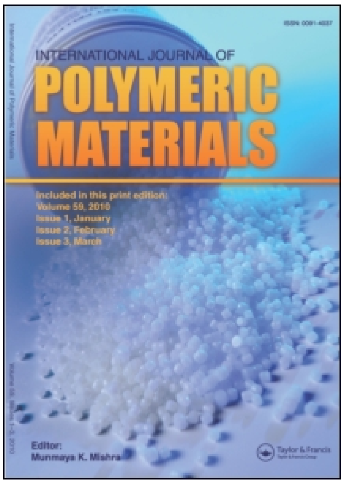

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Thermodynamic Prediction of Molecular Morphology Parameters of Amorphous Regions in Drawn Polymers

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A theory is proposed to predict molecular morphology of amorphous regions in drawn semicrystalline polymers. It is based on the assumption that molecular morphology corresponds to a minimum free conformational energy, provided the size of crystallites and amorphous regions, as well as the degree of macromolecule extension are fixed. The minimization of free conformational energy of amorphous regions was carried out with due regard for the real densities ratio. As a result, portions and the tie chain length distributions, regular folds, random and adjacent reentrant loops as functions of the degree of macromolecule extension and size of amorphous regions were obtained. The Monte-Carlo simulation was used to control the local density distribution within the amorphous regions.

KEY WORDS Semicrystalline polymer, molecular morphology, tie chains, loops, reentry, drawing, computer simulation.

INTRODUCTION

The crystallization of polymers from melt and drawing of melt-crystallized polymers usually leads to the formation of a heterogeneous structure[1,2] containing alternating crystallites and amorphous regions of the order of 100 Å. On the one hand, molecular morphology of amorphous regions depends on the parameters of the resulting heterogeneous structure and on the mechanism of crystallization (or recrystallization in the case of polymer drawing). On the other hand, it may well be that it is the amorphous regions that determine the parameters of heterogeneous supermolecular structure and limit the crystallization and recrystallization processes in semicrystalline polymers under drawing.[3] In addition, the molecular structure of amorphous regions is the essential feature governing their mechanical properties.[4,5] Therefore, experimental and theoretical study of the molecular morphology of amorphous regions in semicrystalline polymers is of primary importance.

The amorphous regions contain chain segments of three types fixed to the crystallite surface: loops, tie chains and free ends[2] (Figure 1a). Depending on the length and positions of loop ends on the crystallite surface, there are three different subtypes of loops:[6–16] regular folds, loose loops with adjacent reentry, and random reentrant loops (Figure 1b). One of the basic problems in a theoretical study of amorphous regions is to determine the portions and length distributions of different chain segments.

The aim of the present theoretical study is to predict the molecular structure of amorphous regions in drawn polymers on the basis of minimization of its equilibrium conformational

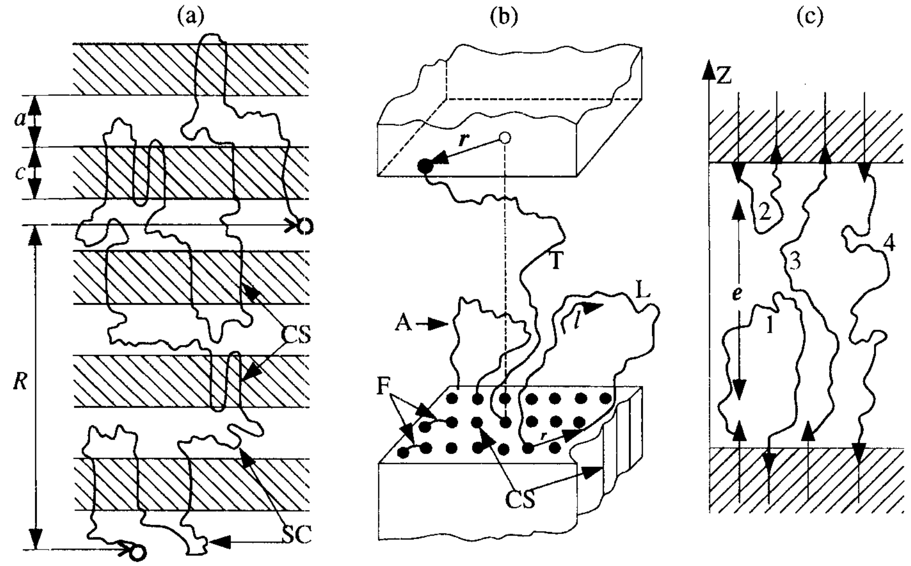

FIGURE 1 Macromolecule in stacked-lamellar model. (a) Stacked-lamellae. c is thickness of lamella, a is thickness of amorphous region, R is end-to-end distance of macromolecule, SC is chain segments in amorphous region, CS is crystal stems. (b) Different types of chain segments. F is regular folds, A is adjacent reentrant loops, L is random reentrant loops, T is tie chains; r and l are parameters of chain segment state. (c) Different types of loops ($n = 1, 2$) and tie chains ($n = 3, 4$) distinguished by direction of vector round at entrance and exit at surface of crystallite. Z is axis of drawing, $\boldsymbol{e}$ is unit vector of macromolecule round.

free energy as a function of chain segments length density distribution:
— at fixed sizes of crystallites c and amorphous regions a,
— with due regard for the real densities ratio d_a/d_c,
— with due regard for the degree of chain extension characterizing of drawing ratio R/L (R is end-to-end distance and L is macromolecule length).

Principal assumption of this study is as follows: the polymer system is believed to have enough time to achieve local thermodynamic equilibrium compatible with the given limitations during crystallization of melt and formation of lamellar or microfibrillar structure (with parameters c, a, d_a/d_c, R/L). The kinetics of drawing and crystallization is assumed to affect the molecular morphology through the parameters of supermolecular heterogeneous structure.

CHAIN SEGMENTS LENGTH DENSITY DISTRIBUTION

Let us consider a macromolecule of length L in a stacked-lamellar model with lamellae of thickness c, separated by amorphous regions of thickness a (Figure 1). Assume that the distance between the end-to-end macromolecule distance is constant and equals R.

Let us imagine the macromolecule as a sequence of crystalline segments and amorphous segments (loops and tie chains in the amorphous region, see Figure 1a, b). We distinguish four types of chain segments (Figure 1c): two types of loop ($n = 1, 2$) and two types of tie chain ($n = 3, 4$), and characterize the chain segment state by a set of variables n, r, l (see Figure 1b).

Our goal is to establish the statistical weight of chain segment states $\rho(n, r, l)$. Each given state of a chain segment has its own free conformational energy $F_s(n, r, l)$. In the present study we use for $F_s(n, r, l)$ the results of the Monte-Carlo calculation and approximations obtained in Reference 17:

$$F = \sum_{n,r,l} \rho(n, r, l) F_s(n, r, l) - TS, \tag{1}$$

where S is the entropy associated with all permissible rearrangements of chain segment in the set of states $\{n, r, l\}$. We obtained

$$\begin{aligned} S = & -T \sum_{n,r,l} \rho(n, r, l) \ln \rho(n, r, l) \\ & + T \left[(\nu_2 + \nu_3) \ln (\nu_1 + \nu_3) + (\nu_1 + \nu_4) \ln (\nu_2 + \nu_4) \right], \end{aligned} \tag{2}$$

where ν_n is a portion of the chain segments of n-type, that is

$$\nu_n = \sum_{r,l} \rho(n, r, l). \tag{3}$$

It is necessary to find a minimum of F under the following limitations:

$$\sum_{n,r,l} \rho(n, r, l) = 1 \tag{4}$$

$$\sum_{r,n,l} \rho(n, r, l) l = \langle l \rangle \tag{5}$$

$$\sum_{r,l} [\rho(1, r, l) - \rho(2, r, l)] = 0 \tag{6}$$

$$\sum_{r,l} [-\rho(3, r, l) - \rho(4, r, l)] = \frac{R(\langle l \rangle + c)}{L(a + c)}. \tag{7}$$

Here (4) is the condition of normalization, (5) is the condition of the average length constancy (actually the condition of d_a/d_c constancy), (6) is the topological condition (see Figure 1c), (7) is the condition of R constancy.

Minimizing F by the Lagrange multiplier method and using the conditions (4)–(7), we obtained

$$\rho(n, r, l) = \frac{\lambda_n}{Z} \exp\left(\frac{F_s(n, r, l) + \beta l}{kT} \right), \tag{8}$$

where

$$Z = 2S_1 + (\lambda_3 + \lambda_4) S_3 \tag{9}$$

$$S_n = \sum \exp\left(\frac{F_s(n, r, l) + \beta l}{kT} \right) \tag{10}$$

$$\lambda_1 = \lambda_2 = 1, \qquad \lambda_3 = \frac{1}{\lambda_4} = \sqrt{\frac{\nu_3}{\nu_4}}. \tag{11}$$

The parameter β is a function of the value R/L (at fixed values of a, c, d_a/d_c and T) and can be found by numerical solution of Equation (7) after (8)–(10) are substituted into it.

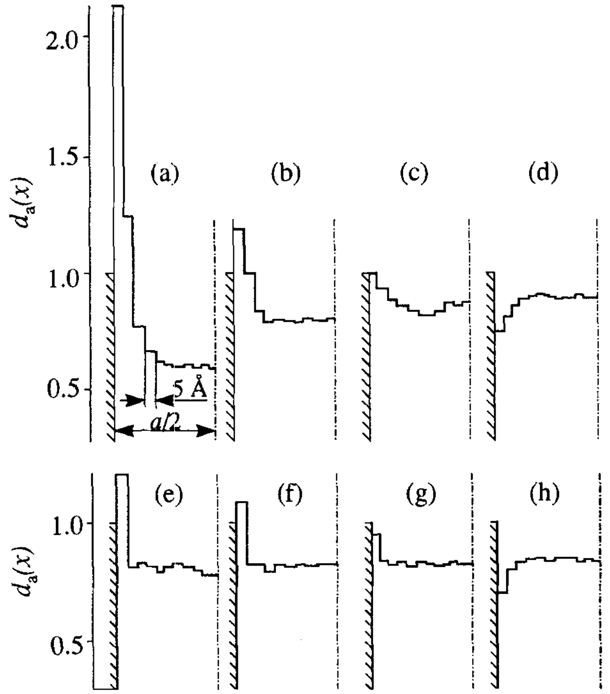

FIGURE 2 Local density distributions within the amorphous region at various values of R/L and various thickness of interfacial layers l_s in CH_2-units. $c = a = 100$ Å, $T = 360$ K. (a–d) $R/L = 0.2$: (a) $l_s = 0$, (b) $l_s = 2$, (c) $l_s = 3$, (d) $l_s = 4$. (e–h) $R/L = 0.7$: (e) $l_s = 0$, (f) $l_s = 2$, (g) $l_s = 3$, (h) $l_s = 4$. The distributions are symmetric relative to a middle of amorphous region.

LOCAL DENSITY WITHIN AMORPHOUS REGIONS

In deriving principle theoretical formulae (1), (2), (7)–(10) the average density of the amorphous regions (5) was assumed to be constant. However, this did not guarantee the constancy of the local density, i.e. the absence of the layers with the density higher or lower than the average one. To control the local density we carried out the Monte-Carlo simulation of chain segments polyethylene in the amorphous region limited by parallel planes: crystallite surfaces according to statistical weights (8) and calculated a local density distribution within the amorphous region.

Figures 2a, e present the calculated local density distribution within the amorphous region at various drawing ratios R/L. In a slightly oriented polymer ($R/L = 0.2$) the density of the layer adjoining the crystallite surface exceeds the density of crystallite by a factor of 2.1 (Figure 2a). As R/L increases, the value of density excess decreases, but even at $R/L = 0.7$ it is still larger than 20% (Figure 2e).

Most likely this density excess is the consequence of the assumption that each chain segment realizes all possible conformations independently. To avoid the density anomaly we assumed that the tie chains and long random reentrant loops retain trans-conformation at a distance l_s from the crystallite surface. As a result of this theory modification the interfacial layer where the unit orientation degree decreases gradually should be introduced.

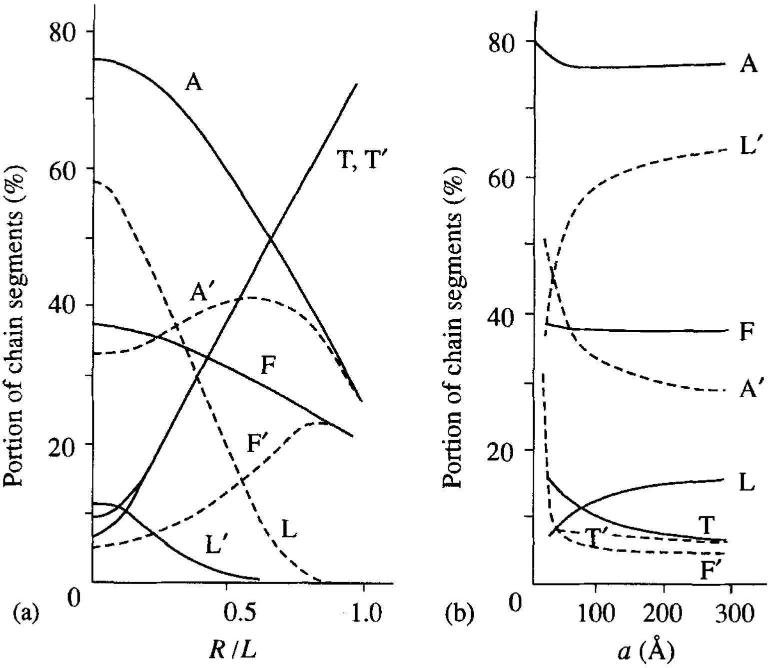

FIGURE 3 Portion of different types of chain segments. (a) Dependences on R/L at $a = 100$ Å. (b) Dependences on a at $R/L = 0.01$. $T = 360$ K, $d_a/d_c = 0.85$. T,T′ are tie chains; L,L′ are random reentrant loops; A,A′ are adjacent reentrant loops; F,F′ are regular folds; $l_s = 0$ (A′, F′, L′, T′); $l_s = 3$ (A, F, L, T).

The thickness of the interfacial layer is a free parameter of the theory. We choose a value of l_s which eliminates any defects in the local density within amorphous regions. According to our calculations the optimum value of l_s is 3 CH_2-units. In this case there is no excess density in the interfacial layer (Figure 2c, g). Further increase in l_s results in the density deficiency in the interfacial layer (Figure 2d, h).

RESULTS

Figure 3 presents the portions of folds, adjacent and random reentrant loops, and tie chains as functions of the R/L and a. It is noteworthy that the dependencies represented by the curves F′, A′, L′, T′ correspond to an unrealistic situation of abnormally high local density in the vicinity of the crystallite surface. We present them only to better understand the influence of the interfacial layer on the date obtained.

As a result of numerous discussion (see References 6–14) a general approach concerning the structure of crystallite surface and interfacial layer was developed. As was shown on different models the degree of adjacent reentrant loops ranges from 74 to 80%. The value $\nu_A = 78\%$ obtained in the present publication using a different approach confirms this result.

The portion of tie chains at $a = 100$ Å and $R/L = 0$ equals $\nu_T = 10\%$. It is nearly three times as big as that in Gambler's ruin model (3% at $a = 100$ Å). With a decreasing

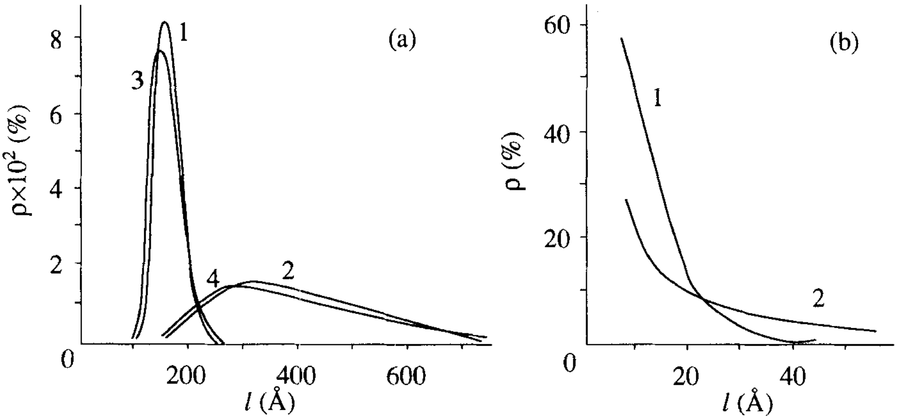

FIGURE 4 Length distributions. (a) Tie chains. (b) Loops (including regular folds). $a = 100$ Å, $d_a/d_c = 0.85$. $R/L = 0.4$ (curves 1, 3), $R/L = 0$ (curves 2, 4), $T = 273$ K (curves 1, 2), $T = 413$ (curves 3, 4).

a this portion grows slower than in Gambler's ruin model (Figure 3b).

As R/L increases due to polymer drawing, the portion of tie chains also grows almost linearly at $R/L > 0.2$. This result is in good agreement with the experimental almost linear dependence of the polymer strength on the drawing ratio.[4,5]

It is noteworthy that at $R/L > 0.2$ any chain segment portion does not actually depend on a.

As distinct from References 15, 16 our model does not predict a pronounced relationship between the parameters of molecular morphology of amorphous region and crystallite thickness c and temperature T.

Figure 4 demonstrates the form of the length distribution of tie chains and loops, their dependence on the ratio R/L and temperature T. Figure 5 shows the average length of tie chains and loops (including regular folds) as a function of a for various values of R/L. For tie chains all the given relationships (Figure 5a) can be approximated with sufficient accuracy by the formula

$$\langle l_T \rangle = \mu a^{\kappa}. \tag{12}$$

Coefficients μ and κ depend on the ratio R/L (see inset in Figure 5a). At $R/L = 0$, index κ is equal to 1.7. In Gambler's ruin model, the average length of tie chains is proportional to a^2. Thus, with the same value of a, our theory predicts a smaller value of the average tie chain length than the one obtained from Gambler's ruin model. For instance, at $a = 100$ Å, l_T is twice as small in our theory as that in Gambler's ruin model.

The mean-square deviation for tie chains length Δl decreases rapidly as R/L increases. According to the experimental data[2,18] Δl for highly drawn polymers is less than 10% of the amorphous region thickness. Our theory predicts such values of Δl at $R/L > 0.8$.

The average length of loops $\langle l_l \rangle$ decreases and its dependence on a disappears as R/L increases. At $R/L > 0.5$ $\langle l_l \rangle$ is less than twice as long as the regular fold.

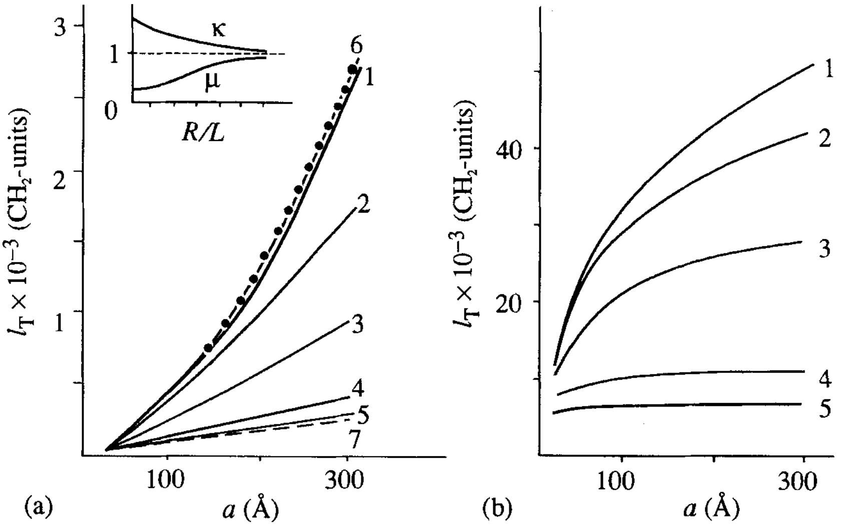

FIGURE 5 Dependences of average length of chain segment on a at various R/L. $T = 360$ K. (a) Tie chains. (b) Loops (including regular folds). $R/L = 0$ (curves 1, 6), $R/L = 0.1$ (curves 2), $R/L = 0.2$ (curves 3), $R/L = 0.5$ (curves 4), $R/L = 0.8$ (curves 5), $R/L = 0.9$ (curve 7). $d_a/d_c = 0.85$ (curves 1–5), $d_a/d_c = 1$ (curves 6, 7). The inset presents dependences of parameters μ and κ on R/L.

CONCLUSION

(i) The theory affords a solution to the problem of molecular morphology of the amorphous region both in isotropic and highly drawn polymers. It is based on the assumption that molecular morphology corresponds to a minimum of the total free conformational energy of chain segments in the amorphous regions, provided the thickness of crystallites c and amorphous regions a, the degree of macromolecule extension R/L and the densities ratio d_a/d_c are given parameters.

(ii) Detailed information on dependencies of tie chains, loops and folds portions on a and R/L is obtained. These dependences are qualitatively similar to those of Gambler's ruin model (in its isotropic and anisotropic variants), though there are considerable quantitative differences.

(iii) The Monte-Carlo calculation of local density distribution within the amorphous region was carried out. It was shown that the concept of interfacial layer between the crystallite and the amorphous region should be introduced into the theory to avoid density excess in the vicinity of the crystallite surface. Within interfacial layer conformations of long chains were limited. The optimum thickness of the interfacial layer was found to be equal to 3 CH_2-units. The introduction of the interfacial layer considerably affects the portions of adjacent and random reentrant loops and their dependencies on a and R/L.

(iv) The value obtained in the theory for portion of adjacent reentry (78%) confirms the agreement reached in this field.

(v) The predictions of a linear dependence of the tie chains portion on the degree of the macromolecule extension R/L and values of mean-square deviation of tie chains length distribution at high values of R/L correspond satisfactorily to the available experimental data.

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