\sim}{\theta})$ and can contribute to the equilibrium distribution of crystal orientations.

The problem of the crystallization-affected free energy of amorphous chains has been approached by several authors. Baranov *et al.* analysed a single polymer chain with fixed ends, subjected to partial intramolecular crystallization (lamellar growth). Minimization of the related free energy vs. orientation angle $\underset{\sim}{\theta}$ yielded the most probable orientation of the crystal with respect to chain axis:

$$F_{\min}(\underset{\sim}{\theta};\underset{\sim}{h} = \text{constant}) \Rightarrow \underset{\sim}{\theta}_{\max} \text{ at } \underset{\sim}{h} = \text{constant} \qquad (1)$$

This analysis did not include any information about the distribution of orientations of crystals in the macroscopic system which is composed of many, differently oriented, and possibly connected chains. The assumption of fixed ends of the chain also seems an overstatement. Even in a permanently crosslinked network, individual chain ends can move in space together with the crosslinks to which they are attached, assuming positions with various free energies. We will show that this is the case with crystallizing networks.

Gaylord[3] discussed the free energy of a single crystallizing polymer chain and then averaged it over the linearily transformed Gaussian distribution function of chain vectors, $W_G(\underset{\sim}{h};\underset{\sim}{\Lambda})$ to obtain the average free energy for a set of many chains in the system:

$$F_{av}(\underset{\sim}{\theta}) = \int F(\underset{\sim}{\theta});\underset{\sim}{h})\, W_G(\underset{\sim}{h};\underset{\sim}{\Lambda})\mathrm{d}\underset{\sim}{h} \qquad (2)$$

This energy, when minimized with respect to $\underset{\sim}{\theta}$ again yielded the most probable orientation $\underset{\sim}{\theta}_{\max}$ as a function of the deformation parameter $\underset{\sim}{\Lambda}$ involved in the chain distribution function W_G. Three objections can be raised to this treatment.

(1) $W_G(\underset{\sim}{h};\underset{\sim}{\Lambda})$ is not the relevant distribution function over which the free energy F should be averaged. The correct equilibrium function should include a Boltzmann factor, $\exp[-F(\underset{\sim}{\theta};\underset{\sim}{h})/kT]$, missing in equation (2).

(2) Because of the symmetry of the functions $F(\underset{\sim}{\theta};\underset{\sim}{h})$ and $W_G(\underset{\sim}{h};\underset{\sim}{\Lambda})$, the integral in equation (2) is identically equal to zero; Gaylord removed this effect by arbitrarily replacing components of the vector $\underset{\sim}{h}$ by their absolute values.

(3) The distribution of crystals in the macroscopic system is not controlled by the average free energy $\langle F\rangle$ but by the average exponential $\langle\exp[-F(\underset{\sim}{\theta},\underset{\sim}{h})/kT]\rangle$. All these points will become clear in the course of our analysis.

The aim of this study was to explain the most important factors responsible for thermodynamically-controlled crystal orientation in crosslinked polymers, and to compare the effect of the orientation effects produced in crosslinked and deformed systems with other mechanisms of crystal orientation (see refs 1, 11). The changes in free energy produced by crystallization derived in this paper will also be used for the analysis of crystallization rates and the thermodynamically most probable morphology of crystals.

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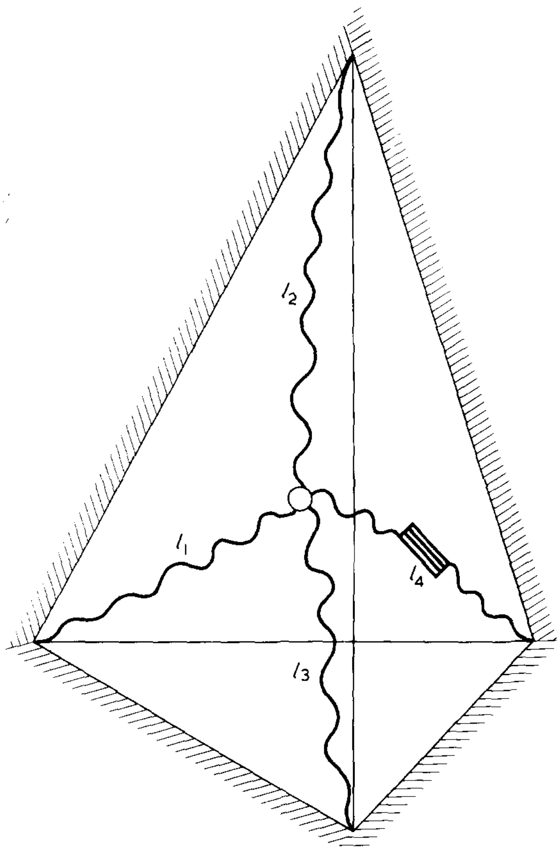

Figure 1 A tetrahedron model of a partly crystallized, crosslinked polymer

The model of a crystallizing network introduced below is simple enough to be treated analytically, and yet involves all the essential festures of a real network with low degree of crystallinity. The network chain to be crystallized is neither fixed at both ends (as assumed in the earlier analyses[2,3]) nor free. Different contour lengths of the network chains can explain effects of molecular weight distribution in real networks. Calculation of the statistical integrals (instead of the minimum free energy discussed in earlier treatments of the problem) also leads to results which are more general and correct from the thermodynamic point of view. It seems that qualitatively our model correctly reflects all features of the crystallization behaviour of real networks. For quantitative calculations the model can easily be extended.

PARTLY CRYSTALLIZED MODEL NETWORK

We will consider a simple, one-junction network, a modification of the Flory–Rehner tetrahedron[4,5]. Four polymer chains exhibiting Gaussian statistics of configurations and contour lengths l_1, l_2, l_3 and l_4, are connected in a central crosslink, the other ends being fixed at the vertices of the tetrahedron (*Figure 1*). The vertices representing the boundaries of the macroscopic system are subjected to uniform boundary conditions defined by the displacement gradient tensor $\underset{\sim}{\Lambda}$. The central junction, representing the whole internal system is free to move and assume any position in the space. No affinity of displacement of the central junction is assumed. This simple model exhibits all the features of a real network, and the small number of degrees of freedom guarantees easy mathematical treatment.

We will consider intramolecular crystallization of one of the four chains, say l_4, in the deformed state. *Figure 2* presents schematically the instantaneous configurations of the system before deformation (*Figure 2a*), after deformation in the amorphous state (*Figure 2b*) and after crystallization (*Figure 2c*). $\underset{\sim}{\mathrm{h}}_i$ (i = 1, 2, 3, 4) denotes end-to-end vectors of the four chains measured from the individual vertices of the tetrahedron to the central junction. We will also define a position 'O' in the tetrahedron which, occupied by the central junction, minimizes the free energy of the system. The chain vectors ending at this point, $\underset{\sim}{\mathrm{h}}_i^{\mathrm{O}}$, satisfy the condition:

$$\sum_{i=1}^{4} \underset{\sim}{\mathrm{h}}_i^{\mathrm{O}}/l_i = 0 \tag{3}$$

In the undeformed state (*Figure 2a*), an instantaneous configuration of the system is thus characterized by the single vector $\underset{\sim}{\mathrm{u}}$, i.e. a deviation of the crosslink from the most probable (affine) position 'O'. We will also assume that lengths of the initial vectors, $\underset{\sim}{\mathrm{h}}_i^{\mathrm{O}}$, correspond to their mean-square values:

$$(\underset{\sim}{\mathrm{h}}_i^{\mathrm{O}})^2 = A_c\langle h_{0i}^2\rangle = A_c l_i a \tag{4}$$

where $\langle h_{0i}^2\rangle$ is the unperturbed length and a is the length of the statistical chain segment. A_c denotes the contraction factor, which, for ideal tetrafunctional networks, amounts to 1/2 (see refs 6, 7).

Vectors $\underset{\sim}{\mathrm{h}}_i$ in any configuration of the system, to the boundary of which a displacement gradient $\underset{\sim}{\Lambda}$ was applied, can be presented in the form:

$$\underset{\sim}{\mathrm{h}}_i = \underset{\sim}{\mathrm{h}}_i^{\mathrm{O}} + \underset{\sim}{\mathrm{u}} = \underset{\sim}{\mathrm{h}}_{i,\mathrm{af}} + \underset{\sim}{\mathrm{u}} \tag{5}$$

where $\underset{\sim}{\mathrm{u}}$ is the actual displacement from the 'affine' position of the junction, and $\underset{\sim}{\mathrm{h}}_{i,\mathrm{af}}$ are linear transformations of the initial vectors $\underset{\sim}{\mathrm{h}}_i^{\mathrm{O}}$ with boundary displacement gradient $\underset{\sim}{\Lambda}$.

The initial contour lengths l_i(i = 1, 2, 3 and 4) are constants and do not change either by deformation or crystallization. The crystal starts at some point on the l_4 chain, characterized by the end-to-end vector $\underset{\sim}{\mathrm{h}}_5$ and contour length l_5. From the other end of the crystal issues a chain characterized by parameters $\underset{\sim}{\mathrm{h}}_6$ and l_6. If ω is the contour

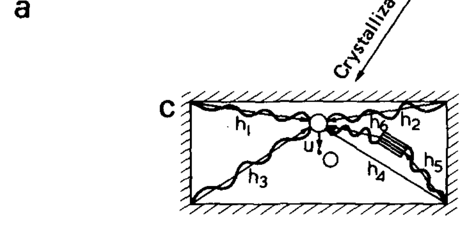

Figure 2 Scheme of the configuration of the model network in three states: (a) before deformation and crystallization; (b) after deformation in the amorphous state; (c) after deformation and crystallization

length of this portion of the chain which is included in the crystal, and $\utilde{r}$ is crystal vector, then the variables $\utilde{h}_5, \utilde{h}_6, l_5, l_6$ satisfy the conditions (see *Figure 2c*):

$$\utilde{h}_5 + \utilde{h}_6 + \utilde{r} = \utilde{h}_{4\mathrm{af}} + \utilde{u} \tag{6}$$

$$l_5 + l_6 + \omega = l_4 \tag{7}$$

The model introduced above involves eight degrees of freedom represented by the multivector $\utilde{\xi} = (\utilde{u}, \utilde{h}_5, \utilde{r})$ with the additional constraint:

$$r^2 = \text{constant} \tag{8}$$

The length of the crystal vector, $\utilde{r}$, the contour length of the chain included in the crystal, ω, and the starting position of the crystal, l_5, are assumed to be predetermined constants.

In the present study we are not interested in 'thermodynamic optimum' morphologies, or 'equilibrium' degrees of crystallinity; rather we are studying free energy and the related crystal orientation distributions for model networks for any given morphology and crystallinity. Hence, the parameters $|\utilde{r}|$, and ω are taken as constants rather than variables subject to optimization.

The characteristics of the initial tetrahedron also form a set of predetermined parameters $\utilde{\kappa} = (\utilde{h}_1^0, l_1, \utilde{h}_2^0, \ldots, l_4)$.

It is evident that our model is intermediate between a free-end and a fixed-end crystallizing chain. Partial crystallization of a free chain hardly affects the conformational entropy of the uncrystallized portions. The entropy of the portion of the chain converted into the crystalline phase is the only quantity that does change being reduced to zero. On the other hand, strong conformational entropy can be expected in crystallizing chains with both ends fixed. In our model, constraints are applied not to the ends of the crystallizing chain, but to the boundary of the system (tetrahedron), as in a real network. Mobility of the central junction makes possible extension or compression of the crystallizing chain l_4, but at the same time affects conformation of the three other, uncrystallized neighbouring chains, l_1–l_3. The competition between the entropy gain in fractions l_5, l_6 of the crystallizing chain, l_4, and entropy loss in the amorphous chains l_1–l_3 determines the overall change of the free energy of the amorphous phase in the same way as in real systems. The assumption that only one out of four network chains develops a crystallite, however, limits our model considerations to systems with a small number of crystallites.

FREE ENERGY OF A PARTLY CRYSTALLIZED TETRAHEDRON NETWORK

The statistical configurational integral, Z, of a deformed and partly crystallized tetrahedron $\utilde{\kappa}$ at some configuration $\utilde{\xi}$ can be presented as a product of the configurational integral for the crystallized chain, $Z_4(\utilde{\xi}\,;\utilde{\Lambda}, \utilde{\kappa})$ and similar integrals for the remaining, uncrystallized chains, $Z_i(\utilde{u}; \utilde{\Lambda}, \utilde{\kappa})$, ($i$ = 1, 2, 3) affected by crystallization of the chain l_4:

$$Z(\utilde{\xi}\,;\utilde{\Lambda}, \utilde{\kappa}) = Z_4(\utilde{\xi}\,;\utilde{\Lambda}, \utilde{\kappa}) \prod_{i=1}^{3} Z_i(\utilde{u}\,;\utilde{\Lambda}, \utilde{\kappa}) \tag{9}$$

It is evident that the integral Z_4 for the crystallized chain depends on the whole set of variables, $\utilde{\xi}$, while Z_i(i = 1, 2, 3) for uncrystallized chains are functions only of the position u of the central junction. For Gaussian chains, the statistical integrals Z_i can be written in the form:

$$Z_i(\utilde{u}\,;\utilde{\Lambda}, \utilde{\kappa}) = 8(3a/2l_i)^{3/2} \exp[(-3/2)(\utilde{h}_{i,\mathrm{af}} + \utilde{u})^2/l_i a] \tag{10}$$

The partly crystallized chain can be treated as two chains l_5 and l_6 and its configurational integral Z_4 as a product of the respective integrals Z_5 and Z_6:

$$Z_4(\utilde{\xi}, \utilde{\Lambda}, \utilde{\kappa}) = Z_5(h_5, l_5)\cdot Z_6(h_6, l_6) \tag{11}$$

which with Gaussian statistics of both subchains and the constraints equations (6)–(8) yields:

$$Z_4(\utilde{\xi}\,;\utilde{\Lambda}, \utilde{\kappa}) = 64[9a^2/4\, l_5(l_4 - l_5 - \omega)]^{3/2} \exp\{-(3/2a)[\utilde{h}_5^2/l_5 + (\utilde{h}_{4,\mathrm{af}} + \utilde{u} - \utilde{h}_5 - \utilde{r})^2/(l_4 - l_5 - \omega)]\} \tag{12}$$

So, the total free energy of the amorphous part of the system, $F_{\mathrm{am}} = -kT \ln Z$, at a given configuration $\utilde{\xi}$ can be written as:

$$2F_{\mathrm{am}}(\utilde{\xi}\,;\utilde{\Lambda}, \utilde{\kappa})/3kT = \text{constant} + \ln[l_5(l_4 - l_5 - \omega)] + \sum_{i=1}^{3} (\utilde{h}_{i,\mathrm{af}} + \utilde{u})^2/l_i a + \utilde{h}_5^2/l_5 a + (\utilde{h}_{4,\mathrm{af}} + \utilde{u} - \utilde{h}_5 - \utilde{r})^2/(l_4 - l_5 - \omega)a$$

Most probable configuration of the tetrahedron, $\utilde{\xi}^*$, and minimum free energy

Using equation (13) we will calculate first the most probable configuration of the system, i.e. the configuration corresponding to the minimum free energy:

$$\partial F_{\mathrm{am}}(\utilde{\xi}, \utilde{\Lambda}, \utilde{\kappa})/\partial \utilde{\xi} = 0 \tag{14}$$

The solution of equation (14) is:

$$\utilde{r}^* = |\utilde{r}|\utilde{e}_4 \tag{15a}$$

$$\utilde{u}^* = [(|\utilde{r}|/|\utilde{h}_{4,\mathrm{af}}| - s)/(1 + S - sS)]\,\utilde{h}_{4,\mathrm{af}} \tag{15b}$$

$$\utilde{h}_5^*/l_5 = [1 + S(1 - |\utilde{r}|/|\utilde{h}_{4.\mathrm{af}}|)]/[l_4(1 + S - sS)]\;\utilde{h}_{4,\mathrm{af}} \tag{15c}$$

where $\utilde{e}_4 = \utilde{h}_{4,\mathrm{af}}/|\utilde{h}_{4,\mathrm{af}}|$. In equations (15a)–15(c), $s = \omega/l_4$ denotes the 'local degree of crystallinity' of the crystallizing chain, and

$$S = \sum_{i=1}^{3} (l_4/l_i).$$

It can be observed that the most probable vectors $\utilde{r}^*$, $\utilde{h}^*_5$ and $\utilde{u}^*$, are all colinear with the chain vector $\utilde{h}_{4,\mathrm{af}}$. The most probable position of the central junction is not affine; however, $\utilde{u}^* \neq 0$. Depending on the 'local crystallinity', s, and $\utilde{h}_{4,\mathrm{af}}$, the junction is shifted forwards ($\utilde{u}^* > 0$) or backwards ($\underset{\sim}{u}^* < 0$) along the vector $\underset{\sim}{h}_{4,\mathrm{af}}$. If crystal growth morphology is strictly determined and constant, then independent of the length of the crystal, the ratio:

$$k = (|\underset{\sim}{r}|/\omega)\epsilon(0,1) \tag{16}$$

can be considered a constant. κ depends on the length and direction of folds in chain-folded crystals and approaches unity asymptotically when the fold length approaches zero. In equation (16) the critical condition for $\underset{\sim}{u}^* > 0$ becomes independent of the local crystallinity, s, or ω:

$$\underset{\sim}{u}^* > 0 \Longleftrightarrow k > |\underset{\sim}{h}_{4,\mathrm{af}}|/l_4 \tag{17}$$

Formally, the end-to-end vector $\underset{\sim}{h}_{4,\mathrm{af}}$ is subject to Gaussian statistics and can assume any values in the range $(-\infty,+\infty)$. Physically, the maximum extension of $\underset{\sim}{h}_{4,\mathrm{af}}$ cannot exceed its contour length, l_4, and the ratio $|\underset{\sim}{h}_{4,\mathrm{af}}|/l_4$ is also confined to the range (0, 1). Consequently, $\underset{\sim}{u}^*$ is positive (the most probable junction position shifted forwards) when k is high, i.e. when the crystal is not substantially chain-folded and/or the relative extension of the chain $|\underset{\sim}{h}_{4,\mathrm{af}}|/l_{\mathrm{af}}$ is small. For highly folded crystals and/or strongly extended chains, $\underset{\sim}{u}^* < 0$ and the junction is shifted backwards – the crystallizing chain is contracted. These two types of crystallization-induced behaviour are related to possible changes in the internal stress of the crystallizing polymers.

If conclusions about the crystal orientation are to be drawn for the most probable configuration $\underset{\sim}{\xi}^*$, the orientation distribution function for crystals should be equal to the distribution of the directions of vectors $\underset{\sim}{h}_{4,\mathrm{af}}$. In the case of a linearily transformed Gaussian distribution $W_G(\underset{\sim}{h}, \underset{\sim}{\Lambda})$ of network chain vectors, the crystal orientation function assumes the form:

$$\Psi(\underset{\sim}{r}/|\underset{\sim}{r}|) = \text{constant} \int_0^{\infty} W_G(\underset{\sim}{h}, \underset{\sim}{\Lambda})h^2\mathrm{d}h \tag{18}$$

Such a distribution was assumed in an early paper by Flory[8]. It corresponds to the distribution resulting from affine rotation of rigid, rod-like elements embedded in an infinitely viscous medium[9–11]. We will show later in this paper that equation (18) also yields the asymptotic case for the thermodynamically-controlled distributions.

The free energy F^*_{am} corresponding to the most probable configuration $\underset{\sim}{\xi}^*$ reads:

$$\begin{aligned} 2F^*_{\mathrm{am}}(\underset{\sim}{\xi}; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa})/3kT = {} & \text{constant} + \ln[l_5(l_4 - l_5 - \omega)] \\ & + \sum_{i=1}^{3} h^2_{i,\mathrm{af}}/l_i a + \Big\{ S(|\underset{\sim}{r}|/|\underset{\sim}{h}_{4,\mathrm{af}}| - s)^2 \\ & + (1-s)[1 + S(1 - |\underset{\sim}{r}|/|\underset{\sim}{h}_{4,\mathrm{af}}|)]^2 \\ & - 2(1 + S - sS)(|\underset{\sim}{r}|/\underset{\sim}{h}_{4,\mathrm{af}}| - s)\Big\} \times \\ & \underset{\sim}{h}^2_{4,\mathrm{af}}/l_4 a(1 + S - sS)^2 \end{aligned} \tag{19}$$

The minimum free energy, equation (19), differs from that calculated by Baranov *et al.*[2], because the authors did not allow any freedom of motion to the ends of the crystallizing chain.

Orientation-dependent free energy from statistical integrals

To find the free energy dependent on the crystal orientation vector, $\underset{\sim}{r}$, but independent of the configurational variables $\underset{\sim}{h}_5$ and $\underset{\sim}{u}$, the statistical integral, Z, from equation (9) should be integrated over the other degrees of freedom:

$$\begin{aligned} Z(\underset{\sim}{r}; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa}) = \int\int & Z_4(\underset{\sim}{r}, \underset{\sim}{u}, \underset{\sim}{h}_5; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa}) \\ & \prod_{i=1}^{3} Z_i(\underset{\sim}{u}; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa})\mathrm{d}\underset{\sim}{u}\,\mathrm{d}\underset{\sim}{h}_5/(4\pi a^2)^3 \end{aligned} \tag{20}$$

For Gaussian chains this yields:

$$\begin{aligned} Z(\underset{\sim}{r}; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa}) = K\exp\Big\{ & -(3/2a)[Ar^2/l_4 - B\underset{\sim}{r}^T\underset{\sim}{h}_{4,\mathrm{af}}/l_4 \\ & + Ch^2_{4,\mathrm{af}}/l_4 + \sum_{i=1}^{3} h^2_{i,\mathrm{af}}/l_i]\Big\} \end{aligned} \tag{21}$$

with dimensionless coefficients:

$K = 512[27Aa^3/8l_1 l_2 l_3 S]^{3/2}$

$A = S/(1 + S - sS)$

$B = 2A(1 + S)/S$

$C = (1 + s + S)A/S$

The orientation-dependent free energy calculated from equation (21) reads:

$$\begin{aligned} 2F_{\mathrm{am}}(\underset{\sim}{r}; \underset{\sim}{\Lambda}, \underset{\sim}{\kappa})/3kT = {} & -(2/3)\ln K + Ar^2/\langle h^2_{40}\rangle \\ & - B|\underset{\sim}{r}|(2\langle h^2_{40}\rangle)^{1/2}\underset{\sim}{e}^T_r\underset{\sim}{\Lambda}\underset{\sim}{e}_4 + \frac{1}{2}C\underset{\sim}{e}^T_4\underset{\sim}{\Lambda}^T\underset{\sim}{\Lambda}\underset{\sim}{e}_4 \\ & + \frac{1}{2}\sum_{i=1}^{3}\underset{\sim}{e}^T_i\underset{\sim}{\Lambda}^T\underset{\sim}{\Lambda}\underset{\sim}{e}_i \end{aligned} \tag{23}$$

$\underset{\sim}{e}_r$ and $\underset{\sim}{e}_i$ denote, respectively, unit vectors along the crystal and along the affinely transformed ith chain vector $\underset{\sim}{h}_{i,\mathrm{af}}$. In the uncrystallized state $s = 0$, $r = 0$, and the free energy reduces to a constant, independent of $\underset{\sim}{e}_r$:

$$2F_{\mathrm{am}}/3kT = -(2/3)\ln K + \frac{1}{2}\sum_{i=1}^{4}\underset{\sim}{e}^T_i\underset{\sim}{\Lambda}^T\underset{\sim}{\Lambda}\underset{\sim}{e}_i \tag{24}$$

It can be observed that the orientation-dependent part of the free energy $F_{\mathrm{am}}(\underset{\sim}{r})$ from equations (13) or (23) is an antisymmetric function of both $\underset{\sim}{r}$ (or $\underset{\sim}{e}_r$) and $\underset{\sim}{h}_{4,\mathrm{af}}$:

$$F_{\mathrm{am}}(\underset{\sim}{r}; \underset{\sim}{h}_{4,\mathrm{af}}) = -F_{\mathrm{am}}(-\underset{\sim}{r}; \underset{\sim}{h}_{4,\mathrm{af}}) = -F_{\mathrm{am}}(\underset{\sim}{r}; -\underset{\sim}{h}_{4,\mathrm{af}}) \tag{25}$$

Consequently, integration of F_{am} with any symmetric function of $\underset{\sim}{r}$ or $\underset{\sim}{h}_{4,\mathrm{af}}$ (such as W_G in equation 2) must inevitably

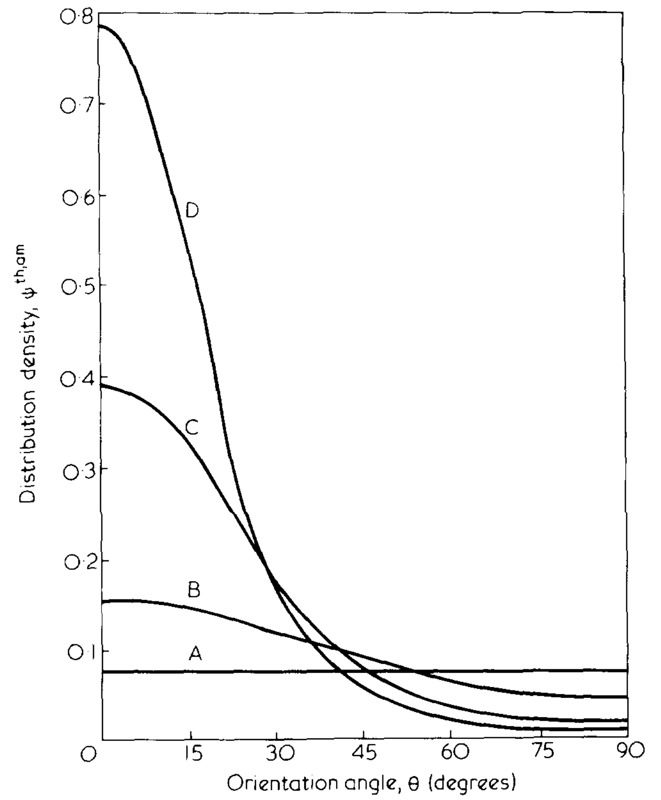

Figure 3 Averaged crystal orientation distribution, $\Psi^{th,am}$ (θ) in a system subjected to uniaxial extension, A_{net} = constant = 2, values of the extension ratio, λ: A, λ = 1; B, λ = 2; C, λ = 5; D, λ = 10

lead to zero. The different result obtaind by Gaylord[3] was due to additional, arbitrary assumptions introduced into the formulae.

The orientation-dependent free energy F_{am} in equation (23) does not depend on the current length of the crystallizing chain, $\underset{\sim}{h}_4$. The integration over $\underset{\sim}{u}$ performed earlier, equation (20), has already taken into account all possible values of the vector $\underset{\sim}{h}_4$. So, F_{am} from equation (23) is physically equivalent (but not identical) to the 'average' free energy obtained by Gaylord[3] from the integral, equation (2), using the incomplete distribution fucntion W_G. F_{am} can further be averaged over $d\underset{\sim}{e}_4$ or $d\underset{\sim}{e}_r$ if macroscopic properties of the network are analysed.

THERMODYNAMICALLY-CONTROLLED ORIENTATION DISTRIBUTIONS OF CRYSTALS IN A CROSSLINKED SYSTEM

In the coordinate system associated with the tetrahedron, the Boltzmann distribution of crystal directions, $\underset{\sim}{e}_r$ reads:

$$\Psi_{tetra} = \text{constant } \times \exp[-F_{am}(\underset{\sim}{e}_r)/kT]$$

$$= \text{constant} \times \exp[A_{net}(\underset{\sim}{e}_r^T \underset{\sim}{\Lambda} \underset{\sim}{e}_4)] \tag{26}$$

where:

$$\text{constant} = (1/4\pi)B_{net}/\sinh B_{net}$$

$$A_{net} = 3|\underset{\sim}{r}|(1+S)/(2\langle h_{40}^2\rangle)^{1/2}(1+S-sS)$$

$$B_{net} = A_{net}(\underset{\sim}{e}_4^T \underset{\sim}{\Lambda}^T \underset{\sim}{\Lambda} \underset{\sim}{e}_4)^{1/2}$$

To obtain an orientation distribution in the macroscopic system, expressed in a fixed-in-space coordinate system, Ψ_{tetra} should be averaged over all equiprobable directions of the vector $\underset{\sim}{e}_4$:

$$\Psi^{th,am}(\underset{\sim}{e}_r;\underset{\sim}{\Lambda}) = (1/4\pi)\int \Psi_{tetra}\,(\underset{\sim}{e}_r;\underset{\sim}{\Lambda},\underset{\sim}{e}_4)d\underset{\sim}{e}_4 \tag{27}$$

This integration can be performed numerically, or, in some cases, analytically. For uniaxial extension along the axis, Z:

$$\underset{\sim}{\Lambda} = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix} \tag{28}$$

$\Psi^{th,am}$ can be obtained as a series of even powers of $\cos\theta$, the angle between the Z-axis and crystal vector $\underset{\sim}{r}$.

Figures 3 and *4* present examples of the distribution function $\Psi^{th,a,}(\theta)$, and *Figure 5* gives examples of the axial orientation factor defined as:

$$f_{or}^{th,am} = 1 - 3\langle\sin^2\theta\rangle/2 \tag{29}$$

The crystal orientation function, $\Psi^{th,am}$ (θ) is controlled separately by two parameters: A_{net} and the elongation ratio, λ. The sharpness of the distribution and the absolute value of the orientation factor increase monotonically with the parameter A_{net} at constant λ (*Figure 4*), and increase with the absolute value of lnλ at constant A_{net} (*Figure 3*).

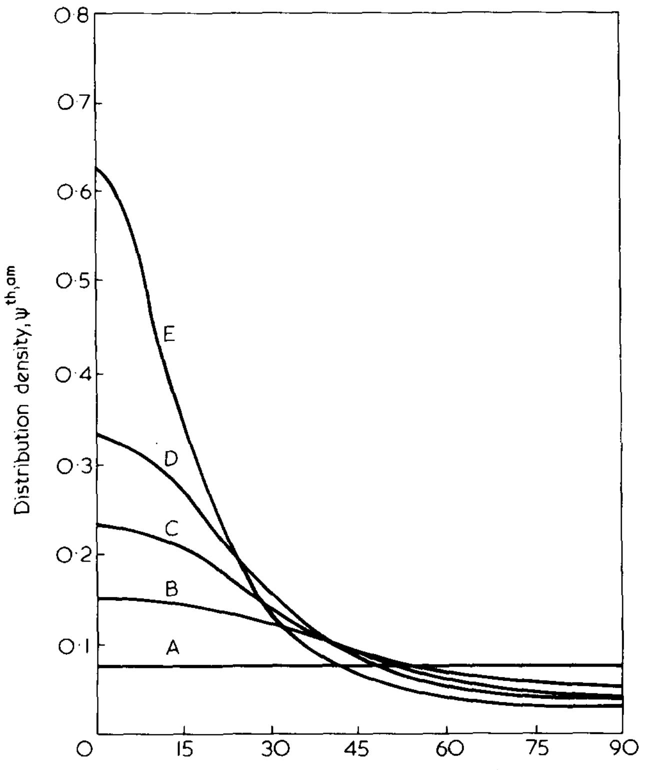

Figure 4 The averaged crystal orientation distribution, $\Psi^{th,am}$ (θ) in a system subjected to uniaxial extension. λ = constant = 2, values of the internal parameter, A_{net}: A, 0; B, 2; C, 4; D, 8. Curve E ($A_{net} = \infty$) corresponds to the asymptotic distribution Ψ_∞ (θ) from equation (30)

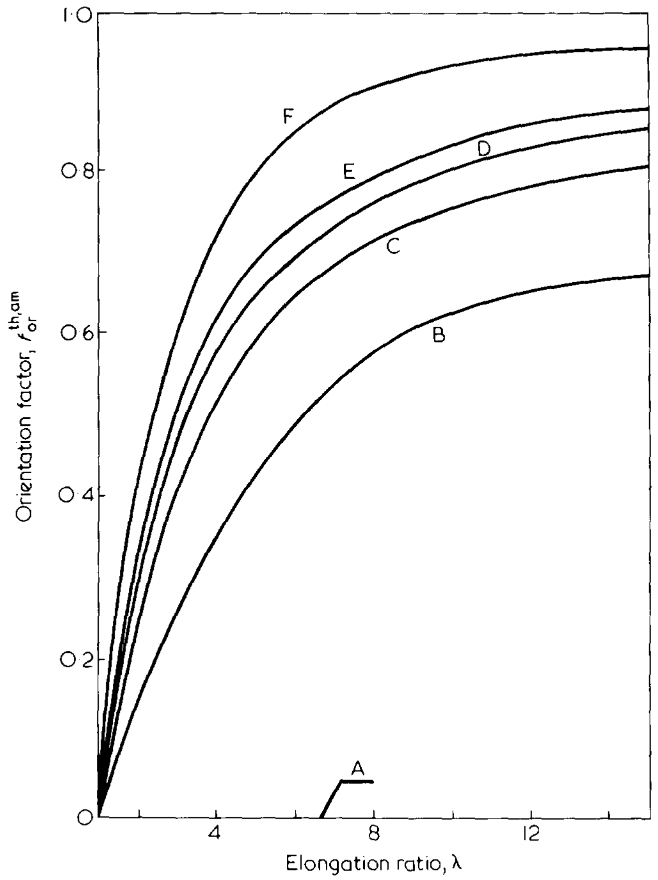

Figure 5 Axial orientation factor $f_{or}^{th,am}$ related to the distribution function $\Psi^{th,am}$ (θ) plotted vs. extension ratio λ. Values of the paramer A_{net}: A, 0; B, 2; C, 4; D, 6; E, 8. Curve F ($A_{net} = \infty$) corresponds to the asymptotic orientation factor, $f_{or,\infty}$

The asymptotic orientation distribution at $A_{net} \rightarrow \infty$, shown in *Figure 4* is equivalent to the orientation distribution of vectors $\underset{\sim}{h}_{4,af}$ in the system of affinely deformed tetrahedra. At $A_{net} \rightarrow \infty$ crystals are all oriented exactly along the vectors $\underset{\sim}{h}_{4,af}$. Such a distribution can be derived either from the Gaussian function of chain conformations integrated over the lengths of the vector $\underset{\sim}{h}$ (equation 18), or from considerations concerning a system of rigid rods embedded in a viscous continuum subjected to affine deformation[11]. The latter approach was applied in late thirties by Kratky[9] and then by Oka[10] to the so-called 'first limiting case' of molecular orientation[9]. Both methods yield for the asymptotic distribution $\Psi_\infty(\theta)$:

$$\Psi_\infty(\theta) = \left\{\frac{\lambda^3/4\pi}{[\lambda^3 + (1-\lambda^3)\cos^2\theta]^{3/2}}\right\} \tag{30}$$

The asymptotic function Ψ_∞ (equation 30) is shown as curve E in *Figure 4*, and the related asymptotic orientation factor $f_{or,\infty}$ as curve F in *Figure 5*.

CRYSTAL ORIENTATION CONTROLLED BY AMORPHOUS AND CRYSTAL FREE ENERGY

It seems important to compare crystal orientation effects related to the free energy of the amorphous, crosslinked polymer F_{am} with similar effects produced by orientation-dependent strain energy of crystals, F_{cr}, and hydrodynamic potential Φ, both discussed in ref 1. The comparison is difficult, since both the strain energy of crystals and the hydrodynamic potential are controlled by stress, while the free energy of network chains, F_{am}, is inherently dependent on deformation (tensor $\underset{\sim}{\Lambda}$, or extension coefficient λ in uniaxial deformation). We will make the comparison using, as a first approximation, the theory of rubber elasticity for uncrystallized networks[5] to convert deformation into stress. The stress tensor p will be related to deformation gradient $\underset{\sim}{\Lambda}$ by the equation:

$$\underset{\sim}{p} = \upsilon kTA_c(\underset{\sim}{\Lambda}\underset{\sim}{\Lambda}^T - \underset{\sim}{I}) \tag{31}$$

in which A_c denotes network contraction factor (in this paper assumed to be ½), υ is the number of elastically effective network chains in unit volume, and $\underset{\sim}{I}$ is the unit tensor. Equation (31) provides first approximation for the stress in partly crystallized networks at low degrees of crystallinity. Actually, the presence of crystallites in the network effects the distribution of crosslinks in space, the free energy and the stress in the system. As a measure of stress in uniaxial extension we will use the difference in normal stress components, $(p_{33} - p_{11})$ which, with A_c = ½ in equation (31) and deformation gradient tensor $\underset{\sim}{\Lambda}$ from equation (28) reduces to:

$$\Delta p = p_{33} - p_{11} = (\upsilon kT/2)(\lambda^2 - 1/\lambda) \tag{32}$$

We will compare stress differences Δp with the extension ratio λ using equation (32) with $\upsilon = 4.82 \times 10^{19}$ cm^{-3}, T = 350K. For polyethylene this corresponds to a molecular weight for network chains $M = 10^4$. The crystal orientation controlled by the free energy of the amorphous crosslinked part also depends on the group of molecular parameters, A_{net}. For our calculations we will take $A_{net} = 2$ and $A_{net} = \infty$ (asymptotic orientation function from equation 30). Orientation factors controlled by the strain energy of crystals and by the hydrodynamic potential (see ref 1) will be calculated with the parameters $V/kT = 7.83 \times 10^{-7}$ cm^2/dyne, and shape factor $\phi = 1.355$, yielding:

$$A_{th} = 2.49 \times 10^{-15}(\Delta p)^2$$

$$A_{hydro} = 1.06 \times 10^{-6}\,\Delta p$$

with Δp expressed in dynes/cm^2.

The results presented in *Figure 6* show that in the range of moderate stresses (up to 3×10^7 dyne/cm^2) orientation effects of crystal strain (see ref 1) are negligible compared both with the effects of deformation in the amorphous surroundings in a crosslinked system or to the effect of hydrodynamic potential in an uncrosslined system. In the range of moderate stresses the effect of strain energy in crystals leads to perpendicular orientation, $f_{or} < 0$, and only above some limit, around $\Delta p = 2.6 \times 10^8$ dyne/cm^2, f_{or} assumes positive values and starts to increase rapidly with the growing stress. The effects of the hydrodynamic potential and of the deformation of amorphous, crosslinked surroundings are comparable one with the other. Orientation of crystals controlled by the crosslinked amorphous surroundings is very senstiive to the internal molecular parameter A_{net}. The orientation factor $f_{or}^{th,am}$ increases monotonically with A_{net}, reaching an asymptotic relation f_∞ (λ) at $A_{net} = \infty$, equivalent to all crystals oriented along the respective network chains. Orientation produced by hydrodynamic effects in uncrosslinked systems, f_{or}^{hydro}, seems to be stronger than

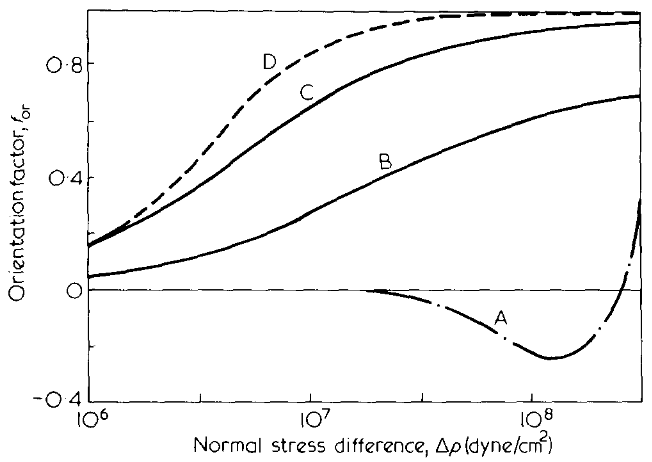

Figure 6 Crystal orientation factor f_{or} plotted vs. the difference of normal stress components, Δp for polyethylene subjected to extensional deformations. Curve A: orientation controlled by strain energy of polymer crystals, with $A_{th} = 2.49 \times 10^{-15}\ (\Delta p)^2$ (ref 1). Curves B and C: orientation controlled by free energy of the amorphous crosslinked phase. Curve B, $A_{net} = 2$; Curve C, $A_{net} = \infty$, asymptotic distribution function from equation (30). Curve D, orientation controlled by hydrodynamic flow potential, with $A_{hydro} = 1.06 \times 10^{-6}$ (ref 1)

$f_{or}^{th,am}$; it depends on the shape of the flowing particles, and disappears for cubical, or spherical crystals. At moderate and high asymmetry of crystals (the curve shown in *Figure 6* corresponds to the axial ratio 2:1), f_{or}^{hydro} is higher than $f_{or}^{th,am}$ at any value of the parameter A_{net}. For the example considered, and similar conditions, stress applied to an uncrosslinked polymer and inducing potential flow produces higher crystal orientation than the same stress applied to a crosslinked system in equilibrium. Since $f_{or}^{th,cr}$ and f_{or}^{hydro} at constant stress, Δp, are independent of the molecular weight of the polymer (see refs 1, 11) and $f_{or}^{th,am}$ shows only a slight dependence, this conclusion seems to indicate a more general regularity.

DISCUSSION

The results obtained in this paper indicate that crystal orientation controlled by the free energy of amorphous chains surrounding crystal in a crosslinked system is different to the effects produced by either the strain energy of the crystal itself, or the hydrodynamic potential of a flowing uncrosslinked system. The magnitude of the effect is different (see *Figure 6*) and so are the main factors controlling the orientation behaviour. It is important to realize to what extent these results are affected by the specific molecular model analysed.

Three assumptions involved in the present treatment limit the applicability of the obtained results, viz:

(i) the crystallization is intramolecular, i.e. involves a single chain only;

(ii) the degree of crystallinity is small, so that only a few network chains, and these only partly, are subjected to crystallization;

(iii) only the effect of crystallization on nearest neighbour chains is considered (a single tetrahedron).

The first assumption limits our analysis to chain-folded crystals or mono-chain helices. It is impossible to think of an extended-chain crystal composed of just one chain, and for such crystals a different model has to be chosen. The present analysis is sensible, provided that the actual crystallization morphology is chain-folded or helical.

The assumption of low crystallinity concerns both the 'local degree of transformations', s, and the fraction of chains which have undergone crystallization. Both these characteristics are assumed small compared with unity. The condition, $s \ll 1$ is necessary to treat both portions of the uncrystallized chain as Gaussian; in our model only one network chain out of four has undergone transformation. For higher crystallinities one should take into account tetrahedra with 0, 1, 2, 3 and 4 crystallized chains. So introduction of non-Gaussian statistics and extension of the one crystallized chain model would be necessary for the discussion of the effect of higher crystallinities on the thermodynamic and orientation behaviour. On the other hand, if a fraction of network chains much smaller than 1/4 is subjected to partial crystallization (i.e. not every tetrahedron includes a crystal) the model should be extended to cover more mobile junctions. This may affect quantitatively, but not qualitatively, the results discussed in this paper.

The limitation of the degrees of freedom of the system to the position of a single junction, $\underset{\sim}{u}$, also distorts the real situation where not only nearest neighbours but also further junctions can experience the influence of the presence of a crystal. Qualitatively, a single vector $\underset{\sim}{u}$ reflects the mechanisms responsible for the change in thermodynamic behaviour. For quantitative analysis, however, the model should be extended to include systems with many junctions.

With the above limitations, our analysis shows that crystal orientation in crosslinked polymers is controlled by the free energy of amorphous chains through two characteristics: deformation of the whole system (displacement gradient tensor $\underset{\sim}{\Lambda}$) and the internal parameter A_{net} which can be written in the following form:

$$A_{net} = [3/(2)^{1/2}]\, ks(n_4)^{1/2}(1 + S)/(1 + S - sS) \qquad (33)$$

$k = r/\omega$ is a morphological characteristic related to the degree of chain folding. $k = 0$ for a chain infinitely folded in a direction perpendicular to crystal axis $\underset{\sim}{r}$, and $k = 1$ for an ideal, extended chain (not realizable in single-chain crystallization). $s = \omega/l_4$ is the 'local degree of transformation' of the crystallizing chain l_4, n_4 is the number of statistical chain segments in the crystallizing chain, and S is a parameter related to contour length distribution and can be represented as:

$$S = 3\langle l\rangle\langle 1/l\rangle \qquad (34)$$

A_{net} linearily increases with the parameter k, and crystal orientation distribution becomes the more sharp, the more extended (the less folded) are the chains within the crystal. A_{net} also increases monotonically with the local crystallinity, s, from $A_{net} = 0$ at $s = 0$ (uniform orientation at the beginning of crystallization) to some limiting value at $s = 1$. At constant 'local crystallinity' s, A_{net} increases, but at constant crystal length, r, A_{net} decreases with increasing contour length of the crystallizing chain l_4, or with the number of statistical chain segments, n_4. Finally, A_{net} monotonically increases with the molecular weight parameter S characterizing the distribution of contour lengths (or molecular weights) of network chains. The effect of S is negligible at local crystallinities, s, up to 0.5. The parameter S depends on the shape and width of the molecular weight distribution. For a monodisperse polymer, $S = 3$, independently of the average molecular weight of network chains. For a normalized 'random' distribution:

$$f(l) = \exp[-(l - a)/(\langle l \rangle - a)]/(\langle l \rangle - a)$$

where a, the length of the statistical chain segment, is the minimum value of l in the system, we obtain:

$$S = -[3\langle l \rangle/(\langle l \rangle - a)] \exp[a/(\langle l \rangle - a)]\, Ei\,[-a/(\langle l \rangle - a)] \tag{34}$$

where $Ei()$ is integral exponential function, and $\langle l \rangle$ is the average contour length of a network chain. Since $\langle l \rangle$ is always much larger than a, equation (35) reduces to:

$$S \cong 3(\ln\langle l \rangle/a - C) \tag{36}$$

where $C = 0.577215\ldots$ is the Euler constant. S from equation (36) slowly increases with the average length of the network chains, $\langle l \rangle$, and practically does not affect the orientation distribution parameter A_{net} with the range $s \in (0, 0.5)$ and $\langle l \rangle/a \in (10^2, 10^5)$. So, the average molecular weight affects A_{net} as $(n_4)^{1/2}$ while molecular weight distribution seems to be of secondary importance.

It seems that the present results throw some light on the mechanisms responsible for thermodynamically-controlled crystal orientation at the beginning of intramolecular crystallization; they indicate the factors responsible for such orientation, and show the effect of this kind of orientation between hydrodynamic and crystal strain effects. The problem involving higher crystallinities and other morphologies will be studied on the basis of different models.

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