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Structure of the tie chains in oriented polyethylene: dependence of all-trans stem lengths on draw ratio

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By the Raman LAM experiments the length distributions of straight all-trans sequences were obtained for oriented polymers films of varied draw ratios λ. A shape of distribution function depended on λ and draw temperature as well: the higher λ the more long trans-stems could be observed in the oriented material. The experimental facts were matched to the results of the computer structure simulation based on 'stencil crystallization' model which was described previously[1]. Large deviation of experimental data from theoretical ones is discussed briefly. In essence, this deviation may be considered as a measure of superstructure imperfection of a real oriented polymer. © 1997 Elsevier Science Ltd.

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According to the current view, both a strength and an elastic module of semicrystalline polymers are determined by the amount of the taut chains in amorphous regions of microfibrils. In a perfect case, the taut chains should be a trans-zigzags placed between two crystallites as between two clamps. In a real polymer a tie chain coiled in unload state may contain gauche-conformers of opposite signs. Only if numbers of 'plus' and 'minus' conformers are equal, the tie chain can transform into perfect trans-stem on stretching. Otherwise the stress-induced annihilation of gauche-conformers would be incomplete and some conformational defects would exist in the straightened segment. Such defective taut chains can bear the load, but their module of elasticity should be expected to be lower than the modulus of the regular trans-zigzag.

Perfect trans-stems (TS) length distribution was determined by measuring the longitude acoustical modes (LAM) in a Raman spectrum[2]. The method is based on the fact that being LAM localized on the TS, their frequency (ν_L) depends on the TS length (L) as:

$$\nu_L = \frac{1}{2cL}\left(\frac{E}{\rho}\right)^{1/2} \qquad (1)$$

where $E = 370$ GPa is the Young's modulus along the chain direction in PE[3]; ρ is the density and c is the light velocity.

The TS length distribution is related to the Raman spectrum intensity via a function[2];

$$F(L) \propto [\exp(hc\nu_L/kT) - 1]\nu_L^2 I(\nu_L) \qquad (2)$$

in the case of anti-Stokes-scattering. Here T is the temperature, and I is the scattering intensity at a given Raman shift.

The low frequency Raman spectra were excited by an ion-argon laser and recorded with the help of a Spex Model Ramalog 5 triple spectometer.

The samples were films of the high-density PE ($M_w = 10^5$) drawn to different draw ratios (λ) at two temperatures 105 and 110°C. The samples characteristics are shown in *Table 1*. As defined by X-ray small angle diffraction all samples possessed the fibrillar structure with long period of 28 nm. *Figure 1* shows the original low-frequency Raman spectra (points) recorded in the region of LAM bands and the result of computer smoothing of these data (solid lines). Dashed lines represent the smoothed background curves that were determined as spectra recorded at the perpendicular that is XZ-polarization (cd-polarization in terms of Snyder *et al.*[2]). The distribution functions calculated from the smoothed spectra are shown in *Figure 2*. Value $F(L)$ is proportional to the number of TS whose length is in the range (L, $L + dL$). It is seen, that with the increase of the draw ratio, λ, from 7 to 20, the LAM band contour in the Raman spectrum and the corresponding TS length distribution profile undergo certain alterations.

The parts of the distributions lying to the right of the main dome are of particular interest because it is that region where the taut chains should give contribution. Coiled chains in the amorphous region may be considered as combinations of all-trans-sequences and kinks formed by gauche conformers[4]. Hence, some all-trans-stems in a crystallite region may be lengthened for account of the adjacent trans-isomers in amorphous regions.

Increase of long TS amount when draw ratio rises as clearly from *Figure 2* seems to be reasonable. It points to supermolecular structure improvement and is in accordance with n.m.r. data on length distribution of tie chains in amorphous regions[5,6]. Particularly sizable right wing in distribution one can see for the sample 4 (*Figure 2d*). In this case an appearance of new TS type was observed, namely, perfect TS passing through two crystallites and an amorphous layer between them. Such long trans-sequences denoted subsequently as 'through trans-stems' (TTS) must be about 45 nm in length and their number is proportional to part of the distribution area in a vicinity of this value. Let us assume as a rough estimation that attributed to TTS part of the distribution may be bounded by symmetrical dome-shape line with the center at 45 nm (dashed line in *Figure 2d*). Then the TTS portions (φ) relative to the total TS number are found to be about 3.5% for the sample 4, not more than 1% for the third one and negligibly small for other two samples.

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Table 1 Characterization of the samples.

Sample number	1	2	3	4
Draw ratio λ	7	15	20	20
Draw temperature (°C)	105	105	105	110
φ(%)	-	-	> 1	3.5

Table 2 Analytical data

β	λ_{cal}	< l > (nm)	α (%)	φ_{cal} (%)
0.16	4.8	524	3	0.4
0.38	11.4	186	8	3
0.56	16.8	121	30	17
0.69	20.7	110	52	32

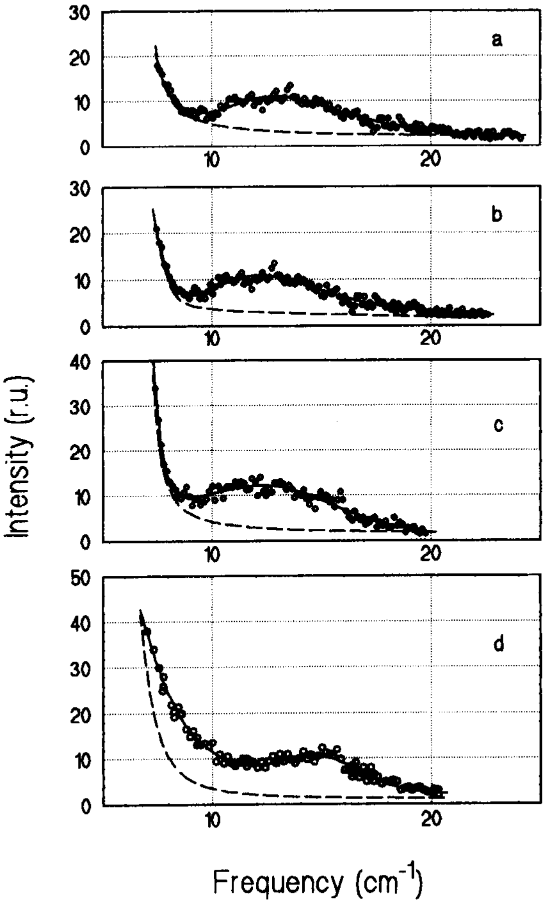

Figure 1 Low-frequency Raman spectra of PE films drawn under various conditions: (a), (b), (c) and (d) correspond to samples 1, 2, 3 and 4 in Table 1, respectively. Points are the experimental data; solid lines are results of their computer smoothing; dashed lines are the background curves

For analytical evaluation of TTS-part in oriented polymers in the perfect case, we shall use the data obtained in Ref. [1] with the help of a computer simulation method denoted as 'stencil crystallization'. In this method a chain of length R (much more than the long period length) is regarded. (Value of R was assumed to be 35 000 links[1].) The chain ends are fixed at a distance r one from another. Average degree of chain straightening, $\beta = r/R$, characterizes the orientation degree of a polymer. Supermolecular structure formation in the tensile force field was simulated in the following manner. For a given β, a chain of 'random' conformation is taken. This chain contains trans and ± gauche conformers which amount and alternation governed by a random number generator. Then a 'stencil' should be applied over the chain. This 'stencil' consists of a linear set of adjacent alternative 'windows' responding to crystalline and amorphous regions in microfibril: C-windows and A-windows, respectively. The windows sizes are chosen in accordance with the X-ray data for a real polymer. By computer-produced command 'Crystallize!' the straightened segments only should remain in C-windows. To do so a dangling segment occurred to be in a C-window must straighten and its length surplus has to be pushed into neibouring A-windows, what forcing the chains in the latter ones to become more coiled. Yet if the excess length is too long (the special criterion is used in the theory), the chain must form a fold (or folds) returning into the C-window and draw from A-windows some deficient links if it is need. Formation of folds in a crystal surface results in the smaller number of tie chains in adjacent amorphous windows.

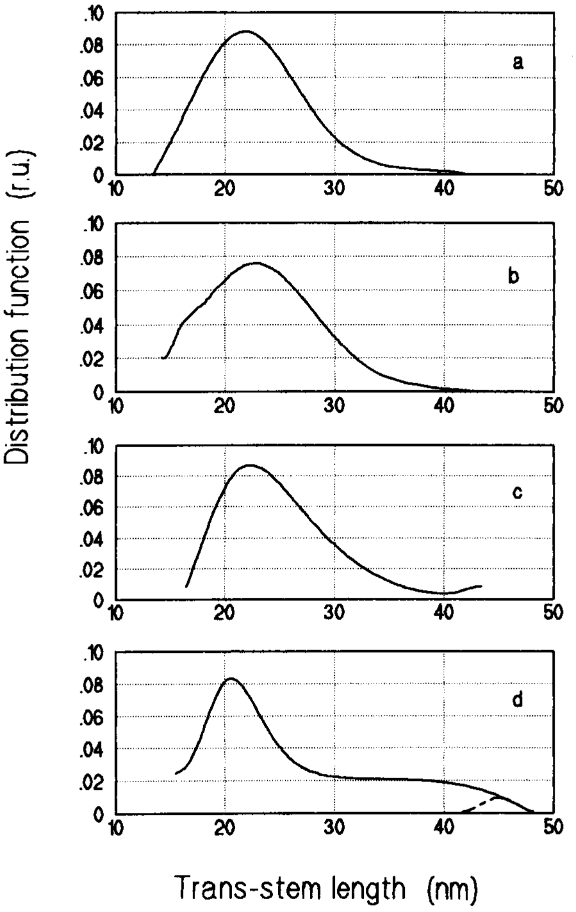

Figure 2 TS length distribution calculated from the spectra shown in *Figure 1* (symbols are the same)

Such procedure must occur over and over for chains with other random conformations but at constant β. In result the tie-chain length distribution, the part of the tie chains in dependence on the value of β, and also the average chain length < l > in the amorphous regions may be obtained theoretically. The distinctive feature of the 'stencil' model is that the long non-interrupted chains are used for the theoretical superstructure building, what is adequate to a real draw process. A specific difficulty may often take place if one seeks to fine a correlation between theoretical orientation parameters and a real draw ratio λ. We have solved this problem as follows. During orientational drawing of isotropic semicrystalline polymer with original spherulite structure, the spherulites transform into microfibril wisps[4]. To evaluate relation between real value λ and theoretical β, let us assume that each microfibril is formed from the part of isotropic spherulite. The volume of this part should be equal to the volume of the microfibril and its size (diameter of the corresponding sphere, D) should be taken as a microfibril dimension in unoriented state, i.e. at $\lambda = 1$. Let us accept a microfibril contains $N = 10^3$ chains in its cross-section and there are 3.5×10^4 links in every chain as in Ref. [1]. Then the theoretical draw ratio λ_{cal} turns out to be connected with the average degree of straightening β by the following relation;

$$\lambda_{\mathrm{cal}} = R.\beta/D = [(\pi R^2)/(6.sN)]^{\frac{1}{3}} \times \beta = 30.\beta \qquad (3)$$

where $s = 25\ \mathring{A}^2$ is the average efficient cross-section of a PE chain. Denoting longitudinal dimensions of the amorphous layer as d_a, and densities of crystal and amorphous regions as ρ_c and ρ_a,respectively, one can determine a part φ_{cal} of the through trans-stems in relation to the number of the chains in a crystal cross-section;

$$\varphi_{\mathrm{cal}} = \alpha[(\rho_a/\rho_c)(d_a/ < 1 >)]100\% \qquad (4)$$

Here α is the part of completely straightened taut chains in the amorphous layers and $d_a = 80$ nm as it was taken in Ref. [1].

Table 2 summarizes the results of simulation. Magnitudes of λ_{cal} and φ_{cal} are calculated with equation (3) and (4), respectively, for different β, the quantities in columns 1, 3 and 4 are taken from[1] ratio ρ_a/ρ_c is assumed to be 0.85. One can see the TTS parts observed experimentally are considerably less than calculated ones (cf. *Tables 1 and 2* data). The reasons of these distinctions we are going to discuss in detail subsequently.

Here we note only two reasons.

(1) The stencil crystallization model was considered as a standard of the 'perfect' supermolecular structure. A real polymer structure could be far from ideal. Therefore, it is hardly surprising that experimental values of φ are less than theoretical ones. Difference of $(\varphi_{\mathrm{cal}} - \varphi)$ may be regarded as a measure of structure imperfection for a real polymer. The cause of such imperfections may be conditioned by defects in initial materials and/or by not the best draw conditions. The experimental results provide support for the letter conjecture: for samples 3 and 4, drawn to the same ratios, values φ are distinguished significantly. It seems likely that micro-Brownian chain mobility becomes retarded at large draw ratios as a result of 'mechanical vitrification'[5]. As a result of this phenomenon further drawing of virtually vitrified polymer without disturbances becomes hard. But even small increase in temperature leads to compensation of mechanical vitrification and to improvement of supermolecular structure in sample 4.

(2) In fact, the stencil model corresponds to an oriented polymer being also under action of tensile stress (as during real drawing process). In this work the theoretical data matched to results of the experiments with unloaded specimens, but one can expect an increase of TTS numbers under load. Indeed, such fact has been observed: in tentative experiments we have recorded a rise of TTS amount depending on elastic deformation. This effect will be taken into account in further investigations.

Mechanical properties of oriented polymers depend in large measure on amorphous layers structure[4]. In this work more attention was focused only on the fully straightened tie taut chains. Investigation of flexible tie chains length distribution can be carried out by n.m.r. methods[5]. However specific information about dangling tie chains is contained in $F(L)$ function contours as well because a shorter trans-segment may be a part of such chains. We are going to use Raman LAM spectroscopy in combination with n.m.r. to study of non-crystalline micro-regions in real 'imperfect' polymers in connection with their mechanical properties.

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