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## Macromolecular Nanotechnology

## Bottom-up self-organizing dissipative polymer nanostructures



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## ABSTRACT

Based on scaling concepts a methodology of research of non-equilibrium polymer systems has been elaborated. Polymers with flexible chains (melt-crystallized linear high density polyethylene is chosen as an example) are solutions in melt as well as in solid state, the ends of a chain serving as a solvent for it. At critical polymerization degree all phases (melt, solid isotropic or oriented state) are identical. The square of the neck draw ratio is equal to the product of the square of the draw ratio at break and the chain ends collision probability. This probability in its turn is proportional to the average thickness of amorphous layers in the isotropic material. Depending on the type of polymer statistics (Gauss or Lévy–Khinchin) and the number of components of an ordering field for the second case, the melt viscosity and the self-diffusion coefficient vs. the molecular weight of linear flexible-chain polymer follow the power laws with the 3.50, 3.41 or 3.33 and  $-2.50$ ,  $-2.05$  or  $-1.65$  exponents, respectively, within the reptation model near the critical point. Vibrational–rotational Brownian motions of chain ends about the polymer melt flow direction were taken into account to find better agreement with the experiment. The recent experimental results of dynamic mechanic and dielectric spectroscopy show the value  $3.5 \pm 0.1$  for the viscosity exponent of long chains, while NMR data result in  $-2.3 \pm 0.1$  for the self-diffusion coefficient exponent of short chains. Possible reasons are discussed.

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## 1. Introduction

The quantitative relationship of structural and macroscopic characteristics (respectively, an average thickness of amorphous layers and draw ratios at neck and at break) is revealed in linear melt-crystallized (MC) polyethylene (PE). This acquires a great significance for modern chemical nanoengineering when it is necessary to understand clearly how to obtain functional nanostructures in order to prepare the material with sought properties by self-organization and self-assembly. The model is associated with such phenomena as drawing polymeric materials and dissipating the energy during the transition from isotropic to oriented state.

It has been revealed experimentally [1] that the neck draw ratio, i.e. the ratio of initial cross-section area to final,

$\lambda_n$ , in linear MC PE decreases with increasing the mean-weight molecular mass,  $M_w$ , as  $\ln \lambda_n = A - \beta \ln M_w$  where  $A$  is a positive constant and  $\beta \approx 0.3$  is the critical exponent of the fluctuation theory of the second order phase transition (PT). It has been also shown [1] that the transformation to the oriented state is the first order PT forming 3 stages: swelling the polymer under applied stress, dissolving crystallites and crystallizing extended macromolecules. From these data one can suppose that no drawing will occur ( $\lambda_n = 1$ ) if the polymerization degree (the number of chain monomers per one macromolecule, PD) is more than a critical value,  $N_{cr}$ . Otherwise, the Helmholtz function of oriented state is less than the Helmholtz function of isotropic state [1] if  $N < N_{cr}$ .

The reptation model [2–4] suggested by de Gennes in 1971 describes the polymer melt viscosity dependence,  $\eta(N)$ . The reptation theory explains why the power law for the melt viscosity relation to the molecular weight of polymer can be observed. However, this is not fully

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supported by the experimental data where the exponent is equal to 3.3–3.4 or even is out of the range compared to the theoretical value of 3. In order to achieve a better agreement with the experiment one may assume that the length of the tube created by entanglement chains, along which a macromolecule can crawl making the reptation motions, can be subjected to fluctuations [3]. Wool [5] obtained a similar result using a different concept. Other attempts have been aimed at modifying the constitutive equations [6,7]. They still continue [8–10]. Similar techniques [8] are believed to be applicable to study more complex systems such as phase-separate polymer solutions, blends, block and graft copolymer mesophases and other fluids. However, in such approaches the number of monomers between neighbor entanglements along the chain,  $N_e$ , is introduced phenomenologically or ignored completely. Moreover, the Monte Carlo results [11] have shown that reptation motions prevail in melts where entropic trapping is absent in contrast to swollen gels [12]. At last, there are models [13,14] in which an exponential increase of the reptation time with increasing PD can be observed if the polymer chains are long enough  $N > N_g^3$ . Thus, the questions dealing with polymer melt viscosity and entanglements have been extensively discussed [8–10,13–19]. This indicates that the problems still exist although the entanglement concentration has been already estimated [5,20].

One of aims of the article is to construct a solution in such a way that would enable to achieve a good agreement with the well-known experimental data within the classical reptation model [2] without any additional simplifying assumptions.

The structure of the article is following. We will define the critical PD or the critical point [1,20–22]. Then we will recall the main principles of the reptation theory [2–4] and try to understand what ways can be used to modify the theory. We will demonstrate that it should be introduced a mechanical field. In that case, the vector connecting the ends of a marked chain can make a vibrational–rotational Brownian motion about the direction of polymer melt flow. Finally, we will obtain a good agreement with the experimental data using the modified reptation theory. Then we will compare correlation radii of concentration fluctuation above and below the melting temperature near the critical point,  $N_{cr}$ . They will be found approximately equal; this would further confirm our theory. Physical clarity of underlying concepts makes this approach very attractive in understanding and explaining the nature of energy dissipation in polymer systems.

## 2. Results and discussion

### 2.1. Calculation of critical polymerization degree

It has been found [20] that the ordering parameter can be defined for the chain with excluded volume as  $w^2 = (B/C) N^{-2\beta}$  and  $w_{cr}^2 = (B/C)^2$  at  $N = N_{cr}$  where  $B \approx 0.2068$  is the constant for the Lévy–Khinchin probability density distribution (PDD) [23],  $C \approx 2842.45$ ,  $C/B \approx 13744.9$ , the

number of components of ordering field [24]  $n = 0$  for the Wilson  $\varepsilon$  – expansion [25]. If we determine

$$\lambda_n^2 = w^2/w_{cr}^2 = (C/B)N^{-2\beta} \quad (1)$$

and use the value [1,20] of  $\nu = 1 - 6^{-1/2}$ ,  $\beta = 0.2998$  then  $\ln N_{cr} \approx 15.89$ . At  $N = N_{cr}$   $\lambda_n = 1$  and the oriented state cannot be observed. These conclusions agree with the results of work [1].

Obtaining (1) it has been assumed [20] that the form of swelling coil is not spherical since there is a fluctuation attraction between the chain ends owing to screening volume interactions. The mechanism of the interaction in polymer solutions [4] as well as in melts [26] was described.

Further let us use the Widom–Kadanoff relation [26]

$$\gamma - 1 + (1 - \nu d) = -2\beta \quad (2)$$

$\nu$  is the critical exponent of correlation radius,  $d$  is the space dimension. We define the mean magnetic correlation for a magnetic system connecting with polymer one [26]

$$\langle M(r_0)M(r) \rangle = (r_0/r)^{1+\zeta} \quad (3)$$

where  $\zeta$  is the critical exponent of ordering field and the following relationship is true [26]  $2\beta = \nu(d - 2 + \zeta)$ . Taking into account that at critical point the correlation radius [26]  $r \sim aN^\nu$  where  $a$  is the diameter of monomer we see from (3) that

$$\langle M(r_0)M(r) \rangle = (r_0/a)^{1+\zeta} N^{-2\beta} \quad (4)$$

We connect this magnetic correlation with  $\lambda_n^2$  (1).

Multiplying  $\nu^{-1} \ln(r_0/r)$  by the Widom–Kadanoff relation (2) we can find the exact thermodynamic equation

$$\langle M(r_0)M(r) \rangle = g_E(r)P_C(r) \quad (5)$$

where  $g_E(r) = (r_0/r)^{d-1/\nu}$  is proportional to the Edwards correlation function,  $P_C(r) = (r/r_0)^{(\gamma-1)/\nu}$  is the des Cloizeaux probability of collision of chain ends [26].

Multiplying  $\nu^{-1} \ln(n_0 r_0 / 100 a N^\nu)$  by the Widom–Kadanoff relation (2) we can obtain the formulae

$$P_C(r) = (\lambda_n / \lambda_{br})^2 = l_a / l_a^{cr} \quad (6)$$

where  $n_0 r_0 / 100 a = (C/B)^{1/(1+\zeta)}$  (compare with (1)),  $n_0 / 100$  is a constant,  $l_a$  is the average thickness of amorphous layer in isotropic material, these layers containing the ends of a marked chain, and

$$\lambda_{br}^2 = (n_0 / 100)^{d-1/\nu} N_{es}^2 N^{1-\nu} \quad (7)$$

$\lambda_{br}$  is the draw ratio at break. If  $n_0 = 18.5$  then  $r_0/a \approx 6.6 \times 10^4$  and  $(18.5/100)^{d/2-1/2\nu} \approx 0.33$ ,  $N_{es} = (r_0/a)^{d/2-1/2\nu} \approx 1430.4$  is another constant, the dependence  $l_a \approx 0.5 l_K (100/n_0)^{(\gamma-1)/\nu} N^{\gamma-1}$  agrees with experimental data [1],  $l_K = 2$  nm is the Kuhn segment in linear PE,  $l_a^{cr} \approx 0.5 l_K (r_0/a)^{(\gamma-1)/\nu} \approx 26.9$  nm is the value of  $l_a$  at  $N = N_{cr}$ . These results (7) are also in accordance with experimental data [27].

We see that at critical PD the isotropic and oriented states are identical since there is no drawing. Consequently, at the melting temperature they are identical to melt [21]. Otherwise, the crystallinity has to tend to zero at the melting point. From this, at critical PD the Helmholtz functions of melt, isotropic or oriented state must be equal

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