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Revisal of the Chain Equilibration Process in Strained Polymer Melts

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Summary

The retraction of stretched molecules explains the intermediate step of relaxation observed at short times with strained polymer melts instead of a single rubberlike plateau.

The stress relaxation following a rapid deformation is derived in this zone of the spectrum from the non linear, quasi elastic response of the transient network formed by the system of entangled chains. This method corrects an approximate calculation of the modulus decline in DOI's original treatment of the molecular equilibration process.

The representation of chain entanglements

We use the slip-link model simulating the topological constraints exerted by its surrounding on one molecule of a polymer melt (DOI and EDWARDS 1978). The polymer is represented by a dense system of **c** identical Gaussian chains per unit volume formed by N_0 monomers with length **b**. They are linked together in the equilibrium state by punctual entanglement junctions. These junctions occur on the average every **Ne** monomers and constitute therefore a set of $N = N/Ne$ segments with length $a = b.Ne^{1/2}$ which will be refered hereafter as the primitive path. Because the entanglement points are in this state of rest randomly located in space, the end-to-end vector $\underset{\sim}{r}_i$ of any segment i belongs to the ensemble $\underset{\sim}{r}_i = a.\underset{\sim}{u}$, $\underset{\sim}{u}$ being a unit vector with isotropic orientation.

In response to a rapid deformation kept constant afterwards, the entanglement points move to other fixed, affine positions imposed by the strain gradient $\underline{\underline{E}}$, so that the segment vectors become $r'_i = \underline{\underline{E}} \cdot \underset{\sim}{r}_i$. The relaxation of the system takes place afterwards by three successive phases respectively corresponding to the connection with the glass transition, the viscoelastic pseudo-plateau and the flow zone.

During the first phase, characterized by a short Rousian time τ_A , the entanglements are assumed to behave as strong cross-links allowing only a transverse diffusion of the monomers relatively to the chain segments.

During a second phase **B** , with relaxation time $\tau_B = (No/Ne)^2 \tau_A$

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they seem to play instead the role of small frictionless rings letting the chains slip back along a distorted primitive path with initial length $L' = L < |\underset{\approx}{E}.\underset{\sim}{U}| >_{U}$, until they have recovered the equilibrium arc length $\tilde{L} = N_o b^2 / a$ (DOI 1980) - Here $< \ >_{\underset{\sim}{U}}$ denotes an average over all directions of vectors $\underset{\sim}{U}$.

During last phase **C**, with relaxation time $\tau_C = (N_o/N_e)^3 \tau_A$ the chains return to an isotropic configuration by a reptation process which completes their disengagement from the primitive entanglements.

In a previous approach of the equilibrium phase **B**, the stress relaxation of the model has been deduced from the sum of the contributions of all the chain monomer units (DOI 1980). But this method incorrectly implies, in order to arrive at a tractable solution,orientations of each monomer unit independent of the chain slipping during the shrinking motion. Such approximations entail significant errors which are avoided in the following revised treatment of the chains equilibration process.

The equivalent quasi equilibrium network

For very short time intervals, the system of entangled chains may be considered at any time $t\ (\tau_A \lesssim t \lesssim \tau_B)$ in a state of quasi equilibrium and should consequently react at this instant like a network of permanent cross-linkages with the same chain configuration. According to the statistical elasticity theory, the stress tensor on this network is (DOI and EDWARDS 1978) :

$$\sigma_{\alpha\beta}(\underset{\approx}{E},t) = 3cN(t)KT \sum_{i=1}^{N} \frac{\underset{\sim}{r}'_{i\alpha}.\underset{\sim}{r}'_{i\beta}}{n_i(t)\,b^2} + P\delta_{\alpha\beta} \qquad \boxed{1}$$

$$\alpha, \beta = x, y, z$$

where **K** is BOLTZMANN constant, **T** the temperature, **N(t)** the number of monomers within each segment **i**, $P\delta_{\alpha\beta}$ the hydrostatic pressure term dropped below by convention, and $\underset{\sim}{r}'_{i\alpha}\cdot\underset{\sim}{r}'_{i\beta} = a^2(\underset{\approx}{E}.\underset{\sim}{U})_{i\alpha}(\underset{\approx}{E}.\underset{\sim}{U})_{i\beta}$ the products of the projections of chain segment **i** on axis **x,y,z**.

The stresses at the beginning and the end of the pseudo-plateau are given by the following expressions derived from equ. $\boxed{1}$ (DOI and EDWARDS 1978), where $G_o = 3\,C\,KTN$:

$$\sigma_{\alpha\beta}(\underset{\approx}{E}) = G_o < (\underset{\approx}{E}.\underset{\sim}{U})_\alpha (\underset{\approx}{E}.\underset{\sim}{U})_\beta >_{\underset{\sim}{u}} \qquad \boxed{2}$$

(when $t \lesssim \tau_B$ because $n_i = N_e$ and $N = N_o/N_e$)

$$\sigma^{\bullet}_{\alpha\beta}(\underset{\approx}{E}) = G_o < \frac{(\underset{\approx}{E}.\underset{\sim}{U})_\alpha\ (\underset{\approx}{E}.\underset{\sim}{U})_\beta}{|\underset{\approx}{E}.\underset{\sim}{U}|} >_{\underset{\sim}{u}} . < |\underset{\approx}{E}\ \underset{\sim}{U}| >_{\underset{\sim}{u}}^{-1} \qquad \boxed{3}$$

(when $\tau_A \gtrsim t \gtrsim \tau_B$ because $n_{i(t)}$ and $N_{(t)}$ become then $n^{\bullet}_i = a|\underset{\sim}{r}'_i|/b^2$ and $N^{\bullet} = N_o / < n^{\bullet}_i >_{\underset{\sim}{u}}$, i.e. $N^{\bullet} = (N_o/N_e) / < |\underset{\approx}{E}.\underset{\sim}{U}| >_{\underset{\sim}{u}}$)

We need at this point a formulation of the diffusion process controlling, between the above bounds, both the chain overall retraction and the diminution of its local state of stretch. Owing to the aleatory distribution of monomer density per segment along the primitive path, no exact solution of the consequent differential LANGEVIN equation seems at present available. However, the uniformisation of this distribution involves a longer length scale than the entanglement distance **a**. This suggests a strong coupling, during the whole chain shrinking, between $n_i(t)$ and the loss $N-N(t)$ of primitive entanglements which should not be moreover much affected by the local stretch equalization.

Assuming therefore a virtually uniform initial monomer density, the solution of the curvilinear diffusion equation giving the change of the arc length is :

$$N(\underset{\approx}{E},t)=N^{\circ}\left[1+\left(\langle|\underset{\approx}{E}.\underset{\sim}{U}|\rangle_{\underset{\sim}{u}}-1\right)\mu(t/\tau_B)\right] \qquad \boxed{4}$$

where μ stands for a time dependent term of the same form as in the flow zone, which decreases from unity to zero in a quasi exponential way.

Notwithstanding the somewhat more progressive diminution of $N(\underset{\approx}{E},t)$ consistent with stricly right boundary conditions, we retain the simple form :

$$\mu(t/\tau_B)\cong\exp(-t/\tau_B) \qquad \boxed{5}$$

On the other hand, the average number of monomers per segment is obviously related to $N(t)$ by : $\langle n_i(t)\rangle_{\underset{\sim}{u}}=N_o/N(t)$ and this condition is fulfilled by :

$$n_i(\underset{\approx}{E},\underset{\sim}{t})\cong n_i^{\circ}\left[1+\left(|\underset{\approx}{E}.\underset{\sim}{U}|-1\right)\mu(t/\tau_B)\right]^{-1} \qquad \boxed{6}$$

The substitution of equ. $\boxed{4}$, $\boxed{5}$, $\boxed{6}$ into the basic expression of the stress tensor clearly allows a smooth transition between the two limits $(t\lesssim\tau_B,\ t\gtrsim\tau_B)$ which are represented by equ. $\boxed{2}$ and $\boxed{3}$.

These limiting cases are described in the earlier treatment of the model by the approximate expressions $\boxed{7}$ $\boxed{8}$ (DOI 1980) :

$$\sigma_{\alpha\beta}\equiv G_o\langle|\underset{\approx}{E}.\underset{\sim}{U}|\rangle^2_{\underset{\sim}{u}}\left\langle\frac{(\underset{\approx}{E}.\underset{\sim}{U})_\alpha(\underset{\approx}{E}.\underset{\sim}{U})_\beta}{|\underset{\approx}{E}.\underset{\sim}{U}|^2}\right\rangle_{\underset{\sim}{u}} \quad \text{for } t\lesssim\tau_B \qquad \boxed{7}$$

$$\sigma^{\circ}_{\alpha\beta}\equiv G_o\left\langle\frac{(\underset{\approx}{E}.\underset{\sim}{U})_\alpha(\underset{\approx}{E}.\underset{\sim}{U})_\beta}{|\underset{\approx}{E}.\underset{\sim}{U}|^2}\right\rangle_{\underset{\sim}{u}} \quad \text{for } t\gtrsim\tau_B \qquad \boxed{8}$$

The magnitude of the errors caused by the latters is shown in the following applications of the theory to two kinds of homogeneous deformation : uniaxial elongation and simple shear, as well as by a comparison with corresponding stress relaxation experiments.

Comparison with experiment

Uniaxial extension

The theoretical variations of the reduced tensile modulus, defined in terms of the extension ratio λ by $Ea/Go = 3\sigma/Go(\lambda^2 - \lambda^{-1})$ are plotted against $1/\lambda$ in fig. 1.

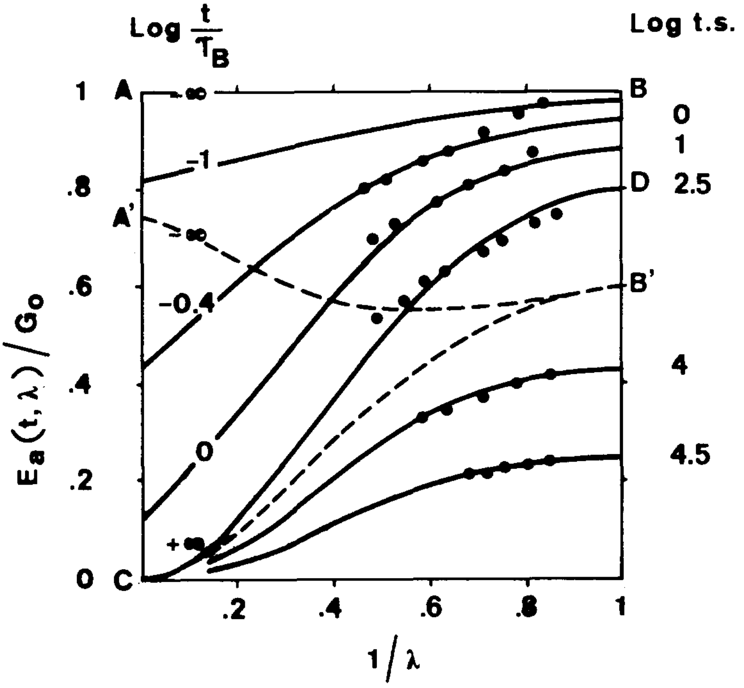

Fig. 1. Plot of the reduced tensile modulus Ea/Go against $1/\lambda$ solid lines : present treatment; dashed lines : Doi's approximation; points : stress relaxation of 1,2-polybutadiene

First, let us look at the limiting cases AB, CD and A'B', B'C where AB, CD represent the responses to a step of extension derived from equ. [2] [3] and A'B', B'C the responses derived from equ. [7] [8]. We see that the exact calculation indicates much larger variations of the tensile modulus of the model than DOI's approximation, especially for small elongations.

The stress relaxation data obtained with a high molecular weight 1,2-polybutadiene in the range of extensions $1{,}1 \leq \lambda \leq 2$ are also plotted on fig.1, both in the pseudo-plateau zone where the isochronous curves diverge and in the flow zone where they converge (NOORDERMEER and FERRY 1976). With estimated values $G_o = 2.10^7$ dynes/cm^2 and $\tau_B \cong 10$ s at a temperature of 0°C for this polymer, equations $\boxed{1}$ $\boxed{4}$ $\boxed{5}$ $\boxed{6}$ of the present treatment successfully describe the experimental results in the short time range of observations between 1 s. and 300 s.

In return, the approximate equ. $\boxed{7}$ $\boxed{8}$ which enclose only a narrow domain of moduli in this moderate range of extension, are quite incompatible with the higher level of the viscoelastic pseudo-plateau of the above polybutadiene.

Simple shear

A similar illustration of the response of the model to a step of shear γ is shown on fig. 2 where the reduced shear modulus $G/G_o = \sigma/G_o\gamma$ is plotted against log γ for different reduced times t/τ_B.

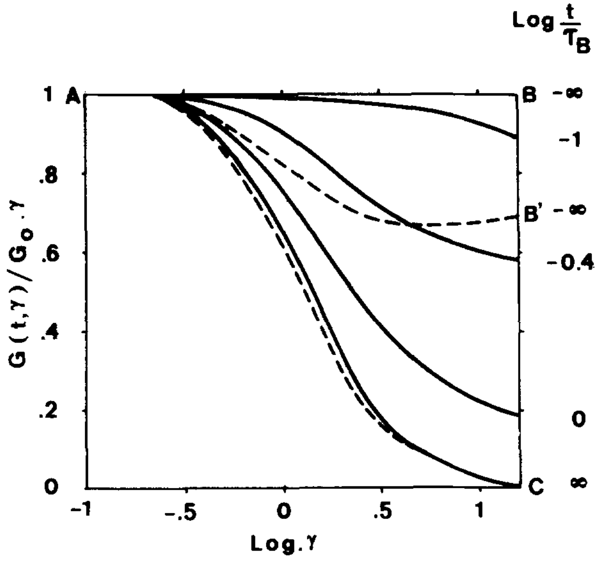

Fig. 2. Strain dependence of the reduced shear modulus $\sigma/G_o\gamma$ against log γ .
Solid lines : present treatment; dashed lines : Doi's approximation

The lines AB and AB' refer again to the upper limits of moduli respectively derived from equ. $\boxed{2}$ and equ. $\boxed{7}$ and the curves AC, which practically coïncide , to the lower limits of moduli deduced from equ. $\boxed{3}$ $\boxed{8}$. We see that both treatments predict in this case a negligible diminution of modulus with time until shear strains of about 0.4. For larger shears, the approximate equ. $\boxed{7}$ entails still a significant contraction of the model pseudo-plateau but the discrepancy is less marked than for uniaxial elongation.

A fit of the other theoretical isochronous curves of fig. 2 with shear stress relaxation data obtained with concentrated solutions of polystyrene (OSAKI and KURATA 1980) has not been attempted owing to the unsufficiently short times covered. The characteristic shoulders found by these authors on the curves of shear relaxation indicate however, as a function of time, a visible transition from the pseudo-plateau to the flow regime. Such shoulders are not observed in uniaxial extension, as expected from the shift of the earlier theoretical isochrones of fig. 1.

CONCLUSION

The slip-link model of chain entanglements do not require the introduction of empirical memory functions in the molecular theory of polymer rheology and presents in this respect a decisive advantage over former representations by non permanent cross-links at fixed points along the chain contour (WAGNER 1978).

There remains to assess, in a more general way than by a direct comparison with step deformations experiment, the validity of the present treatment of slip-link model yielding the exact limits of the viscoelastic pseudo-plateau. Other strain histories, such as constant rate of elongation and stress relaxation after stopping shearing flow are currently considered for this purpose in this laboratory.

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