

A hybrid model of rubber elasticity in simple extension

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Abstract

A thermodynamically related continuum model developed for describing elastic rubber-like behavior of amorphous and crystallizing polymers is exemplified for simple extension. This model is based on a new concept of extendable dynamic segment (DS) whose unperturbed size is roughly evaluated for several polymers. The extension of the DS's hinders the cooperative rotations of monomer groups and contributes to the internal energy of chains. Therefore, in description of macroscopic elastic rubber deformation, this approach takes into account the motions of chains caused by both the entropy and internal energy. The model displays a continuous transition from entropy to energetic elasticity, without common singularity related to finite extensibility of polymer chains. A multi-scale molecular approach, based on the concept of extendable DS's, has been employed for evaluations of continuum parameters. In case of crystallizing polymers, a simple model is developed for the strain-induced crystallization based on local calculations of energetic gain caused by the formation of needle-like (NL) crystals. Then the strain-induced crystallization for a crystallizing rubber is described on continuum level taken into account the reinforcement effects of emerging NL crystals.

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1. Introduction

Amorphous and crystallizing polymers demonstrate different types of mechanical and optical behavior above T_g . The amorphous polymers display the rubber-like behavior in both the cross-linked and not cross-linked states, the latter just above T_g . In case of cross-linked rubbers, the importance of energetic component of deformation has been discussed long ago (e.g. see Ref. [1]), but to the author knowledge, the energetic effects have never been involved in rubber theories. In case of not cross-linked polymers, the energetic component(s) of deformation, along with common entropy component, could also significantly contribute in reversible part of stress tensor in rubbery region due to the high level viscosities in the low temperature region above T_g . A 'hybrid', energetic/entropy approach could facilitate understanding of specifics of

rubbery behavior at large strains, with possible applications for evaluations of strength and strain-induced crystallization. A hybrid continuum constitutive model [2,3] of relaxation type with additive energetic and entropy stresses has been elaborated for describing rheological behavior of amorphous polymers near the glass transition.

The statistical description of polymer behavior commonly uses the 'coarse-graining' approach, where the polymer chains consisting of monomers with correlated small-scale motions is represented as statistically independent elements of chain. This approach describes well the chain motion in the length scales larger than the correlation length of monomer interaction along the chain. The independent elements are usually established by partitioning a polymer chain in equal parts whose sub-chain lengths are not less than the correlation length along the chain. This way of description of large-scale polymer macroscopic properties assumes its independence (or invariance) of partitioning. A good example of such coarse-graining approach is the well-known Rouse bid-spring model [4,5], which describes well the linear macroscopic relaxations of polymer chains in dilute polymer solutions independently of partitioning the molecular chain in bids, however, within a restricted

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frequency region. The recent papers [6,7] among others experimentally revealed that there is a certain partitioning specific for a given polymer that describes the linear macroscopic dynamics of polymer chains in the whole observable, very wide frequency region. Thus this preferential partitioning defines the ‘dynamic segments’ (DS) or the bids with a certain average number of monomer units n_d , specific for a given polymer. There is currently no understanding why it happens, and the ways of calculations of the DS size are currently unknown.

The classical rubber elasticity employs Kuhn coarse-graining approach [1], which is far stiffer than the Rouse approach. Kuhn defined the freely jointed (FJ) segments using two conditions: (i) the mean-square end-to-end distances as well as (ii) the contour lengths for the real and FJ chains should be equal. These two conditions allowed determining both the length and mass of Kuhn segment using experiments or more detailed theories. Although the Kuhn segment is often viewed as a real ‘kinetic unit’, i.e. a small part of a chain participating in kinetic processes, it was recently shown (e.g. see Ref. [8] and references there) that the concept of Kuhn segments [1] is inconsistent with many experimental data. For example, for polystyrene the mass of kinetic unit established by neutron scattering is several times higher than the mass of the Kuhn segment. The authors of Ref. [8] argued that the reason for this difference is arbitrary assumption (ii) in the Kuhn theory. Therefore, they suggested using only the above condition (i), where the mass of the statistic segment should be determined from other data or more detailed theories. In this regard, keeping in mind that the description by using only the Kuhn segment is not unique, one has to show that the description of rubber elasticity in the Gaussian region is independent of partitioning the polymer chain in more large FJ parts, and that there might exist a ‘dynamic segment’ which could provide a uniform description of Gaussian and non-Gaussian behavior of rubber elasticity.

The earlier analysis of flow data for polymer melts [9] showed that the concept of Kuhn segment could not explain the well-known fact of independence of activation energy of the length of polymer chain. Therefore, the flow or dynamic segment was defined in Ref. [9] as a part of macromolecule that participates in rotational cooperative motions of monomer units, when keeping the connectivity of macromolecular chains. The results of paper [9] when applied to evaluation of the dynamic segment size, might serve as an example of choosing the size of dynamic segment if this description is consistent and does not contradict other, e.g. neutron scattering data. According to Ref. [9], the mass of dynamic segment is an intrinsic property of a polymer. To explain high frequency dynamic data for dilute polymer solutions another approach [10] considers the increase in initial Kuhn segment mass due to dynamically induced ‘rigidity’.

The ideas in papers [9,10] can be interpreted as a rough

attempt to understand the cooperative motions of monomers inside the dynamic segments as the source of ‘energetic elasticity’. This type of elasticity has been mentioned many times in the literature (e.g. see Refs. [1–3]). Several more fundamental theoretical and computational approaches have also been developed to understand the kinetics of conformational transitions of parts of macromolecules on microscopic level (e.g. see Refs. [11–13]). However, the important effect of cooperativeness, more difficult for theoretical treatment, has not been understood.

In simple extension of crystallizing polymers, the strain-induced crystallization could happen at high stretching ratios. The needle-like (NL) polymer crystals that emerge in this type of crystallization have been observed long ago at high extensions of natural and synthetic crystallizing cross-linked rubbers [1] (ch. 1). These crystals are quite different from the common type of folded, thermal crystals occurred in the stress free crystallization. Flory [14] developed a statistical model for the strain-induced crystallization based on the classical entropy (Gaussian) statistical calculations that neglected the non-Gaussian effects of finite extensibility of polymer chains, and internal energy contribution. The dependence of extension force on stretching ratio in strain-induced crystallization calculated in Ref. [14] displays lesser stress in NL crystalline region as compared to that for amorphous case. However, the experimental data [15,16] clearly demonstrated increasing stress in the crystalline region and were explained as reinforcement of rubber by the emerged rigid crystals. Later, Flory’s theory has been modified with introducing two new aspects: (1) non-alignment of the crystalline chains along the tensile axis [17], and (2) combination of NL and common folding-like crystallization in cooling [18]. It should be mentioned that the modification (2) could contradict the experimental data, where the opposite effects unfolding the folded polymer crystals under stretching, were reported (e.g. see Refs. [19,20] and references there).

This paper is organized as follows. We first introduce the concept of extendable dynamic segments and develop a general equilibrium, continuum approach for simple extension to obtain the hybrid stress–strain constitutive relation. Then we specify thermodynamic functions responsible for entropy and energetic contributions. In the following we roughly evaluate macroscopic parameters in the continuum model through molecular parameters, and demonstrate that the description of entropy elasticity in Gaussian region is independent of partitioning the chain in FJ segments. Assuming that the semi-empirical approach [9] provides the correct values for the size of DS n_d we present for three polymers, PE, PS and PBD, some numerical examples. In the final part of the paper we extend the previous results on crystallizing polymers. Here we first develop a local thermodynamic description of formation of NL crystals and evaluate their parameters. We then develop a continuum model of stress-induced crystallization.

2. Qualitative description of structure

In this paper the Kuhn concept is not used because of its inconsistency with many data in defining the mass of kinetic segment mentioned before. The second reason, which also follows from arbitrary assumption (ii) of Kuhn's theory, is the rigidity of Kuhn segment consisting of fully stretched part of chain contour with corresponding monomer numbers. Therefore, in non-Gaussian region, the Kuhn approach is incapable to involve the internal energy contributions in deformation of polymer chains, and describes only entropy effects with singular behavior at high stretching.

Underlying the continuum approach in this paper is a multi-scale molecular model, which is qualitatively described as follows. For low and moderate stretching ratios, the macromolecules are viewed on the large scale as consisting of N_d freely jointed 'dynamic segments' (or 'bids') consisting of n_d monomer units each so that $N = N_d n_d$. Here N is the degree of polymerization and n_d is considered below as known parameter. A possible method of n_d estimations that might be valid in the non-Gaussian region is discussed in Appendix A. Another important geometrical parameter of dynamic segments is their effective length l_d . Although as a rule, $l_d N_d < L$, where L is the contour chain length, the condition for preserving Gaussian statistics in this region determines l_d via the mass of dynamic segment (Section 5).

According to the present approach, at small and moderate stretching ratios, the large-scale motion responsible for the entropy elasticity can be viewed as a conformational motion of macromolecules consisting of FJ bids or DS's with length l_d and number of monomer links n_d . This macroscopic coarse-graining description of entropy elasticity, being independent of the polymer chain partitioning is similar to the Kuhn approach but with more realistic value n_d .

The inter-segmental motion of macromolecules is an activation process, where macromolecules move by small parts consisting of several connected monomers, performing very fast collective crankshaft-type rotations [12]. Under higher stretching ratios when even small parts of polymer chains are extended, the rotational mobility of monomer units is increasingly suppressed. At very high extensions, when the monomer units are almost aligned, the relative rotations are almost suppressed because they need energy supply close to its maximum, roughly estimated as the barrier value of trans-gauche transition for every link [10]. In order to model the high stretching behavior this paper employs a concept of extendable DS's, which have constant masses and could be schematically viewed, as deformable bids needed higher forces for their small-scale deformations. These small-scale deformations of the DS's occur when the entropy elasticity begins saturating.

When the monomer units in a dynamic segment are maximally oriented along the stretched chains, another, fine-scale, motion of monomer units is still possible. This

motion, caused by distortion of valence angles between adjacent monomer units, is responsible for the solid like infinitesimal elasticity of the same type as in low molecular weight crystals.

Both the small- and fine-scale deformations are two different types of energetically related elasticity. Nevertheless, the term 'energetic elasticity' will often be used below only for the less stiff energetic deformations related to collective rotations of monomer units. The other, extremely stiff energetic elasticity caused by distortion of valence angles between adjacent monomer units will be called the crystal-like (CL) elasticity.

On the continuum level, there are three macroscopic Hookean moduli, entropic G_s , energetic G_e , and CL one G_c , that characterized these types of elasticity, such that

$$G_s \ll G_e \ll G_c \quad (1)$$

In summary, the present model views the polymer chains as consisted of free jointed, deformable DS's. On the macroscopic level, the large-small- and fine-scale motions of monomer units produce the entropic and energetic components of deformations, which are not independent. The behavior of the deformable bids in two-scale (entropy/energetic) bid-spring model is sketched in Fig. 1.

It should be mentioned that the above qualitative picture as well as inequalities (1) are not applicable to silicon rubbers, because the energy change of valence angle for these rubbers is less than the typical rotation energy (see discussion in Ref. [9]).

The above multi-scale model can also be mechanistically pictured as three consecutively connected springs, the first one ('entropic') being soft, another ('energetic') stiff and the third one ('CL') extremely stiff. If this hybrid spring is extended by a relatively small force F its full displacement is the sum of entropy $\Delta l_s = F/\kappa$, energetic $\Delta l_e = F/\kappa_e$, and CL $\Delta l_c = F/\kappa_c$, components, i.e. $\Delta l = \Delta l_e + \Delta l_s + \Delta l_c$, where κ_s , κ_e and κ_c are, respectively, the entropy, energetic and CL spring constants. The hybrid's force-displacement relation $F = \kappa \Delta l$ with the hybrid spring constant $\kappa = (\kappa_s^{-1} + \kappa_e^{-1} + \kappa_c^{-1})^{-1}$ clearly shows that under condition $\kappa_s \ll \kappa_e \ll \kappa_c$, the

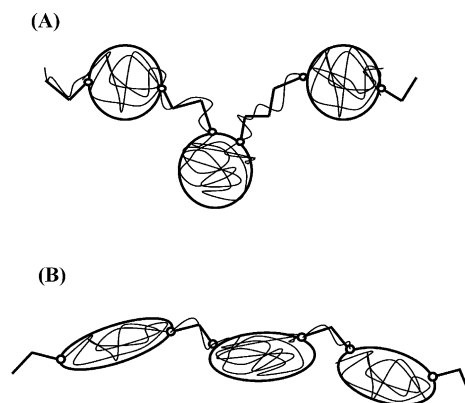


Fig. 1. (A) Common bid-spring model, (B) bid-spring model with extensible bids.

entropy spring overwhelmingly contributes in the total displacement of the spring.

3. Thermodynamic hybrid model in simple extension

We neglect here for simplicity the volume deformations, i.e. consider $\rho = \rho_0 = \text{constant}$, and assume that in the thermodynamic relation $\Delta f = \Delta e - T\Delta s$, where f is the Helmholtz free energy (density), the changes in the internal energy Δe and entropy Δs are represented as:

$$\begin{aligned} \rho_0 \Delta e &= \frac{1}{2} G_e(T) \psi_e(\lambda_e) + \frac{1}{2} G_c(T) \psi_c(\lambda_c), \\ -\rho_0 T \Delta s &= \frac{1}{2} G_s(T) \psi_s(\lambda_s) \end{aligned} \quad (2)$$

Here λ_s , λ_e and λ_c are, respectively, the entropic, energetic and CL elastic stretching ratios. Eq. (2) means:

$$\begin{aligned} \rho_0 f(\lambda_e, \lambda_s, \lambda_c, T) \\ = \frac{1}{2} G_s(T) \psi_s(\lambda_s) + \frac{1}{2} G_e(T) \psi_e(\lambda_e) + \frac{1}{2} G_c(T) \psi_c(\lambda_c) \end{aligned} \quad (3)$$

The specific dependencies (2) and (3) of internal energy and entropy on their own, stretching components is the main assumption of the hybrid approach. It is physically meaningful if the inequalities (1) are valid.

The relation between the entropic λ_s , energetic λ_e , CL λ_c and total λ stretching ratios, evident from the picturesque of the multi-scale model, is postulated as:

$$\lambda = \lambda_s \lambda_e \lambda_c \quad (4)$$

In the regions of dominancy of either entropic or both energetic elasticities, the respective true stresses are represented as:

$$\begin{aligned} \sigma_s(\lambda_s, T) &= G_s \lambda_s \frac{d\psi_s}{d\lambda_s}, \\ \sigma_e(\lambda_e, T) &= G_e \lambda_e \frac{d\psi_e}{d\lambda_e}, \quad \sigma_c(\lambda_c, T) = G_c \lambda_c \frac{d\psi_c}{d\lambda_c} \end{aligned} \quad (5)$$

According to the physical sense of the hybrid modeling, the entropy and both energetic stresses are not additive but related to the total stress $\sigma(\lambda, T)$ as:

$$\sigma_s(\lambda_s, T) = \sigma_e(\lambda_e, T) = \sigma_c(\lambda_c, T) = \sigma(\lambda, T) \quad (6)$$

The relations (3)–(6) are compatible with the common definition of the total stress-stretch relation

$$\sigma(\lambda, T) = \rho_0 \lambda \frac{\partial f}{\partial \lambda} \Big|_T \quad (7)$$

Indeed, using identity

$$\lambda_e \lambda_c \frac{d\lambda_s}{d\lambda} + \lambda_s \lambda_c \frac{d\lambda_e}{d\lambda} + \lambda_s \lambda_e \frac{d\lambda_c}{d\lambda} \equiv 1$$

obtained by differentiating (4) with respect to λ , and

calculating the right-hand side (7) with account of (3) yields:

$$\begin{aligned} \sigma &= \rho_0 \lambda \frac{\partial f}{\partial \lambda} \Big|_T = \lambda_s \lambda_e \lambda_c \sum_{i=s,e,c} G_i \left(\frac{d\lambda_i}{d\lambda} \right) \frac{d\psi_i}{d\lambda_i} \\ &= \sigma_s \lambda_e \lambda_c \frac{d\lambda_s}{d\lambda} + \sigma_e \lambda_s \lambda_c \frac{d\lambda_e}{d\lambda} + \sigma_c \lambda_e \lambda_s \frac{d\lambda_c}{d\lambda} \\ &= \sigma \left(\lambda_e \lambda_c \frac{d\lambda_s}{d\lambda} + \lambda_s \lambda_c \frac{d\lambda_e}{d\lambda} + \lambda_s \lambda_e \frac{d\lambda_c}{d\lambda} \right) \equiv \sigma \end{aligned}$$

The constitutive equation (CE), $\sigma = \sigma(\lambda, T)$, can now be readily established using the functions $\sigma_s(\lambda_s, T)$, $\sigma_e(\lambda_e, T)$ and $\sigma_c(\lambda_c, T)$ defined in (5). The assumption that the hybrid model is thermodynamically stable results in the fact that the three stress functions $\sigma_s(\lambda_s, T)$, $\sigma_e(\lambda_e, T)$ and $\sigma_c(\lambda_c, T)$ are monotonically increasing. Then using (6), one can introduce the three inverse functions, $\lambda_s = \sigma_s^{-1}(\sigma, T)$, $\lambda_e = \sigma_e^{-1}(\sigma, T)$ and $\lambda_c = \sigma_c^{-1}(\sigma, T)$, and obtain with the aid of (4) the inverse hybrid CE in the general form:

$$\lambda(\sigma, T) = \sigma_s^{-1}(\sigma, T) \sigma_e^{-1}(\sigma, T) \sigma_c^{-1}(\sigma, T) \quad (8)$$

To specify relation (8), some physical models for entropic, energetic and CL elasticity should be introduced.

4. Specific thermodynamic functions and hybrid CE's

4.1. Entropy elasticity

When the Gaussian statistics is valid, there are the familiar expressions for the classic entropic elasticity:

$$\begin{aligned} -\rho_0 (s - s_0) T &\equiv W_s(\lambda_s, T) = \frac{1}{2} G_s(T) \frac{\lambda_s^2 + 2}{\lambda_s - 3}, \\ \sigma &= G_s(T) \frac{\lambda_s^2 - 1}{\lambda_s} \end{aligned} \quad (9)$$

When stretching ratio is high enough and non-Gaussian effects are important, fractioning of macromolecular chains in the dynamic segments employed in our multi-scale model plays a pivotal role. This is because as compared to the Kuhn segment statistics, the onset of non-Gaussian behavior for dynamic segments may begin much earlier for chains consisting of DS's, which are generally larger than the Kuhn segment. In the following, we simply use the semi-empirical Warner–Gent potential [21,22], which describes the finite extensibility of polymer chains in terms of Finger strain tensor. In simple extension, the elastic potential and related stress are presented as:

$$\begin{aligned}
-\rho\Delta sT &\equiv W_s(\lambda_s, T) \\
&= -\frac{1}{2}G_s(T)(I^* - 3)\ln\left[1 - \frac{(I_{1s} - 3)}{(I^* - 3)}\right] \\
&\quad \times \left(I_{1s} = \lambda_s^2 + \frac{2}{\lambda_s}\right) \quad (10a)
\end{aligned}$$

$$\sigma = \sigma_s(\lambda_s, T) = G_s(T)\left(\frac{\lambda_s^2 - 1}{\lambda_s}\right)\left[1 - \frac{(I_{1s} - 3)}{(I^* - 3)}\right]^{-1} \quad (10b)$$

Here, $I^* = I_{1s}(\lambda_{*})$, and λ_* is the strain related to complete aligning the DS's but without taking into account their internal stretching. Keeping in mind that the analysis of entropy elasticity in our hybrid model is based on the fractioning of polymer chains in DC's whose size exceeds the size of Kuhn segment, one can conclude that the value I^* in (10) should be less than that when using the Kuhn segment approach. Note that involving in this model a possible dependence of λ_* on λ_e , which contradicts the basic assumption (2), makes the analysis needlessly more complicated. When $\lambda_s \gg 1$ (and always when $\lambda_* \gg 1$), the stress in (10b) is expressed in the simplified form:

$$\sigma = \sigma_s(\lambda_s, T) \approx G_s(T)\frac{\lambda_s^2}{1 - (\lambda_s/\lambda_*)^2} \quad (\lambda_s \gg 1) \quad (10c)$$

4.2. Energetic elasticity

To characterize this type of elasticity we employ the simplest approach described in terms of Cauchy–Green strain tensor. This approach is valid even for the relatively soft energetic case when $n_d \gg 1$. In simple extension, it is presented as:

$$\begin{aligned}
W_e(\lambda_e, T) &= \frac{1}{2}G_e(T)\psi_e(\lambda_e) \\
&= \frac{1}{2}G_e(T)(2\lambda_e + \lambda_e^{-2} - 3) \quad (11a)
\end{aligned}$$

$$\sigma = G_e(T)(\lambda_e - \lambda_e^{-2}) \quad (11b)$$

In cases of rigid and soft energetic elasticity, relation (11b) takes the respective forms:

$$\sigma \approx 3G_e(\lambda_e - 1) \quad (\lambda_e - 1 \ll 1) \quad (11c)$$

$$\sigma \approx G_e\lambda_e \quad (\lambda_e \gg 1) \quad (11d)$$

4.3. CL elasticity

This is an infinitesimal elasticity, where

$$W_c(\lambda_c, T) = \frac{1}{2}G_c(T)\psi_c(\lambda_c) = \frac{3}{2}G_c(T)\varepsilon_c^2 \quad (12a)$$

$$\sigma = 3G_c(T)\varepsilon_c, \quad \lambda_c = 1 + \varepsilon_c \quad (0 < |\varepsilon_c| \ll 1) \quad (12b)$$

Note that the temperature dependencies $G_s(T)$ and $G_e(T)$

(or $G_c(T)$) are qualitatively different. Unlike slightly increasing function $G_s(T)$, the energetic moduli $G_e(T)$ and $G_c(T)$ are slightly decreasing function of T , having a maximum about T_g and being independent of T at higher temperatures in the rubbery region.

4.4. Hybrid CE's

Formula (8) along with the expressions for stress in (10) and (11) constitutes the hybrid CE, $\sigma(\lambda)$, that could rarely be explicitly expressed. Two cases will be considered below to illustrate this constitutive behavior under conditions (1).

We first consider the transition from entropic to the energetic elasticity assuming that the contribution of the CL elasticity in stress is negligible, i.e. that crystal-like 'springs' are rigid. To illustrate the features of this transition it is appropriate considering the large entropic strain approximation (10c). Then CE (8) for hybrid elasticity takes the forms:

$$\hat{\lambda} \approx \left(1 + \frac{\hat{\sigma}}{3\xi}\right)\sqrt{\frac{\hat{\sigma}}{1 + \hat{\sigma}}}, \quad (\hat{\sigma} \ll \xi) \quad (13a)$$

$$\hat{\lambda} \approx \frac{\hat{\sigma}}{\xi}\sqrt{\frac{\hat{\sigma}}{1 + \hat{\sigma}}}, \quad (\hat{\sigma} \gg \xi) \quad (13b)$$

$$\hat{\lambda} = \frac{\lambda}{\lambda_*}, \quad \hat{\sigma} = \frac{\sigma}{G_s\lambda_*^2}, \quad \xi = \frac{G_e}{G_s\lambda_*^2}$$

Here parameter ξ is the measure of relative contributions of entropic and energetic parts in the total hybrid elasticity. When $\hat{\sigma} \ll \xi$, due to (13a) $\lambda_e \approx 1$, i.e. the energetic contribution in the hybrid elasticity is negligible. Therefore, this case is described by (10c) with $\lambda_s \rightarrow \lambda$. When $\hat{\sigma} \gg \xi$, formula (13b) describes the hybrid elasticity with large stretches for arbitrary value of parameter ξ . At the crossover point $\hat{\lambda}_\xi$ between two asymptotic behaviors in (13), the stress and strain characteristics are:

$$\hat{\lambda} = \hat{\lambda}_\xi : \lambda_s = \lambda_*\frac{3}{2}\sqrt{\frac{3\xi/2}{1 + 3\xi/2}}, \quad \sigma_s = \frac{3}{2}G_e, \quad (14)$$

$$\lambda_s^{(\xi)} = \lambda_*\sqrt{\frac{3\xi/2}{1 + 3\xi/2}}, \quad \lambda_e^{(\xi)} = \frac{3}{2}$$

Consider now the dependence $\sigma(\lambda; \xi)$ of the hybrid CE on parameter ξ . When $\xi \gg 1$, the dynamic segments are almost non-deformable up to very high stresses. Thus in this case the entropy elasticity dominates over large deformation region. When $\xi \leq 1$, the dynamic segments are significantly deformable even at moderate strains. The behavior of dependence $\hat{\lambda}(\hat{\sigma})$ for various values of ξ is sketched in Fig. 2. It is clearly seen from the above analysis that the model describes a smooth transition from the pure entropy elasticity to the pure energetic one, with no singular behavior common for pure entropy approach.

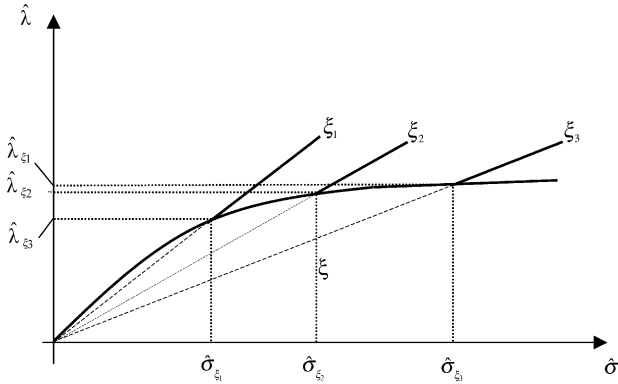


Fig. 2. Schematic plots of $\hat{\lambda}(\hat{\sigma}; \xi)$ for various values of ξ : $\xi_1 < \xi_2 < \xi_3$.

The situation when the stretching of chains in dynamic segments is close to their limit is still well described by the relation (13b). Using (11d), where $\hat{\sigma} \gg 1$, this relation can be equivalently represented in the form:

$$\lambda \approx \lambda_* \lambda_e, \text{ or } \sigma \approx G_e \frac{\lambda}{\lambda_*} \quad (\sigma \gg G_s \lambda_*^2) \quad (15a)$$

Formula (15a) describes the intermediate case when the entropy elasticity is already saturated ($\sigma \gg G_s \lambda_*^2$) but the stretching effect of the CL elasticity is still very small. If this small effect is not neglected, the asymptotic formula of hybrid elasticity is:

$$\lambda \approx \lambda_* \lambda_e (1 + \epsilon_c) \quad (15b)$$

Consider now the transition from the energetic to the CL elasticity. Near the transition, formula (11d) is generally invalid. Nevertheless, we can still approximately describe this transition using (15b) assuming that near this transition the energetic elasticity is almost saturated, i.e. the chains in the dynamic segment are almost completely extended, with λ_e value reaching maximum λ_{em} . As soon as the equality $\lambda_e \approx \lambda_{em}$ is achieved, the CL elasticity, however, it is small, cannot be ignored. Then using (12b) and (15b) the strain–stress relation in the region of the CL elasticity, is given by:

$$\lambda \approx \lambda_* \lambda_{em} (1 + \epsilon_c), \text{ or} \quad (15c)$$

$$\sigma = 3G_c \left(\frac{\lambda}{\lambda_* \lambda_{em}} - 1 \right), \quad (\lambda > \lambda_* \lambda_{em})$$

The relation (15c) approximately describes the continuum transition from the energetic to CL elasticity with a kink at $\lambda_e \approx \lambda_{em}$.

5. Evaluation of parameters

5.1. Evaluation of chain parameters

Two chain parameters need to be evaluated, the number of monomers n_d in and the unperturbed length l_d of the

dynamic segment. The relation between them is:

$$l_d \approx l \sqrt{C_\infty n_d} \quad (16)$$

Here the parameter C_∞ ($\approx n_k$) characterizing the stiffness of ‘infinite’ real chain is calculated using experimental data or the detailed statistical approach [23]. Eq. (16) can be obtained in the following way [8]. The Gaussian statistics of macromolecular coils yields: $\langle R_0^2 \rangle \approx C_\infty N l^2$, where l is the length of monomer link and N is degree of polymerization. Using here the Gaussian statistics for the description of polymer chain with the DS’s, $\langle R_0^2 \rangle \approx N_d l_d^2$, and the condition $N = N_d n_d$ results in (16).

Note that the condition $N = N_d n_d$ preserving the mass conservation for model and real chains is always valid for any type of partitioning. In particular case of the Kuhn segment when $n_d = C_\infty$, relation (16) yields $l_d = l_k = C_\infty l$, and $l_d N_d = l_d N / n_d = N l$. It means that the Kuhn segment is rigid because it consists of the fully stretched arc of contour chain containing C_∞ monomers. In case of polymer chains with rigid valence angles the inequality $n_d > n_k \approx C_\infty$ yields: $N l > l_d N_d$.

Parameter n_d treated as ‘kinetic unit’ has been experimentally evaluated in many papers ([4,5,8–10] and references there). Calculations of n_d , based on semi-empirical model [9] in Appendix A, are presented in fourth column of Table 1. The first three columns in this table show the literature data for values of activation energy of viscous flow E_p , the number N_e of monomers in polymer sub-chain between entanglements [24] and the values of C_∞ [23].

Five parameters have been employed in the continuum modeling of polymer rubbery behavior: (i) the modulus of entropy elasticity G_s , (ii) the stretching ratio λ_* for finitely (non-Gaussian) extendable polymer coils, fractioned in the non-perturbed DS’s of length l_d , (iii) the ultimate energetic stretching ratio λ_{em} , (iv) the energetic modulus G_e , and (v) the modulus G_c of CL elasticity. These parameters are evaluated below, using scaling arguments that follow from the multi-scale modeling and the values n_d from Table 1.

- (i) Evaluating entropy elasticity modulus G_s for DS approach in the same way as for Kuhn segments, yields the well-known expression:

$$G_s(T) = \alpha k T = \frac{\rho R T}{M_c} \quad (17)$$

Here α is the number of cross-links (or entanglements) in unite volume, k is the Boltzmann factor, ρ is the density, R is the gas constant, T is the Kelvin temperature, and M_c is the molecular weight of polymer chain between cross-links (or entanglements). Relation (17) distinctly shows that the description of entropy elasticity in the Gaussian region is independent of partitioning the polymer chain in FJ segments. Note that the values of G_s for cross-linked elastomers are commonly in the interval: 0.1–1 Mpa.

Table 1
The values of parameters for PE, PS and PBD [9]

Material	E_p (kJ/mol)	N_e	C_∞	n_d	λ_*	λ_{em}	G_c/G_s
PE	25	135	6.7	8.8	8.7	1.15	7480
PS	150	170	10	33	5.5	1.82	440
PBD	34	60	~5	32	4	2.5	180

- (ii) Evaluation of stretching ratio λ_* for finitely (non-Gaussian) extensible polymer coils consisted of the dynamic segments. With known length l_d of dynamic segment, the gyration diameter D_d of the polymer coil consisting of the N_d dynamic segments, and the maximum conformational length L_{conf} , i.e. the length of completely aligned chain consisted of not stretched dynamic segments, are evaluated as:

$$D_d \sim l_d \sqrt{N_d}, \quad L_{conf} \approx l_d N_d$$

Then the value λ_* is evaluated, as:

$$\lambda_* \approx \frac{L_{conf}}{D_d} \sim \sqrt{N_d} = \sqrt{\frac{N}{n_d}} \quad (18)$$

- (iii) Evaluation of ultimate energetic stretching ratio λ_{em} . It is calculated for the DC fully extended to its maximum limit length $s_m = l_d n_d$ as:

$$\lambda_{em} \approx \frac{s_m}{l_d} = \frac{l_d n_d}{l_d} \approx \sqrt{\frac{n_d}{C_\infty}} \quad (19)$$

Note, that if the CL energetic elasticity is considered as very stiff, the total ultimate strain, λ_u is evaluated, using (18) and (19) as:

$$\lambda_u \approx \lambda_* \lambda_{em} \approx \sqrt{\frac{N}{C_\infty}} \quad (20)$$

The evaluation (20) also directly follows from the definition:

$$\lambda_u \approx \frac{Nl}{\langle R_0^2 \rangle} = \frac{Nl}{\sqrt{C_\infty N l^2}}$$

Formulae (18)–(20) allow estimating the values of λ_* and λ_{em} under assumption [22] that $\lambda_u \approx 10$. These estimations for the three polymers are presented in Table 1.

- (iv) Evaluation of energetic modulus G_c . The highly stretched amorphous polymers with dominant energetic behavior could be viewed as consisting of almost extended set of DS's. Following [10] we assume that the energetic free energy e spent for limit deformation λ_{em} is fully compensated by the limit rotational energy of monomers. Since, in this case the energy spent for rotation of every link approaches the rotational barrier ΔE_r between the trans and gauche

states, we obtain:

$$\frac{1}{2} G_c \psi_e(\lambda_{em}) \approx \beta \Delta E_r \quad (21)$$

Here β is the number of monomers in unit volume. It is related to parameter α in (17) as $\beta \approx \alpha N_e$, where N_e is number of monomer unit in polymer chain between cross-links or entanglements. For flexible polymers, $\Delta E_r/kT \approx q$, where at usual temperatures $q \approx 1.5$ – 7 , depending on type of polymer [25]. Then relation (21) is reduced to:

$$\frac{G_c}{G_s} \approx 2q \frac{N_e}{\psi_e}(\lambda_{em}) \quad (22)$$

Here according to (10a) $\psi(\lambda_e) = 2\lambda_e + \lambda_e^{-2} - 3$. The rough evaluations of moduli ratio in (22) using the (arbitrarily but uniform) values $N_e = 100$, $q = 2$ and calculated parameters λ_{em} are shown for the three polymers in Table 1.

- (v) Evaluation of CL modulus G_c . Near the transition from energetic to CL elasticity the energetic and CL stretching parameters cannot be considered as independent. Nevertheless, using the simplified molecular modeling in Ref. [12], we still can obtain a rough evaluating of G_c , considering only the motion due to the distortion of valence angle θ_0 for a single bond with the following potential:

$$U(\theta) = \frac{1}{2} u_\theta (\cos \theta - \cos \theta_0)^2 \approx \frac{u_\theta \sin^2 \theta_0}{2} (\delta\theta)^2 \quad (23)$$

Here θ_0 is the valence angle between two neighboring bond vectors and $\delta\theta \equiv \theta - \theta_0$ is the valence angle distortion for the bond. We considered the potential (23) near the minimum, $\theta = \theta_0$ for the fully stretched chain, when the variations in the expressions (23) for different bonds are negligible. The force applied along the fully stretched chain causes the longitudinal displacement of chain, calculated as the sum of equal displacements due to the distortion of valence angles in each bond. The axial displacement for each bond is calculated as

$$l_c - l_0 \equiv b \left[\cos\left(\frac{\theta}{2}\right) - \cos\left(\frac{\theta_0}{2}\right) \right] \approx \frac{1}{2b} (\delta\theta) \sin\left(\frac{\theta_0}{2}\right)$$

For the zigzag configuration of chain, the stretching

ratio is:

$$\varepsilon_c = \frac{(l_c - l_0)}{l_0} = \frac{1}{2}(\delta\theta)\tan\left(\frac{\theta_0}{2}\right)$$

Here l_c and l_0 are the projections of the bond on zigzag axis with disturbed and undisturbed values of the valence angle, respectively. For the helix configuration, the result is almost the same. Expressing $\delta\theta$ via ε_c and substituting the result into (23) yields:

$$U(\theta) = 8u_\theta\varepsilon_c^2\cos^4\left(\frac{\theta_0}{2}\right) \quad (24)$$

Here $U(\theta)$ is the energy of stretching per one monomer unit due to the distortion of valence angles. The energy (24) multiplied by the number β of monomers in unit volume should be equal to the crystal-like energy density (12a), $\beta U_\theta \approx W_c = 3/2G_c\varepsilon_c^2$ which gives:

$$G_c \approx u_\theta \frac{(3 + 4 \cos \theta_0 + \cos 2\theta_0)}{l^3} \quad (25)$$

Here we used the formulae, $\cos^4(\theta_0/2) = 1/8(3 + 4 \cos \theta_0 + \cos 2\theta_0)$, and $m \approx \rho l^3$.

Typically, the values of energies u_θ are not more than two orders of magnitude higher than the energies ΔE_r of rotational barriers [11]. It means that for PE, the Hook modulus could approach the modulus of steel. This result is known (see Tables 11–13, p. 429 in Ref. [26]). The results of numerical evaluations of moduli for the three polymers are consistent with the data in the Tables 11–13 in Ref. [26].

6. Crystallizing polymers: stress-induced crystallization

6.1. Formation of the needle like (NL) crystals

New effect, the strain-induced crystallization, which occurs in stretching of crystallizing rubbery polymers, is described below using the following hypothetical scenario. It is assumed that the special type of NL crystals emerge when some parts of macromolecules in well-stretched fibrils randomly come very close to each other. As soon as it happens, the attractive forces cause these fibrils to suddenly collapse in rigid NL crystals, whose shape is maintained by the emerged surface energy γ acting on the crystal sidewall.

Consider two deformed states for the same parts of macromolecules before and after formation of a NL crystal. The free energy density W_e/ρ for amorphous fibrils before NL formation is described as: $W_e(\lambda_c) = 1/2G_c\psi_e(\lambda_c)$, where we assume $\lambda_c \gg 1$. After formation of NL crystal, when the surface energy emerges, the Gibbs's energy of a NL crystal

is given by:

$$G_c = \pi r_c^2 l_c W_e(\lambda_c) - 2\pi r_c l_c \gamma, \quad (26)$$

$$\lambda_c = \frac{l_c}{l_0}, \quad l_0 \approx \frac{\lambda_c l_d n_{\parallel}}{n_d}$$

Here r_c and l_c are the radius and length of the crystal, l_0 is the length of stretched fibril before crystallization, and n_{\parallel} , an unknown parameter, is the number of monomer units in fibrils forming the crystal length. Minimizing (26) with respect to r_c and l_c yields:

$$\left(\frac{\partial}{\partial r_c}\right)G_c = 0 : r_c = \frac{\gamma}{W_e}(\lambda_c); \quad \lambda_c = \lambda_{em} \approx \sqrt{\frac{n_d}{C_\infty}} \quad (27)$$

$$\left(\frac{\partial}{\partial l_c}\right)G_c = 0 : \sigma(\lambda_c) = \frac{\gamma}{r_c} \quad (28)$$

In obtaining (28) we used (27) and the definition of stress: $\sigma(\lambda_c) = \lambda_c \partial W_e / \partial \lambda_c$. We also used in (27) and (28) the relation, $\lambda_c = \lambda_{em}$, because the macromolecular parts including in NL crystal are completely stretched.

On the other hand, the value of stress $\hat{\sigma}$ for a cylindrical rod stretched with the ratio λ , having a current radius r , and being under action of surface energy on the sidewall is:

$$\hat{\sigma} = \sigma(\lambda) - \frac{\gamma}{r} \quad (29)$$

Formula (29) shows that the squeezing effect of surface tension produces the release of the true stretching stress. Comparing (28) and (29) yields the conclusion: just formed a NL crystal is completely released from the elongation force. This reveals the compensatory mechanism of extensional strain release by surface energy and describes the occurrence of NL crystals as a stress induced spontaneous transition from oriented polymer to the NL crystals. As soon as the NL crystal is formed, it is loaded once again in the axial direction from the outside macromolecules, causing, however, almost no deformation in NL crystal. The important consequence of this analysis is that just formed NL crystals can be viewed in the following deformation history as rigid fillers. The rigidity of the NL crystal means that the additional (infinitesimal) stretching of formed NL crystals could only be caused by the fine motions of monomer units due to the distortion of valence angles.

Because the asymptotic formulae (21) derived for highly stretched DS's are also valid in the case of NL crystal formation, substituting the value of G_c from (21) into the left-hand side of (25), reduces (25) to the form:

$$\beta \frac{\Delta E_r \lambda_{em} \psi'_e(\lambda_{em})}{\psi_e(\lambda_{em})} = \frac{\gamma}{r_0}, \quad \text{or} \quad (30)$$

$$r_c = r_0 = \frac{\gamma}{\beta \Delta E_r} \frac{\psi_e(\lambda_{em})}{\lambda_{em} \psi'_e(\lambda_{em})}$$

In case of validity (11d) and $\lambda_{em} \gg 1$, relation (30) is

simplified to:

$$r_c = \frac{\gamma}{\beta \Delta E_r} \quad (31)$$

Here r_c is the equilibrium radius of NL crystal.

The remarkable simple result (31) could also be readily derived when considering the Gibbs' energy function $G_c = \pi r_c^2 l_c \beta \Delta E_r - 2\pi r_c l_c \gamma$ for the single NL crystal. The first term in the right-hand side of this expression is the ultimate stretching energy equal to the energy of rotational barriers, approaching by monomer units confined in the NL crystal volume. The second term there is the surface energy of the single NL crystal. The value of the crystal radius r_c , which minimizes the Gibbs energy G_c , is found from (31), and respective minimum value of G_c is represented as: $\min G_c = -\pi l_c \gamma^2 / (\beta \Delta E_r)$.

Although the equilibrium length l_c of NL crystal cannot be quantitatively found in the above 1D approach, simple qualitative considerations show that

$$l_c \sim l_m = l_n \quad (32)$$

Indeed, the possible case, $l_c \ll l_m$, is improbable because of the high rigidity of DC's. The opposite case, $l_c \gg l_m$, is improbable too, because to form the NL single crystal of that high length, several moderately extended DS's should be almost perfectly aligned in the stretching direction.

Two conclusions could be drawn from our model of the NL crystal formation.

- (i) The grow of a formed single NL crystal in the direction of extension is highly improbable, because at the instant of its formation, the crystal is relieved from the stretching. Although due to the action of the environmental polymer chains, the tension in the stretching direction occurs, it should be in general not enough to cause the grow of just formed NL crystal. Growing a single NL crystal in the lateral direction is also improbable due to the surface energy caused by the attractive intermolecular forces.
- (ii) Similarly to the thermally formed crystals obtained under cooling, the NL crystals formed under stretching create the dispersed 'crystal phase' surrounded by amorphous chains. The difference, however, is that in strain-induced crystallization the concentration of NL crystals gradually increases with growing strain.

6.2. Hybrid model for crystallizing rubbers

Developing this hybrid model needs specifying only the energetic part of free energy and related expression for stress. Two other components of hybrid model, entropic and CL ones have been established in Sections 4 and 5. In case of crystallizing rubbery polymers, the energetic component of elasticity might be simplistically considered as a type of elasticity for the filled system with NL crystals being the rigid filler. Then taking into account that the energetic

elasticity happens in amorphous region of polymer deformation, and that in our simple model the NL crystals are oriented along the stretching direction, proposed modeling of energetic elasticity is:

$$W_e^c(\lambda_e, T) = \frac{W_e(\lambda_e, T)}{(1 - \phi)} = \frac{1}{2} G_e(T) \frac{(2\lambda_e + \lambda_e^{-2} - 3)}{(1 - \phi)} \quad (33)$$

$$\begin{aligned} \sigma^c(\lambda_e) &= \lambda_e \left. \frac{\partial W_e^c}{\partial \lambda_e} \right|_{\phi=\text{const}} = \frac{\sigma(\lambda_e)}{(1 - \phi)} \\ &= G_e(T) \frac{(\lambda_e - \lambda_e^{-2})}{(1 - \phi)} \end{aligned} \quad (34)$$

Here ϕ is the degree of NL crystallinity, $W_e^c(\lambda_e, T)$ and $\sigma^c(\lambda_e)$ are free energy and stress, respectively, for crystallizing rubbers in 'energetic' region of deformations, $W_e(\lambda_e, T)$ and $\sigma(\lambda_e)$ are the corresponding variables for the amorphous polymers defined in (11a) and (11b). Since, in equilibrium $\phi = \phi(\lambda_e)$, the simplest phenomenological modeling of this dependence is:

$$\phi(\lambda_e) = \frac{\chi \lambda_e}{\lambda_{em}} \quad (35)$$

Here λ_{em} is the ultimate energetic stretching ratio defined in (20) and χ (< 1) is the maximal possible degree of crystallinity, which depends of monomer stereochemistry and treated here as an empirical factor. Substituting (35) into (34) yields:

$$\sigma^c(\lambda_e) = \frac{G_e(\lambda_e - \lambda_e^{-2})}{1 - \chi \lambda_e / \lambda_{em}} \quad (36)$$

In the limit of saturated energetic elasticity, when $\lambda_e \rightarrow \lambda_{em} \gg 1$

$$\sigma^c(\lambda_{em}) \approx \frac{G_e \lambda_{em}}{1 - \chi} \quad (37)$$

Using general expressions (4) and (6), reveals the asymptotic behaviors of hybrid elasticity for crystallizing rubbers, similar to those discussed in the Section 4.4. We consider here the case of soft energetic elasticity when $\lambda_e \gg 1$, with the relation (11d) and, therefore, (10c) being valid. Then the strain–stress relation obtained using (4) is:

$$\lambda = \lambda_* \sqrt{\frac{\hat{\sigma}}{1 + \hat{\sigma} \alpha + \chi \hat{\sigma} / \lambda_{em}}} \left(1 + \hat{\sigma} \frac{G_e}{3\alpha G_c} \right) \quad (38)$$

Here the parameters $\hat{\sigma}$ and α have been defined in (13a) and (13b). Note that similarly to relations (13a) and (13b), formula (38) is strictly valid when $\hat{\sigma} \gg \alpha$, or equivalently, $\lambda_e \gg 1$. However, one can start approximately using it when the variables in (38) have passed the crossover values defined in (14). Thus relation (38) describes the smooth transition from entropy to energetic elasticity for crystallizing rubber-like polymers. Note that all the formulae for amorphous rubbers in Section 4 could be formally obtained from (38) and similar relations in the limit $\chi \rightarrow 0$. Note that

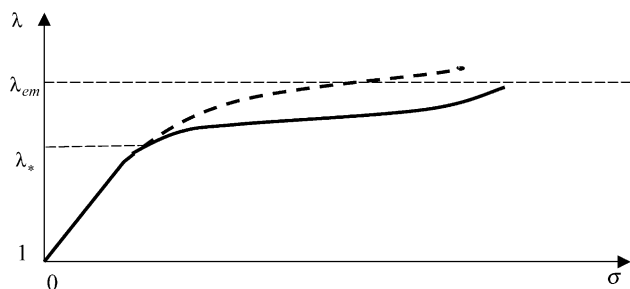


Fig. 3. Schematic plots of strain–stress dependences $\lambda(\sigma)$ for crystallizing (solid line) and amorphous (dashed line) rubber-like materials.

due to (37), the formula (15c) that describes the transition from energetic to CL elasticity is also valid for the case of crystallizing rubbers in the vicinity $\lambda_e \approx \lambda_{em}$. Comparing the first two terms in the product in (38) with (13b) clearly shows that (38) describes the effect of reinforcement in stress-induced crystallization.

The result of analysis of the hybrid constitutive relation for crystallizing rubbers is sketched in Fig. 3, where the strain–stress relations are shown by the solid/dashed lines for in crystallizing/amorphous cases. The effect of the strain-induced crystallization is well seen in Fig. 3.

Analysis of another function, $\lambda_c(\lambda)$, based on the CE's of hybrid elasticity resulted in the dependence of the degree of crystallinity on the total stretching ratio, $\phi(\lambda) = \chi \lambda_c(\lambda) / \lambda_{em}$, sketched in Fig. 4. This plot obtained using modeling (35), demonstrates the occurrence of a quasi-threshold for onset of the stress-induced crystallization, because the 'energetic' stretching ratio λ_e is noticeable only when the entropic elasticity is well developed and/or almost saturated.

Both the qualitative predictions in Figs. 3 and 4 seem realistic as compared to the data in Ref. [1] (ch. 1).

7. Discussion

The present paper develops a model of hybrid entropy/energetic elasticity on the example of simply stretching. The model employs a version of bid-spring model with deformable bids treated as dynamic segments (DS's). The extension of bids is attributed to the energetic

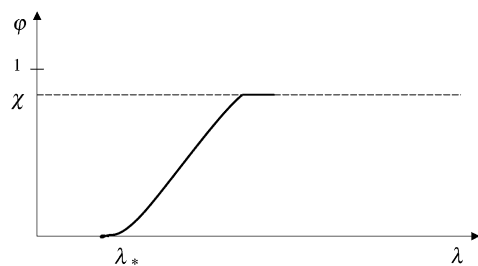


Fig. 4. Sketch of dependence $\phi(\lambda)$ of degree of crystallinity on the stretching ratio, qualitatively predicted by the hybrid approach.

elasticity dominated inside of DS's, and is caused by collective rotational motions of connected monomer units.

The key element in this modeling is evaluation of the number n_d of monomers in dynamic segment. Along with experimental evaluations of this parameter by neutron scattering, one of the possible ways of evaluation of n_d is using the kinetic model [9] shown in Appendix A. In due regard the pioneering Kuhn's contribution in rubber elasticity, his choice of segment treated as kinetic unit, being the same arbitrary as other choices, is worse than others, because it presents the rigid, a fully stretched arc of contour chain consisting of C_∞ monomer units, which contradicts the measurements of kinetic units. More appropriate approach to this problem was established by Rouse in non-equilibrium statistical mechanics of polymer chains [4,5]. In his bid-spring model the bids are treated as sub-chains with bid mass dependent on the partition, but with equivalent description of averaged statistical property (relaxation function), independent of the chain partition in a particular frequency region. The same result, independence of rubber elasticity modulus on the chain partitioning in the region of Gaussian statistics shown in (17), is valid for Gaussian region of rubber elasticity. As mentioned in the Introduction, recent experimental evidence of the uniqueness (specified for a polymer) in the partition of bids allowed the researchers to describe linear relaxation dynamics of dilute polymer solutions in a very wide frequency region [6,7]. Hopefully, the same uniqueness (specified for a polymer) in the partition of chain could extend the non-Gaussian description of rubber elasticity.

Three different types of elasticity have been taken into account in formulation of the hybrid CE for amorphous polymers: (i) entropy type with finitely extendable chains, (ii) energetic type with finite elasticity known from description of low molecular weight hard materials, and (iii) crystal-like very tough elasticity known for minerals and metals. A scaling approach was developed to evaluate macroscopic parameters in the theory via microscopic ones. Some numerical examples of evaluations for PE, PS and PB, using the kinetic approach [9] briefly exposed in Appendix A, seem to be realistic. These evaluations show that PS and PB with the values of n_d , more than three times exceeding C_∞ , have a mutual feature, very large side blocks in the chain, e.g. for PS, the molecular weight of this block C_6H_5 is almost 3/4 of the molecular weight 104, of the monomer unit. The physical reason for these effects is unknown.

This paper also developed a model of strain-induced crystallization in crystallizing rubbery polymers, based on the assumption that in crystallizing polymers, highly oriented macromolecules could collapse in the needle-like crystals. It was shown that there is an energy gain in this strain-induced crystallization. Then the phenomenological type of modeling has been employed that treats the stress–strain behavior of a polymer crystallizing under force similarly to the filled polymers, with reinforcement effect caused by the needle-like rigid crystals.

The equilibrium type of modeling presented in this paper could be applied to more detailed description of large elastic deformations in amorphous and crystallizing rubbers and also could be useful for evaluations of rubber strength.

The non-equilibrium effects, such as relaxations (for cross-linked polymers), and both relaxation and flow effects (for not cross-linked polymers above T_g) could also highly affect the mechanical and optical behavior of amorphous polymers in rubbery state. In case of modeling the non-equilibrium properties of crystallizing rubbers, the kinetics of stress-induced crystallization should also be taken into account along with relaxations and flow effects.

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Appendix A. Kinetic evaluation of number of monomers in dynamic segment

The kinetic approach used for evaluation, employs the rate theory and considers the segmental motion of macromolecules as an activation process. It means that macromolecules move by small parts of several connected monomers, performing very fast collective crankshaft-type rotations. Because the activated rotations happen in very small time intervals Δt of order of nanosecond [12] only one motion in the chain is probable during this time interval. The activation barrier E_n in this motion is proportional to number n of monomers participating in elementary act of rotation, because the traveling group of monomers needs to readjust their conformation to another, ‘hole’ conformation, using the relative rotations in neighboring monomer links.

Based on this physical picture the probability distribution of activated rotation of connected group containing n monomer in a chain of N monomer units is established as:

$$P_N(n; p) = p^n \frac{(1-p)}{[p(1-p^N)]}, \quad (0 < p < 1; \quad n \geq 1) \quad (A1)$$

Here p is the transitional probability of attaching one monomer to the group. Expression (A1) yields:

$$\sum_{n=1}^N P_N(n; p) = 1$$

We also roughly consider the limit $n \rightarrow 1$ in (17) as valid, although it is not true. The average number $\langle n(p) \rangle_N$ over distribution (A1),

$$\langle n(p) \rangle_N = \frac{1}{1-p} - \frac{Np^N}{1-p^N} \quad (A2)$$

monotonically increases with growing N , and for very long chains, $N \rightarrow \infty$, is independent of DP:

$$\langle n(p) \rangle_\infty = \frac{1}{(1-p)} \quad (A3)$$

The activation energy for transition of n monomers is: $E_n = E_0 n$. Here E_0 is characteristic activation energy of low molecular weight pre-polymer. Then the activation energy of polymer chain with DP equal to N is defined as: $E(N) = E_0 \langle n(p) \rangle_N$. It is seen that there is finite activation energy $E(\infty) = E_0 \langle n(p) \rangle_\infty = E_0 / (1-p) \equiv E_p$ for ‘infinite’ chain. Although the parameter p is unknown, this model could be tested on the example of slow Newtonian flow of polymers with activation energies measured for polymer homological series with increase in DP. It was experimentally found that the activation energy of viscous flow in the Newtonian region grows with increasing DP and is saturated at higher values of DP. Then using (A2) the value p was evaluated in Ref. [9] as a fitting parameter in description of experimental normalized dependences $E(N)/E_p = E_p \langle n(p) \rangle_N / \langle n(p) \rangle_\infty$ for five polymers. Here $E_p = E(\infty)$ is activation energy of viscous flow for very high DP’s.

In paper [9] instead of (A3), the incorrect expression $p/(1-p)$ was written. This misprint, however, did not change values of n_d in Ref. [9] because the numerical values of parameters p are very close to the unity. Surprisingly, the model also realistically predicts the value $n_d \approx 2.65$ for PDMS with $C_\infty \approx 6-7$ [23].

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