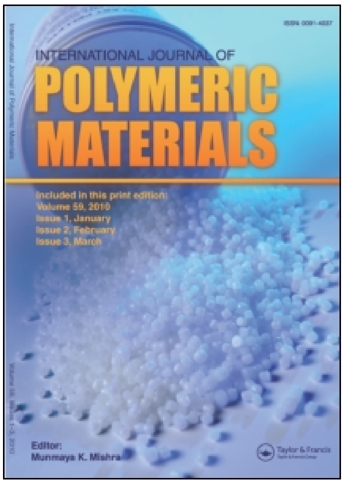

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# A Globule in a Stretching Field. The Role of Partial Melting During Drawing of Crystalline Polymers

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# A Globule in a Stretching Field. The Role of Partial Melting During Drawing of Crystalline Polymers

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The statistical theory of solid polymers (without a solvent) is presented. Such problems as the neck formation, the $\alpha$-relaxation transition, the calculation of the scale critical exponents are considered. The experimental data obtained are in excellent agreement with the theory. It is found that the dynamic properties of dilute polymer solutions in a good solvent are influenced by entanglement interactions. Therefore it is not necessary to introduce a new dynamic critical exponent. Ethylene-acrylic acids copolymers with the co-unit content *ca* 0.1 mol % and linear polyethylenes are studied by WAXS, SAXS, and infrared spectroscopy. Drawing and shrinkage behavior of these materials are also investigated. It is shown that the copolymer branches can be aggregated through intramolecular attraction. The entanglement concentration as revealed by SAXS and from shrinkage data is 0.07–0.08 mol % in high-oriented polyethylene.

KEY WORDS Drawing, scaling, entanglements, polyethylene, copolymer.

## 1. INTRODUCTION

Embedding of a small number of side groups in a linear polyethylene macromolecule gives some additional information about the structure and physical properties of both copolymers and polyethylenes to be extracted.

It has recently been shown that in ethylene-ethylacrylic acid copolymer (EEAA), which contained 0.1 mol % side groups as estimated by infrared spectroscopy (IRS), the branches are aggregated with the formation of a network.[1,2] The topology of the network as revealed by radiothermoluminescence (RTL)[1,2] influences the EEAA relaxation spectrum. Consequently, one can expect some differences in the deformation process of copolymers compared to linear polyethylenes.

The main purpose of the present study is to investigate the transition from isotropic to oriented state in ethylene-acrylic acid (EAA), ethylene-propylacrylic acid (EPAA) copolymers, in EEAA, and in linear PE.

## 2. THEORY

### 2.1. Model problem

Edwards was the first to successfully apply quantum mechanics methods to solve problems of polymer statistics.[3] Let us consider the behavior of a polymer globule in the stretching axial uniform field without a solvent. It is assumed that the continuous spectrum can be observed. Neglecting the interaction potential we may get the one-dimensional equation for Green's function of $G$:[4,5]

$$\nabla^2 G + \frac{2d}{a^2}\left(E + \frac{fx}{T}\right) G = 0, \tag{1}$$

where $d$ is the space dimension, $a$ is the monomer diameter, $E$ is the "energy" of the globule, $f$ is the force applied, $x$ is the coordinate, one of the polymer chain ends is fixed at $x = 0$; $T$ is the temperature in energy units. The equation is solved[6] by substitution of another variable, $X$, for $x$:

$$X = \left(x + \frac{ET}{f}\right)\left(\frac{2df}{a^2T}\right)^{1/3}. \tag{2}$$

We write the solution, finite for all $x$ (at $X \to +\infty$), as

$$G = \frac{A}{X^{1/4}}\sin\left(\frac{2}{3}X^{3/2} + \frac{\pi}{4}\right), \tag{3}$$

where $A$ is a normalizing coefficient. The following expression for $A$ is obtained by Landau's normalization method[6]

$$A = (2d)^{1/3}\left[\pi a\left(\frac{fa}{T}\right)^{1/3}\right]^{-1/2}. \tag{4}$$

Substituting $r/a$ for $(fx/T + E)/(fa/T)^{(3-d)/3}$ and $N$ for $X$ in (2), we obtain the expression

$$r = (2d)^{-1/3} N a \left(\frac{fa}{T}\right)^{(d-1)/3} \tag{5}$$

which coincides with the solution received for the drawing of an isolated chain in a good solvent[4] (here $N$ is the number of chain monomers, $r$ is the end-to-end distance).

## 2.2. Neck formation theory

Let us write the following equation for the applied force:

$$f = 6\pi\eta r v + mNv\frac{v}{r}\frac{nN_A}{p_N(a)V}, \tag{6}$$

where $\eta$ is the rate, $v$ is the drawing velocity, $m$ is the monomer weight, $p_N(a)$ is the probability of a neighbor location of the chain ends, $V \sim R^d$ is the "fluctuation" volume, $N_A$ is the Avogadro number, $nN_A$ is the number of monomers influenced by $f$. In order to take into account the fluctuation effects we choose the scaling relationships[4] for $\eta$, $p_N(a)$ and $R$:

$$\eta = \frac{\eta_0 c V}{N} \tag{7}$$

$$p_N(a) = \text{const}\, a^{-d} N^{1-\gamma-\nu d} \tag{8}$$

$$R = aN^{\nu}. \tag{9}$$

Here $c$ is local monomer concentration, $\gamma$ and $\nu$ are the exponents which depend only on space dimension. Substituting (7), (8), and (9) into (6), defining the neck draw ratio, $l_{\mathrm{n}}$, as $r/(aN^{1/2})$, where the value of $r$ should be taken from the condition $\partial f/\partial r = 0$, we find:

$$l_{\mathrm{n}} = BN^{-\beta}, \tag{10}$$

where the critical exponent, $\beta$, is expressed in terms of the well-known similarity laws[7] as:

$$2\beta = \nu d - \gamma, \tag{11}$$

and $B = [(nN_{\mathrm{A}} v a \rho)/(6\pi\eta_0\Phi^2)]^{1/2}$, $\rho$ is the polymer density, $\Phi = ca^d$.

## 2.3. Entanglement concept, $\alpha$-relaxation transition theory

We write Fisher's equation for the probability density of self-avoiding walks[8]

$$P_N(r) = \text{const}\left(\frac{r}{R}\right)^{\varphi} \exp\left[-\left(\frac{r}{R}\right)^{\delta}\right]. \tag{12}$$

Here

$$\varphi = \frac{0.5}{1-\nu} + \frac{1}{\nu} - d \tag{13}$$

$$\delta = \frac{1}{1-\nu}. \tag{14}$$

From the condition $\partial(F/T)/\partial r = -\partial[\ln P_N(r) + fr/T]/\partial r = 0$ we can obtain

$$r = R\left(\frac{(f + f_{\mathrm{add}})R}{T\delta}\right)^{1/(\delta-1)}, \tag{15}$$

where $F$ is the total energy of a chain,

$$f_{\mathrm{add}} = -\frac{\partial U}{\partial r} = \frac{\varphi T}{r} \tag{16}$$

is some additional force, $U$ is the interaction potential. If $f_{\mathrm{add}} = 0$ it is easy to find $\delta$. Comparing (15) and (5) we see that $\delta^{-1/(\delta-1)} \approx \delta^{-(d-1)/3} \approx (2d)^{-1/3}$ and

$$\delta = (2d)^{1/(d-1)}. \tag{17}$$

Now we may calculate the value of $\varphi$ from (13), (14), and (17), and conclude that $\varphi < 0$ for $d > 2$. It means that $f_{\mathrm{add}}$ counteracts $f$ when $d = 3$. We suppose that (self-) entanglements are responsible for the additional force and shrinkage of the test samples after the drawing is completed. From (16) one can obtain the expression for the shrinkage $l_{\mathrm{el}}$:

$$\ln l_{\mathrm{el}} \approx \frac{\sigma}{E} = \frac{U(T)}{T} = \frac{U_0(T)}{T} - \varphi \ln r = \frac{U_0(T)}{T} - \varphi \ln a - 0.5\varphi \ln N, \tag{18}$$

where $\sigma$ is the stress, $E$ is the elastic modulus. We assume that the temperature dependence of entanglement interaction or $U_0 = U_0(T)$ is the $\alpha$-relaxation transition.

## 2.4. Computation of the critical exponents at $d = 3$

It should be expected that $p_N(a)$ is connected with the entanglement interaction. We write the following equation for the probability of the binary collision:

$$N^{-1}V(a^3N)^{-1} = \frac{p_N(a)}{(VN^{\nu\varphi})^{-1}}. \tag{19}$$

From (13), (14), (17), and (19) we determine $\gamma$, $\varphi$ and $\nu$ for $d = 3$

$$\gamma = -\frac{5}{2} + \frac{6}{\delta} + \frac{\delta}{2} = 1.1742 \tag{20}$$

$$\varphi = \frac{\delta}{2} + \frac{\delta}{\delta - 1} - 3 = -0.0854 \tag{21}$$

$$\nu = 1 - \delta^{-1} = 1 - 6^{-1/2} = 0.5918. \tag{22}$$

Critical exponents can also be calculated within the framework of the fluctuation theory of phase transitions.[9] The second order $\epsilon$-expansion results in $\nu = 0.5918$ and $\gamma = 1.1758$ in the case of 3-dimensional space. From (11) we find

$$\beta = 0.3006. \tag{23}$$

## 2.5. Dynamic scaling problem

Let us take the following equation for the true stress:

$$\sigma = \frac{2\eta v/l_0}{1 + vt/l_0} \approx 2\eta s \Phi_0 l^{-1}, \tag{24}$$

where the viscosity $\eta$ is expressed by means of (7), $l_0$ is the initial length of the sample, $vt = ll_0$ is the sample length at time $t$, $l$ is the draw ratio, the microscopic velocity gradient $s$ is proportional to $v/l_0$, $\Phi_0 = Na^3/r^3$, $r = aN^{1/2}$. We use the equation for the draw ratio:

$$l = l_\mathrm{f} l_\mathrm{el}, \tag{25}$$

where $l$ and $l_\mathrm{f}$ are the draw ratios prior to (under stress) and after shrinkage, respectively, and $l_\mathrm{el}$ is elastic component after drawing. It is difficult to experimentally extract the entanglement interactions in the case of dilute polymer solution in a good solvent. Therefore, we introduce the entanglement contribution in expression (7) for the viscosity and obtain $\eta_\mathrm{e} = \eta/l_\mathrm{el} = \mathrm{const}\, N^x$ using (9), (18), (21), (22), (24), and (25). Here

$$x = \nu d - 1 + \nu\varphi = 0.7247. \tag{26}$$

Thus, our theoretical speculations show that it is not necessary to introduce a new dynamic critical exponent.[4] One can explain some experimental results[4] in terms of the conventional scaling concepts, provided entanglement interaction does take place.

TABLE I
Molecular and structural characteristics of polymers ($M_w/M_n$ = 3.0–3.5 in all polymers)

| Sample | MFI (g per 10 min) | $M_w \times 10^{-3}$ (kg kmol$^{-1}$) | $K$ (%) | $L_l$ (nm) | $\langle l_c \rangle$ (nm) | $T_m$ (°C) |
|---|---|---|---|---|---|---|
| EEAA | 3.01 | 105 | 66 | 20 | 13.2 | 133 |
| EPAA | 2.07 | 125 | 63 | 22 | 13.9 | — |
| EAA | 0.21 | 250 | 58 | 20 | 11.6 | 132 |
| PE1 | — | 35 | 68.5 | 20.5 | 14.0 | — |
| PE2 | 1.20 | 155 | 61 | 21 | 12.8 | 134 |
| PE3 | — | 300 | 58 | — | — | — |
| PE4 | — | 800 | 53 | 24 | 12.7 | — |

## 3. EXPERIMENTAL

EEAA as well as EAA and EPAA were prepared with the vanadium-based Ziegler–Natta catalyst.[10] The copolymers were partially neutralized. Polyethylenes (PE2 and PE4 in Table I) were synthesized under the same conditions. PE1 and PE3 were prepared with a Ti+Mg-based catalyst.[11] The molecular weight was characterized by the melt-flow index (MFI). The MFI of PE correlated to $M_w$ obtained by GPC. The $M_w$ of copolymers was estimated from the polyethylene relation of MFI to $M_w$. No dependence of the studied physical properties upon the bulk size of co-units was observed in the copolymers.

Isotropic sheets of 1 mm thick were prepared by compression of the reactor powders at 175°C and the subsequent quenching in an ice water bath. Dumb-bell samples with the gauge dimensions $5 \times 2$ mm were cut from the sheets and drawn at cross head speed of 10 mm min$^{-1}$. The draw ratios obtained were determined from the spacing of ink marks applied to the samples prior to drawing.

The crystallinity $K$ was measured by WAXS and IRS. The lamellar long spacing $L_l$ was obtained from the SAXS data after the Lorentz-factor correction.[12] The lamellar thickness of $\langle l_c \rangle$ was estimated from the product of $K$ and $L_l$. The length of the amorphous region $\langle l_a \rangle$ was found from the difference of $L_l$ and $\langle l_c \rangle$. The melting temperatures (DSC, 20°C per min) are given in Table I together with other structural and molecular characteristics.

## 4. RESULTS AND DISCUSSION

The structure of amorphous regions in isotropic samples has been studied by WAXS, SAXS, RTL and IRS.[1,2] There are side polar groups in the vicinity of the folded chain surfaces of crystalline lamellae in the copolymers. The densities of both crystalline and amorphous regions do not practically change compared to PE.

The average lamellar thickness of $\langle l_c \rangle$ is equal to 12.8±1.3 nm for all polymers. The following dependences of $K$ and $\langle l_a \rangle$ on $M_w$ are observed for the copolymers and polyethylenes: $K = (1.20 \pm 0.04) - (0.049 \pm 0.005)\ln M_w$; $\ln(\langle l_a \rangle/(2 \pm 1)) = (0.17 \pm 0.06)\ln M_w$. (In this and following relations the values of $l_a$, $l_n$, $l_{el}$, and $M_w$ are dimensionless).

It is likely that the aggregates of the side groups hinder the development of Peterlin's plastic deformation[13] in the copolymers. Therefore it has been recently assumed[14] that the local melting of crystallites takes place during yielding and the subsequent drawing of

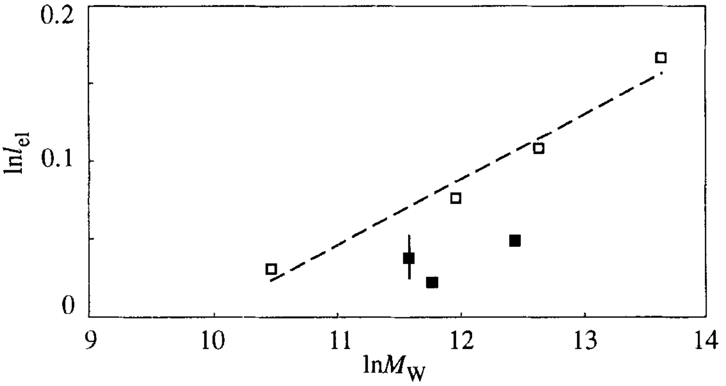

FIGURE 1 The shrinkage of the neck drawn samples at 20°C as a function of $M_w$. Copolymers (■), linear polyethylenes (□). The vertical bar corresponds to the value of experimental errors.

the materials. In this case, being an analog of MFI, the neck draw ratio of $l_n$ has to be proportional to the weight of the 'melted' material and hence to depend upon $M_w$ to the $n$-th power where $n = -(3.3\text{–}3.4)$.

In PE, $l_n$ proved to decrease with increasing $M_w$ as $\ln l_n = (5.3 \pm 0.3) - (0.29 \pm 0.02)\ln M_w$ in accordance with (10), (23) and to be 7.6±0.3 in the copolymers. Thus, melting previously discussed in many publications[15–20] occurs in neither of the above cases. Since recrystallization phenomena are observed during the drawing,[14] the transformation to the oriented state is a phase transition.[21] It has been found that there are three transition stages: swelling of polymer under stress, dissolution of crystallites and subsequent crystallization of extended molecules.

Figure 1 shows the relationship of $\ln l_{el} \sim (0.0428 \pm 0.0012)\ln M_w$ for PE. The result is in excellent agreement with (18) and (21). The temperature of the $\alpha$-relaxation transition is 331 K provided $a = 0.127$ nm. $l_{el}$ tends to 1 at extrapolation to $M_e = 20\,000$. It is assumed that $M_e$ corresponds to the molecular weight of a chain segment between the neighboring entanglements of molecules. $M_e$ is five times larger than the critical $M_w$ at which the change of the exponent in the melt viscosity relation to $M_w$ is usually observed. In the copolymers $l_{el} = 1.035 \pm 0.015$.

The superlong spacings in drawn single crystal PE mats have recently been assumed to be of entanglement origin.[22] In order to observe the scattering from melt-crystallized polymers the drawing of oriented materials (the draw ratios were as high as 30) was performed under stress of 50–80 MPa and at 120°C.

The meridional SAXS curve for PE3 is shown in Figure 2. This curve reveals more than seven reflection orders. The superlong spacing calculated from the difference in the positions of the neighboring orders is 150 nm, hence the entanglement concentration is 0.08 mol %. This value is in accordance with the result obtained from $M_e$ (0.07 mol %). The single maximum at 8 arc min is observed in EAA. This reflex is related to the aggregates of the side polar groups (to the knots of the network). Owing to the intramolecular nature of the branch interactions the concentration of the knots calculated from the peak position is two times higher than that of the side groups. From the data obtained it is possible to estimate the longest crystalline segment in the direction of chains. This value is 150–180 nm for PE and 65 nm for EAA.

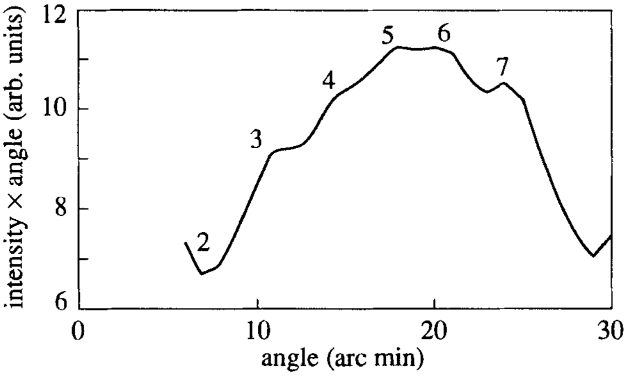

FIGURE 2 The meridional SAXS curve of PE3 in the region of the ordinary small-angle reflex; the reflection orders are numbered at the curve.

## 5. CONCLUSION

The transformation from an isotropic to an oriented state is connected with critical phenomena. We can see from Equation (10) that a neck draw ratio is equal to 1 when $N_{\mathrm{crit}} = B^{1/\beta}$. It means that the free energy of an isotropic state has a minimum of polymerization degree is more than $N_{\mathrm{crit}}$. Otherwise the free energy of an oriented state is less than that of an isotropic state. The experimental value of critical molecular weight for linear PE is $M_w = 87 \times 10^6$.

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