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Elastic moduli of highly stretched tie molecules in solid polyethylene

Zdenko Špitalský, Tomáš Bleha*

Department of Molecular Thermodynamics, Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 84236 Bratislava, Slovak Republic

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Abstract

The elastic properties of interlamellar bridges in semicrystalline polyethylene (PE) were estimated from the molecular-mechanics calculations on the assumption that the energy loading of a chain backbone represents the principal deformation mechanism. The calculations result in the force–length functions featuring abrupt discontinuities due to sequential annihilation of the defects by the conformational transitions. The correlation of the chain elastic moduli E with the concentration of defects in the chain and with the chain extension ratio x were established. The distribution functions $\zeta(E)$ of Young's moduli of interlamellar bridges in semicrystalline PE were calculated by using the literature data on the chain length distributions of tie molecules. The impact of the distribution function of moduli $\zeta(E)$ on the overall elastic response of solid PE materials was examined, particularly in cases of the stacked lamellae morphology involving so-called hard elastic PE.

Keywords: Interlamellar phase; Mechanical properties; Semicrystalline polymers

1. Introduction

Molecular description of elasticity of semicrystalline polymers is of considerable importance due to technical and biological applications of a variety of such materials, ranging from thermoplastics such as polyethylene to biological fibres such as spider silk. On a molecular scale the structure of semicrystalline polymers can be approximated as consisting of two phases: crystalline regions and a noncrystalline matrix material. The quantitative modelling of mechanical properties of semicrystalline polymers is not a straightforward task because of the complexity in their structural and morphological hierarchy. Still, in recent years the theory and modelling provided new insights on the molecular mechanisms underlying the deformation of these materials [1–7]. The elastic properties of crystalline phase, typically consisting of thin crystal lamellae formed by folded chains, can be fairly well predicted [8]. According to the current view the Young's elastic modulus and the strength of semicrystalline polymers are primarily affected by the structure of quasi-amorphous interlamellar (IL) regions where several types of molecules, such as loops, which start and end in the same lamella, tails with one free end, and bridges (tie molecules) which join up two lamellae, can be distinguished.

Tie molecules that traverse the noncrystaline regions play a central role in transferring stress effectively from one lamella to the next when strained. Thus, the various models of deformation of semicrystalline polymers [9] are in large part focused on the properties of tie molecules, especially in polyethylene (PE). The concentration of tie molecules interconnecting crystallites in an undeformed solid PE can be estimated from the chain dimensions and the lamellar microstructure [10,11]. During tensile drawing of PE the spherulite-lamellar morphology of semicrystalline polymers is transformed into an oriented fibrous structure [9]. On drawing, tie molecules are pulled out and become more taut and the entire amorphous regions more oriented. In PE at high drawing ratios the intrafibrillar taut tie molecules involve long (zig-zag) sequences of all-*trans* bonds. It was argued that the fraction of the load-carrying taut tie molecules determines the elastic modulus of PE fibrils and of ultra-high molecular weight PE fibres [9,12].

Detailed atomistic modeling of elasticity of extended tie molecules in the noncrystalline IL phase is usually based on the axial mechanical loading of polymer chains containing the conformational defects [1,13–18]. In highly extended

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* Corresponding author. Tel.: +421-2-54777414; fax: +421-2-54775923.

E-mail address: upoltble@savba.sk (T. Bleha).

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tie chains the kink defects, involving coupled *gauche* bonds of opposite orientations, are assumed. In contrast, the uncorrelated *gauche* defects are supposed in the moderately extended PE molecules. The static potential energy of the selected PE tie chain stretched by an external axial force F was computed by the molecular mechanics (MM) (force-field) methods of different parameterisations [19,20]. The loading of the tight and slack interlamellar bridges by an external force is accompanied by an accumulation of the elastic energy into the chain. The calculations revealed that the transition of defect chains into more extended conformations proceed by abrupt changes of the deformation potential $U(R)$. A flip-flop interconversion of backbone torsional angles brings about a change from the shorter into the longer state and liberates the stored elastic energy. Abrupt discontinuities due the *gauche–trans* conformational transitions were established on the force–length curves $F(R)$ as well [17,18]. Sequential annihilation of the chain defects on stretching resulted in a sawtooth-like profile of the $F(R)$ curve of PE tie chains. It was argued [17] that the sawtooth-like profile is a common feature of mechanochemistry of bridging polymers with a restricted number of conformations, in the same way as in some biopolymers, where compact domains unfold on stretching.

The deformation response of specific conformers of a PE chain computed by the MM method is based on the energy changes only. Disregard of the entropy factor is entirely substantiated for highly extended tie chains. In addition, the energy-elastic deformation is crucial even in a fairly coiled tie chains under conditions of restricted thermal equilibrisation, due to a reduction in the chain mobility. This situation may happen when the conformation dynamics in the IL phase is either partly blocked by neighbouring macromolecules or when the loss of entropy due to straightening of chains brings about their 'mechanical vitrification' at high deformations [16,21]. Then, the strain energy cannot be fully dissipated through conformational motions and should be at least partially stored in the tie chain backbone parameters. The entropy changes at deformations are fully accounted for in the traditional treatment of rubber elasticity by a statistical theory [22]. Similar type of statistical-mechanical averaging of all allowed conformations of tie molecules would only be appropriate for a purely amorphous IL phase. However, spatial configurations of tie molecules at high draw ratios substantially differ from ideal melt-like structure. Consequently, the energy-elastic functions of PE chains, ensuing from the single chain loading and from the statistical averaging, differ considerably [18].

The present paper is focused on the estimation of elastic properties of interlamellar bridges in semicrystalline PE under conditions where the energy loading of a chain backbone represents the principal deformation mechanism. The calculations result in the toothsaw-like profile of the force–length function. The longitudinal Young's moduli E of tight and slack tie molecules involving various conformational defects are calculated. An average modulus of the IL phase E_{IL} is evaluated for the chain length distributions of tie molecules $\tau(N)$ reported in literature.

2. Model and method

In a slit-like model of interlamellar (IL) phase (Fig. 1) the chains are spatially restricted by the presence of impenetrable surfaces of crystal lamellae. The slit width is given by the (undeformed) interlamellar layer thickness L_{IL}, and L_{c} denotes the thickness of crystal lamellae. The tensile force F, acting in the direction of the normal to the lamella, increase the IL layer thickness to $(L_{\mathrm{IL}})_d$. Four types of disordered chains are assumed: (a) tails with one free end; (b) loops, which start and end in the same lamella; (c) bridges (tie molecules) which join up two lamellae and (d) floating molecules which are unattached to any lamellae. Mechanical properties of the IL phase depend on the distribution of chains into all four categories. Still, it is believed that tie bridges threading the disordered IL are crucial for the transfer of stress between crystal lamellae. It is assumed that tie chains are firmly fixed to the lamella surface and no pull-out from the lamellae interior is allowed. Thus, the end-to-end length of tie molecules R is equal to layer thickness L_{IL}. However, individual tie molecules involve a different number of monomers N in dependence on their coiling, i.e. they are of different 'lengths' N. Tie chains shown in Fig. 1 may effectively represent also entangled loops and similar topological bridges that realize an indirect transmission of force between the lamellae.

Linear alkanes up to $N = 40$ carbon atoms served as models of PE tie molecules in the calculations. The distance of terminal C atoms was regarded as the length of a molecule, R. The length of defect molecules can be expressed relative to the contour length R_z of all-*trans* (T form) by the chain extension ratio $x = R/R_z$. Obviously, the contour length of the chain zig-zag $R_z(N)$ depends on the polymerisation degree N. The model molecules involved a variable number of coupled or uncorrelated *gauche* defects in a chain. The coupled defects comprise several three-bond

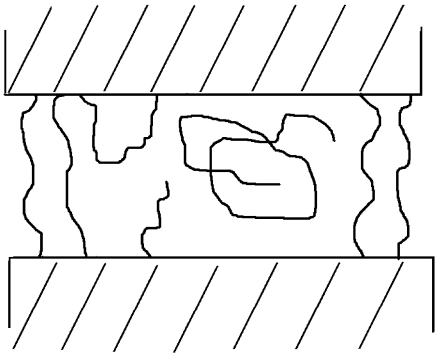

Fig. 1. Sketch of the different types of chains in the interlamellar phase of semicrystalline PE.

sequences g^+tg^- (the kink defects) or five-bond sequences g^+tttg^- (the jog defects). A rather high chain extension, typically of about $x > 0.85$, applies for these molecules assumed to occur as tight PE bridges in more ordered zones of the IL phase. For taut tie molecules the ratio x should approach unity. The uncorrelated *gauche* defects form more loose, 'slack' bridges of $x < 0.85$, typical for disordered zones of the IL phase.

The static potential energy of molecules involving conformational defects was calculated by the Allinger MM + molecular-mechanics method [20] by the procedure described in previous papers [17,18]. The static potential energy of a molecule U is expressed in the method as the sum of several contributions

$$U = U_r + U_\theta + U_\phi + U_{\mathrm{vdW}} \tag{1}$$

where the terms U_r and U_θ represent the bond length and bond angle deformation, respectively, U_ϕ is the inherent ethane-like torsional potential respecting the cosine type periodicity of torsion angle ϕ. The term U_{vdW} is a summation of all nonbonded pair interactions in the molecule. The individual energy terms in MM + methods are expressed by simple analytical functions involving numerous adjustable parameters. The parameters, specific for a given class of compounds, were determined [20] by fitting an extensive set of experimental data and optimised to give the best performance of the method. The MM + method provides reliable predictions of the structural and thermodynamic data of long-chain alkanes at ambient temperature.

A molecule was stretched by a gradual increase in R. An implicit deformation force F is collinear with the vector of the end-to-end distance R. The energy of a stretched molecule, almost rigidly constrained at given R, is optimised and the equilibrium static energy U and the valence parameters (torsional angles ϕ_i, bond angles θ_i and bond lengths r_i) are obtained. The force F and the Young's modulus E were computed as a function of the length R by the first and second differentiations of the static energy U according to R. The results obtained for chains of $N > 20$ were fully compatible with the previous data [17,18] for C_{20} models.

3. Results and discussion

3.1. Force–length relations in tie molecules

Stretching of PE tie chains containing the multiple defect bonds results in the energy potentials $U(R)$ exhibiting numerous discontinuous *gauche–trans* transitions [17,18]. Stretching favours the longer and more stable *trans* conformations. At the critical strains $\varepsilon_c = (R - R_d)/R_d$, where R_d is the length of an undeformed defect molecule, the chain undergoes an activated transition from a hypersurface of the deformed defect molecule into a hypersurface corresponding to another form with higher R_d. In this way, the conformational defects in a chain are sequentially annihilated on deformation. A common 'reaction' path, nearly independent of the stretching history and the chain length, was observed. The elastic energy accumulated in a strained molecule is released at the transitions.

The force–length functions $F(R)$ can be obtained by the differentiation according to R of the deformation potentials $U(R)$. In Fig. 2 the related functions of stress σ vs x are presented for two typical cases of tight and slack bridges. The axial chain stress $\sigma = F/A$ was computed by assuming $A = 0.1824\ \mathrm{nm}^2$ for the defect chain cross-section. This value of A corresponds to the zigzag PE chains packed in an orthorhombic crystal [1]. The cross-section A may be a slightly higher in molecules containing the numerous kink and *gauche* defects, however, the mentioned value of A was used to facilitate the comparison with the previous determinations of the PE chain moduli.

The stress–extension curves $\sigma(x)$ of the kink and the *gauche* defect chains, i.e. of tight and slack bridges, are

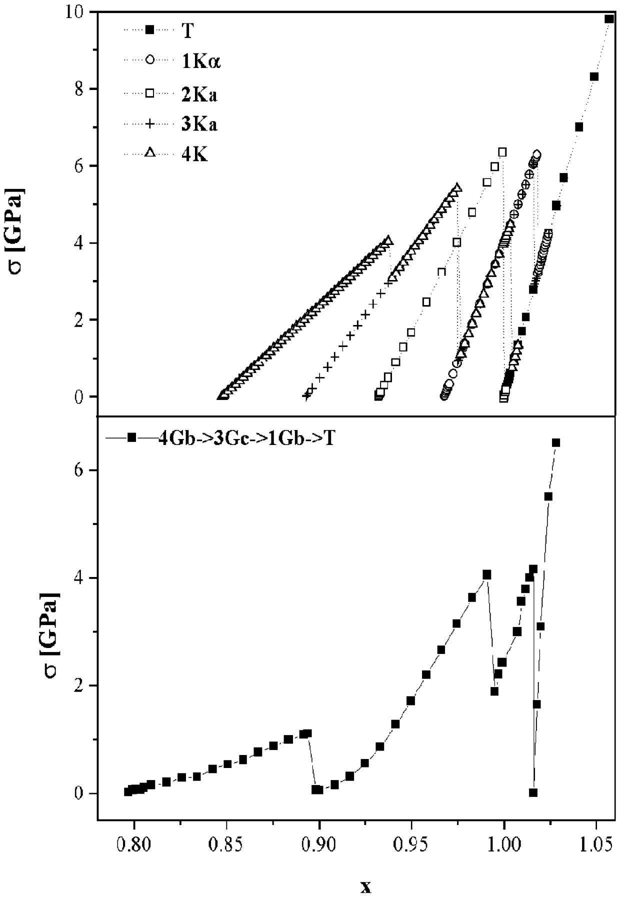

Fig. 2. Stress (σ)–chain extension ratio (x) curves of PE tie molecules. The upper panel: the transformation of a chain with four kinks (4K) into the three- two- and one-kink forms (3K, 2K and 1K, respectively) and subsequent stretching of the T form. The lower panel: the transformation of a chain with four random *gauche* defects (4G) into the 3G and 1G defect chains and to the T form by an annihilation of the *gauche* defects on stretching.

compared in Fig. 2. In the upper panel the transformation of a four-kink (4K) chain into the three- two- and one-kink forms (3K, 2K and 1K, respectively) and subsequent stretching of the ultimate T form is seen. In the lower panel a similar annihilation of the *gauche* defects on stretching is shown in a sequence from the four-*gauche* defect (4G) into the 3G and 1G defects and the final T form. The deformation of tight and slack bridges in Fig. 2 follows a common pattern. The stress–extension curves $\sigma(x)$ are divided into several portions by abrupt drops in stress. The individual portions of the $\sigma(x)$ curves of the kink chains are nearly linear whereas in *gauche* chains the deviations from linearity are evident. The segments of the $\sigma(x)$ curves become steeper after every elimination of the defect. A sawtooth-like profile of the function $\sigma(x)$ is noticeable particularly in the case of kink chains. The stress at the transition point σ_c represents the maximum load that a chain can bear prior to 'yielding' by a conformational interconversion. The tight bridges of chain extension $x > 0.85$ can bear the stress σ_c of about 4–6 GPa. Conversely, by the stress up to about 1.1 GPa, a quite sizeable elongation of the slack bridges can be achieved in the region around $x = 0.85$. A further extension of the tie chains stretched to their contour length R_z proceeds by the energy-elastic deformation of the bond lengths and bond angles. The portion of these overloaded tie chains of the chain extension ratio $x > 1$ increases by drawing of polymers up to the chain break.

Fig. 2 and previous data [17,18] show that conspicuous jumps in stress–strain curves are displayed when rather high forces are needed to achieve a conformational interconversion. The magnitude of forces is governed by the mechanical torque generated in the process and by the resistance of the chain backbone towards force-driven interconversions. In PE this resistance is evidently higher for kinks than for the *gauche* defects. Minor forces can be expected to activate interconversions in molecules featuring shallow minima in the backbone torsional potentials. In these cases it might be difficult to discern the discontinuities on $\sigma(x)$ curves.

Additionally, the elastic response of fairly extended chains depends on a choice of the length or the force as an independent variable in calculations. The MM method predicts a sawtooth-like profile of the force–length function only when R is used as the independent variable in so called R-fixed ensemble [23,24]. In a conjugated F-fixed ensemble, the force F is used as an independent variable and R is adjusted accordingly. The resulting length–force function $R(F)$ may show the jumps in the length analogous to jumps in force at the $F(R)$ curve [17]. Several consecutive jumps in the length in multidefect chains can amalgamate to a quasi-plateau on the length–force curve. Such a variability in the representation of elastic properties, from the sawtooth-like to plateau-like profiles was convincingly demonstrated [25] by AFM measurements of unravelling of compact single biomacromolecules. Apparently, one can picture the two interrelated mechanisms of a quasi-plateau formation on the force–length curves originated in an abrupt increase in the length of macromolecule: (a) the conformational interconversions into a longer conformations at the constant number of chain segments N, as described in the above MM calculations, and (b) an increase of effective number of segments N by their pulling out from a reservoir [26], such as by unwinding of the collapsed chains [27] or a globule [23] on stretching.

3.2. Young's moduli of tie molecules

The longitudinal Young's moduli E of the PE chains were calculated from the initial slopes of $\sigma(x)$ curves. The reference modulus $E_T = 185.4$ GPa of the all-*trans* T form was determined from the plot of E against $1/N$ for the chain lengths $N = 20–100$, by the extrapolation to an infinitely long molecule. Theoretical studies of the ultimate modulus of PE by the force fields and quantum chemical methods [28,29] resulted in a broad distribution of values of E_T. Still, it seems that the values of E_T of about 50% higher than the above MM + result prevail in the literature data. To eliminate this problem, the ratio E/E_T will be used henceforth since we are interested mainly in the influence of the defects on the chain modulus. This relative measure also suppresses uncertainties in the selection of a proper value of the chain cross-section A. Since stretching of the T-form in Fig. 2 follows the Hooke law, the ultimate value E_T calculated for $x = 1$ should also be appropriate for the overstressed tie molecules in the range of $1 > x > 1.1$. The chain modulus may start to diminish over x about 1.1, as molecules approach the limiting extension at break.

The moduli of PE tie chains determined from the initial parts of the stress–strain curves were correlated with the respective chain extension ratio x (Fig. 3). Ignoring some scatter of points the plot in Fig. 3 validates the notion that an introduction of a defect into the all-*trans* chain brings about a shortening of the molecule and a reduction of the modulus. The data in Fig. 3 can be fitted by the power-law expression

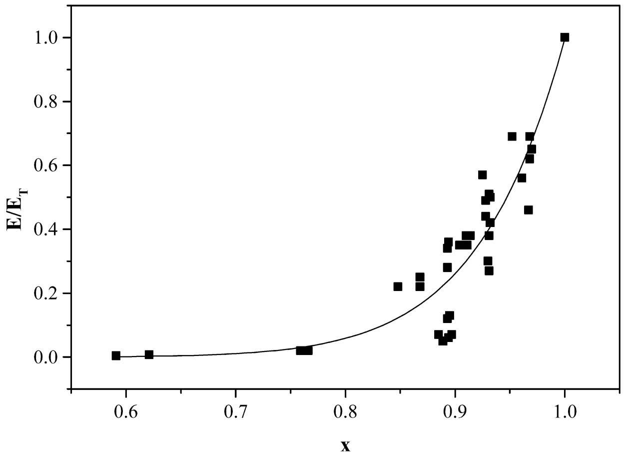

Fig. 3. Variation of the relative modulus E/E_T of PE tie molecules with their chain extension ratio x.

$E/E_T = 0.9952x^{12.694}$. Three regions can be identified in the plot: the low-module region ($x < 0.85$) where partly coiled chains involving uncorrelated multigauche chains are located, the high-modulus region ($x > 0.95$) formed by the highly extended kink defects and the region in-between ($0.85 < x < 0.95$). In this intermediate region mainly the chains with jog defects or with a high concentration of kink defects are situated. The calculated correlation E/E_T vs x shown in Fig. 3 should apply for tie molecules of any length N i.e. for any interlamellar thickness L_{IL} in solid PE.

The straightening of tie chains can alternatively be assessed by the chain orientation function P_2 defined as

$$P_2 = (3\langle\cos^2\theta\rangle_{av} - 1)/2 \tag{2}$$

where $\cos\theta = \mathbf{a}_i\cdot\mathbf{b}$ is given by the dot product of vectors. The vectors $\mathbf{a}_i$ are specified by co-ordinates of the first and fourth carbon atoms in the chain backbone ($x_{j+3} - x_j$; $y_{j+3} - y_j$; $z_{j+3} - z_j$) for each torsional angle ϕ_i. The chain-end vector $\mathbf{b}(x_n - x_1;\ y_n - y_1;\ z_n - z_1)$ defines the orientation of the force F. Averaging over all backbone torsional angles ϕ_i is carried out. At full parallel or antiparallel alignment of vectors $P_2 = 1$. From the MM data a linear proportionality $P_2 = -0.99 + 1.90x$ was established between the orientation factor P_2 and the extension ratio x. This proportionality underlies the correlation of the defect chain moduli and the P_2 factor reported earlier [18] that resembles the plot in Fig. 3. It should be noted that high values of x or P_2 imply an enhanced packing of tie chains and their ordering in the IL phase.

As a rule, the relative chain stiffness, given by the ratio E/E_T, decreases with the amount of defects in a molecule. However, a quantitative relation can be deduced from the calculated data only for the kink chains. The dependence of the relative chain modulus E/E_T on the increasing concentration of the kink defects $\phi = n_k 3/(N-1)$ in the molecule is shown in Fig. 4. The moduli of the defect chains can approximately be analysed [1,10] by assuming additivity of compliances (reciprocal moduli) of the mechanical elements in the chain, in line with the Reuss averaging [30]:

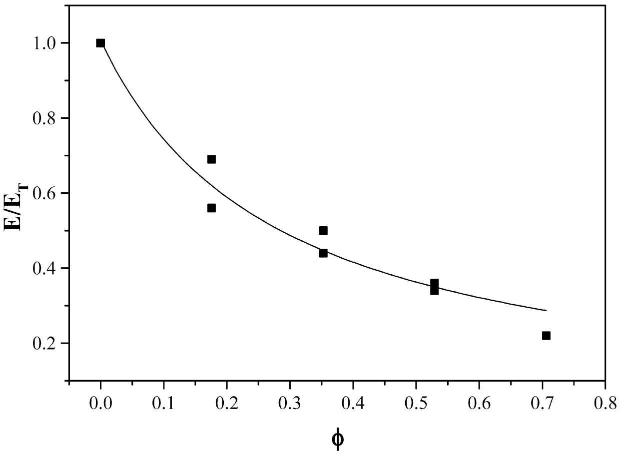

Fig. 4. Variation of the relative modulus E/E_T of tie molecules involving kinks with the fraction of the kink defects ϕ in the PE chain.

$$1/E = \sum \phi_i/E_i \tag{3}$$

The chain compliance E^{-1} for kink chains is given as a compositional average of the bare kink defect compliance E_k^-, pertaining to the three bond sequence *gtg*, and the compliance of the remaining all-*trans* portions of chains. Then, the Eq. (3) can be recast into the form

$$E/E_T = 1/[1 + (E_T/E_k - 1)\phi] \tag{4}$$

The data in Fig. 4 were fitted by the above equation and the fit yielded the ratio $E_k/E_T = 0.222$. Overlooking some scatter of points in Fig. 4 it seems that the additivity principle behind the Eq. (3) is fairly well obeyed in the kink chains. The bare kink defect is an element mechanically about four or five times softer than the all-*trans* T-form; the uncorrelated *gauche* defects are structural elements even much softer than the kink defects.

The computed reduction of the relative chain modulus E/E_T with an increase of the concentration of kinks is much slower than estimated earlier [1]. Originally, the modulus E (in GPa units) of kink chains was represented [1] by the equation $E = 2.6(N_t + N_g)/N_g$, where N_t and N_g are the numbers of *trans* and *gauche* bonds in a molecule. For 100% population of kinks in a chain this equation gives $E = 3.9$ GPa.

Previous calculations [15] by a different version of the MM method predicted a slightly lower relative modulus E/E_T around 0.5 for a single-kink PE chain. Majority of molecular-mechanics calculations so far were focused on the crystallographic defects [31,32]. These defects are associated with the diffusion, translation and rotation of molecules inside the PE crystals. The chain moduli in the range of 30–70 GPa were calculated for some six- or seven-bond defects [32]. In another set of eight defects, with the length of the defect regions up to 19 bonds, two groups of defects were distinguished: the moduli in one group were almost identical with the all-*trans* chain (around 177 GPa) whereas the moduli in the other group were by 25–40% lower than the all-*trans* chain [31].

The chain modulus E is proportional to the second derivative of the deformation potential $U(R)$, i.e. it depends on a steepness of ‘walls’ in this potential. This curvature (rather than the height of appropriate energy barriers) defines torsional stiffness of the defect bonds and controls the elastic response of a macromolecule. As seen from Fig. 2 the torsional stiffness of interconverting bonds in the multidefect PE chains increases on stretching; a higher modulus results by each annihilation of a defect. The curvature of the $U(R)$ potential may be affected by neighbouring molecules in the IL phase. In hypothetical case of the fully disordered IL phase, structurally resembling melts or amorphous networks, the deformation could be described by the molecular theory of rubber elasticity. According to assumptions in this theory [22] intermolecular interactions do not affect the chain deformation and the spatial configurations of chains in a melt are described by the conformational statistics of a single chain in the theta solvent. The single-chain Monte Carlo simulations provide a useful limiting description of the mechanics of tie chains in a supposed purely amorphous IL phase [18]. However, the conformational statistics of fairly extended tie chains in the IL phase of PE differ considerably from those in the ideal amorphous phase: sub-chains in the IL phase are much shorter than in a polymer melt and more oriented.

A possible influence of embedding molecules in the IL phase of solid PE on the functions of the relative chain modulus E/E_T shown in Figs. 3 and 4 was assessed roughly by the MM method using two simplified approaches: (a) by examining proper multichain systems or (b) implicitly, by assuming an additional constraining potential at the energy minimization. In employing the first approach two or three PE chains with a kink defect in the middle of each molecule were considered. Position of molecules was fixed by constraining the interchain distance of the terminal carbon atoms to an equilibrium value of $R_{int} = 0.44$ nm but leaving translational mobility unrestricted. At interchain distances smaller than R_{int} the chain centres protrude into a free space due to repulsive interaction. On the other hand, at larger R_{int}, the chains are bowed inwards in midpoints due to attraction interaction. Any deviation of R_{int} from the equilibrium value reduces the stabilisation energy U_{st} and brings about chain shortening and reduction of the P_2 factor.

The deformation potential calculated by simultaneous stretching of two or three PE chains with a kink defect in the middle of chain is shown in Fig. 5 up to the conformation interconversion. The single chain potential and its two and three-fold multiple are also included. Mutichain systems are stabilized by the energy U_{st} relative to a single chain. The conformational transition occurs in all systems at the the same value of ε_c. Multichain systems show a steeper increase in energy with distance than a single chain. However, when the multiple of the chain cross-section nA is allowed for in calculation of the stress–strain curve, this increase is found to be practically identical to an increase in the two and three-fold multiples of the potential, i.e. the modulus of the kink chain is about $E = 121$ GPa, regardless of the number of molecules stretched. This results are in line with the previous study [2] of thermomechanical behaviour of interacting tie molecules in PE which found negligible effect of chain–chain interaction on the force–displacement relation. The same result was regained [2] when interchain interaction in PE were modeled by enclosing a tie molecule in a tube which restricts the lateral motions of its atoms.

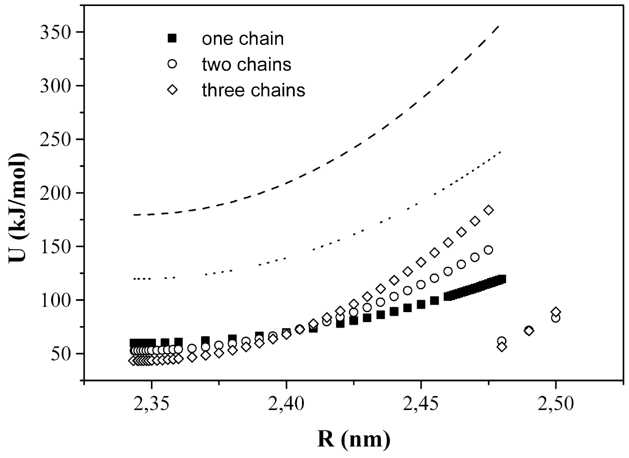

Fig. 5. The deformation potential of one, two and three molecules involving a central kink defect by their elongation to the length R. Dotted and dashed curves represent two- and three-fold multiples of the single-molecule deformation potential.

Furthermore, the influence of surrounding chains on the curvature of the $U(R)$ potential was tested indirectly, by a variation of the torsional constraining potential U_{cnst} that in the MM + method holds a molecule in a pre-selected *gauche* conformation during the energy optimisation. An increase in U_{cnst} may simulate an enhanced packing of neighbouring medium, in an analogy with a similar procedure used earlier [16]. The modulus of a kink chain calculated by assuming the high values of U_{cnst} was found to differ insignificantly from the value for an isolated chain. However, the *gauche–trans* interconversions are considerably hindered by an increase in the constraining potential U_{cnst}. It seems that the effect of local packing on the steepness of the $U(R)$ potential can be quite complex. For example, in a related problem of the rotational barrier of the methyl group in polymers [33] some barriers were higher in the solid state than in an isolated chain, but some barriers were lower. The primary effect of the packing interactions was to broaden the range of the barrier heights. At any rate, the dependence of the relative chain modulus on the chain extension ratio x shown in Fig. 3 should represent at least the lower bound of reality. In case that the chain packing effects actually rise the steepness of the $U(R)$ potential, the function in Fig. 3 will converge to higher values of the ratio E/E_T in the region of $x = 0.6–0.8$.

3.3. The moduli of tie molecules of variable lengths

Tie molecules represent only one of four categories of chains assumed in the IL phase (Fig. 1). Usually only a small portion of chains in the IL region belongs to this category, their population is defined by the number fraction τ. In the model assumed all tie chains must have the end-to-end span R identical with the width of interlamellar layer L_{IL}. However, the chain length, given by the polymerisation degree N, differs in individual tie molecules and the chain length distribution $\tau(N)$ has to be introduced. From such a distribution function the populations of the taut and coiled bridges in the IL layer can readily be find out. The length distribution function $\tau(N)$ implies that the contour lengths of molecules R_z vary with the length N. The contour length of chains of N methylene units can be calculated from the backbone geometry parameters as $R_z(N) = (N-1)r_{CC} \times \sin(\theta/2)$. It is obvious that there is a minimum all-*trans* length $N_{\min}$ of the chain, exhibiting the contour length $(R_z)_{\min} = L_{IL}$ that ensure a formation of a bridge between crystal plates. Then, the extension ratio x of tie molecules in the IL layer can be expressed as $x = (R_z)_{\min}/R_z(N)$.

In the literature two types of the dependence of tie molecules population on the chain length are encountered. In the often-used distribution function of Huang and Brown [10], a probability is calculated that the end-to-end distance of a coil in a melt is greater than the sum $2L_c + L_{IL}$, where L_c is the crystal lamella thickness. In this case the relative tie-chain concentration depends on properties of both the crystalline and IL phases and on crystalline fraction. In an alternative approach, the distribution function $\tau(N)$ is based on the specifications of the IL phase only. The function $\tau(N)$ for PE tie chains was already determined from the wide-line NMR measurements [21,34] or from Monte Carlo (MC) simulations [35,36].

In off-lattice simulations by Balijepalli and Rutledge (BR) [35] the microscopic structure of the IL layers of PE-like chains was examined. Their distribution functions $\tau(N)$ for two multichain systems are re-plotted in Fig. 6(a). These systems (denoted as II and V in Ref. [35]) represent PE molecules of relative molecular mass of about $M = 8000$ and 30 000, respectively. Both BR systems are characterized by the interphase width $L_{IL} = 3.81$ nm corresponding to the minimal chain length $N_{\min} = 30$. In the system II only 2.9% of chains form bridges; populations of loops and free tails is an order of magnitude higher. The population of tie molecules increases to 10.3% in the system V of higher average M.

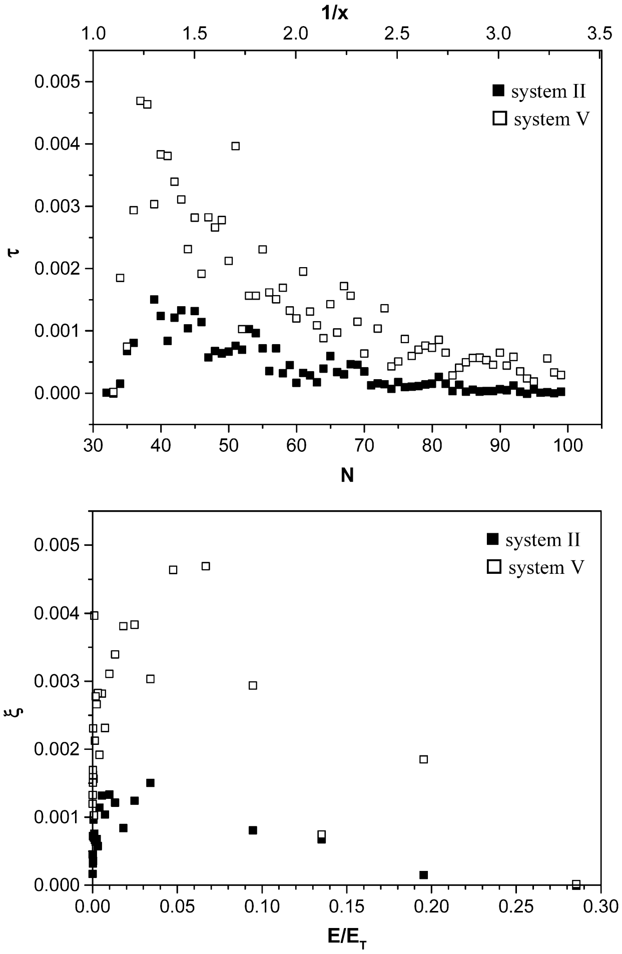

Fig. 6. The distribution of PE tie molecules τ according to their length N (or the inverse of the chain extension ratio x) replotted from the simulation data in Ref. [35] (a) and the corresponding distribution function ξ of relative chain moduli E/E_T (b).

The functions $\tau(N)$ in Fig. 6(a) give an allocation of the average number fraction of tie molecules into the various chain lengths N. No overstressed chains of $x > 1$ (or $N < N_{\min}$) are present at the lower bound of the BR distributions in Fig. 6(a). Then, the distributions go though a distinct maximum at x about 0.8 before decaying exponentially at large N. The fairly extended chains are located on the left side of a maximum of the distribution. The concentration of long, coiled bridges in the tail part of distributions is a quite considerable. Analogous distributions $\tau(N)$ were also reported [36] for the model of the IL phase where PE molecules were tilted to the lamellar normal. An increase in the chain tilt angle resulted in some enhancement of the population of bridges.

The individual tie chains of variable lengths in the IL layer obviously differ in their elastic moduli. The length distribution of tie molecules $\tau(N)$ can be converted into a related distribution of moduli $\zeta(E)$ by using the correlation between the chain extension ratio x and the relative chain modulus E/E_T from Fig. 3. The $\zeta(E)$ function resulting from such a transformation of the BR length distributions is plotted in Fig. 6(b). It is seen that the distribution $\zeta(E)$ emphasizes the weight of high-modulus, load-bearing chains; the maximum of the distributions is situated in the region around $E/E_T = 0.05$. The input of long bridges, with rubber elastic response, is hidden in the lower bound of this plot.

The length distribution of tie chains can be estimated from measurements on semicrystalline polymers by using a procedure described for oriented samples of nylon 6 [21] and PE [34]. The distribution functions $\tau(N)$ for various oriented samples of PE of $M = 1.05 \times 10^5$ determined by this technique [34] are re-plotted in Fig. 7(a) for the drawing ratio $\lambda = 7$ and 28. As expected, the number of longer bridges decreases on drawing of samples: the position of a peak shifts on drawing to the shorter bridges and its height increases. The chain extension ratio x cover in Fig. 7(a) approximately the region $0.8 < x < 1$. Such a shape of distribution functions $\tau(N)$ may suggest that either only the highly extended tie molecules are present in the drawn samples or the experimental technique used does not detect properly the more coiled tie chains. The narrow span of the tie-chain length distribution in Fig. 7(a) strikingly contrasts with a considerable width of the BR distributions in Fig. 6(a). Whatever the case may be, the $\tau(N)$ functions of drawn PE were again transformed into the functions $\zeta(E)$ (Fig. 7(b)) by using the correlation from Fig. 3. Since the $\tau(N)$

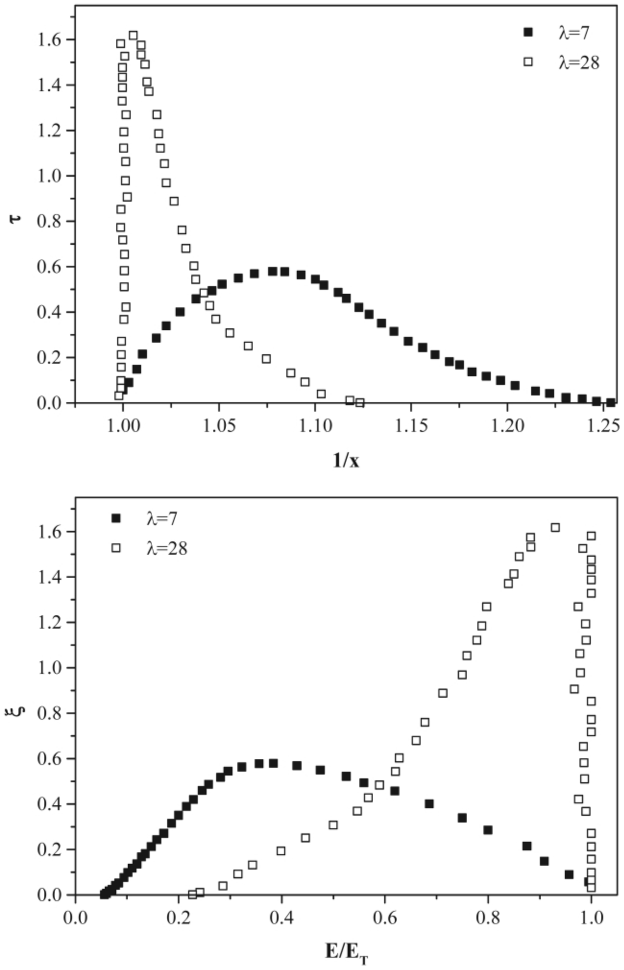

Fig. 7. The length distribution of PE tie molecules, expressed through the inverse of the chain extension ratio x, replotted from the experimental data in Ref. [34] (a) and the corresponding distribution function ξ of relative chain moduli E/E_T (b).

distributions comprise solely the highly extended chains, rather excessive relative moduli are predicted for oriented PE samples in this case. The maximum at curves in Fig. 7(b) is situated at $E/E_T = 0.35$ for the sample of $\lambda = 7$ and close to the ultimate value of 1 for the sample of $\lambda = 28$. Thus, even though the distribution functions $\tau(N)$ in Fig. 7(a) reflect correctly the changes on drawing in qualitative terms, they yield the unrealistically high chain moduli.

The distribution functions $\tau(N)$ and $\zeta(E)$ in Figs. 6 and 7 characterize a situation before the deformation of the IL phase in the slit-like arrangement in Fig. 1. An elongation of the interlamellar width L_{IL} by an external force F normal to the lamellae may bring an irreversible change in the shape of the $\tau(N)$ function. The taut tie chains of lengths close to $x = 1$ may be overstressed by deformation and finally broken at $x \gg 1$. Accordingly, the $\tau(N)$ distributions and ultimately the stress–strain curve may differ for the first and second deformation cycle.

The distribution functions $\tau(N)$ and $\zeta(N)$ in Figs. 6 and 7 represent a kind of extremes that may be encountered in various types of solid PE. The BR distributions featuring wide tails of long bridges may represent a situation in common types of PE. In contrast, the narrow distributions from Fig. 7(a) should be symptomatic of highly drawn PE fibres. In between, the whole spectrum of shapes of $\tau(N)$ function can be envisaged, differing in the peak maximum, width and asymmetry of the distribution. In this way the distribution $\tau(N)$ represent an essential parameter affecting the properties of the IL phase and of the PE samples as a whole. The distribution $\tau(N)$ should depends on the sample preparation, modification, morphology, history, etc. In all cases, the transformation of the chain length distribution $\tau(N)$ into the chain modulus distribution $\zeta(E)$, via the E vs x correlation in Fig. 3, should be viable.

The mean modulus $\langle E \rangle$ of the multichain system in the IL layer can be determined by averaging the distribution $\zeta(E)$. The Voigt averaging [30] of the chain moduli, $\langle E \rangle = \sum \zeta_i E_i$, is proper for parallel model in Fig. 1 under isostrain conditions; here ζ_i represents the fraction of individual types of bridges. The mean modulus of tie chains $\langle E/E_T \rangle$ in the systems II and V calculated from $\zeta(E)$ functions in Fig. 6(b) is about 0.08 and 0.10, respectively. The computed mean moduli are based on a simple slit-like model of the IL phase and thus can directly be related to the solid PE materials of similar simple morphologies only. An additional, orientation averaging [3,6,30] would be indispensable for more complex lamellar systems such as spherulites. The mechanical properties of oriented low-density PE with the lamellar stack morphology were recently reported [37]. In a correspondence to the slit-like model in Fig. 1, this material consisted of extended stacks of thin platelike crystals separated by layers of the noncrystalline phase. The modulus of amorphous phase $E_a = 0.61$ GPa at -55 °C was deduced for this polymer [37] by using the experimental tensile modulus 2.85 GPa and the composite laminate model, i.e. the value almost one order lower than the values of $\langle E \rangle$ computed above from BR distributions.

Mechanical properties of PE materials with the stacked lamellae superstructure depend also on the stiffness of the crystal lamellae and their tendency to disintegrate into smaller blocks under deformation. In so called hard elastic PE prepared by melt extrusion and annealing [38], no disintegration, but bending of lamellae under tension, is supposed in the leaf-spring model of this polymer. This material is characterized both by a rather high elastic modulus and by a high elastic recovery typical of elastomers. In contrast to entropy elasticity of rubbers, the energy elasticity mechanism of lamellar bending under tension is presumed here by the leaf-spring model. However, the energy-elastic stretching of highly extended molecules bridging the lamellae, by the mechanism detailed in this paper, undoubtedly should also be operative at the deformation of hard elastic PE.

4. Concluding remarks

The elastic properties of PE chains bridging the noncrystalline layers between crystalline lamellae are calculated by the molecular-mechanics method on the assumption that their deformation is controlled by the internal energetics rather than by the conventional rubber-like entropy elasticity. The deformation potentials and stress–chain extension curves show abrupt discontinuities due to sequential annihilation of the defects by the conformational transitions. The longitudinal Young's moduli E were calculated for a set of typical extended tie chains. A distinct reduction of the PE chain modulus with the kink defect concentration was observed and the relationship between the modulus E and the chain extension ratio x was established. The computed moduli of tie chains were used to convert the chain length distribution functions $\tau(N)$ reported in the literature into the distribution functions of chain moduli $\zeta(E)$ in the IL phase. The influence of the above distribution functions on overall elastic response of solid PE was examined, with a particular focus on the stacked lamellae morphology. It is believed that the above description of the energy elasticity and the estimation of the chain modulus is relevant also to other situations of highly stretched molecules connecting two surfaces, such as bridging two adjacent surfaces in the adhesion joints or in the domains of block copolymers, in cases of fibrillar structures bridging crazes, bimodal polymer networks with one component stretched almost to the full length, filled reinforced elastomers, etc.

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