Macromolecular Internal Viscosity. The Role of Stereoregularity

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Summary: Macromolecular dynamics at the scale of a few chain bonds is largely controlled by the "internal viscosity" effect if the energy barriers hindering the skeletal rotations are sufficiently large. In an extensive spin-echo neutron scattering analysis, Richter and co-workers (A. Arbe, M. Monkenbusch, J. Stellbrink, D. Richter, B. Farago, K. Almdal and R. Faust, *Macromolecules,* **2001**, *34,* 1281) investigated the dynamic properties of polyisobutylene (PIB) and polydimethylsulfoxide (PDMS) in toluene solution, the latter polymer being currently assumed to have very small rotational barriers. Analysis of the data according to a theory proposed by this author enabled them to obtain realistic values both of the rotational barrier around C-C bonds (~3kcal/mol) and of the natural frequency of the rotational jumps. - A problem related to chain internal viscosity concerns the *iso-* and *syndio*-tactic forms of polystyrene (respectively i-PS and s-PS): After a careful conformational analysis it is shown that i-PS has very large *effective* energy barriers due to interactions between phenyl rings (S. Brückner, G. Allegra and P. Corradini, *Macromolecules*, **2002,** *35,* 3928). This effect is compounded with that of the intrinsic rotational barrier and helps explaining the kinetic difficulty to crystallise of i-PS as compared with s-PS.

Keywords: polymer internal viscosity; rotational barriers; stereoregularity

Introduction

The motion of a long polymer chain is bound to take place via rotations around chain bonds, see Figure 1. In turn, each rotation implies that a conformational energy barrier must be surmounted, see Figure 2, and the process entails energy dissipation for reasons analogous to those discussed by Eyring in his viscosity theory from a system of heavy spheres[(1)].

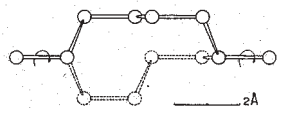

Figure 1. Any deformation of a polymer chain propagates via chain rotations.

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The dynamical-statistical description of this phenomenon has been the subject of a large body of investigations [2-4]. In the present paper we shall discuss the results in the light of a theoretical approach due to the present author and his coworkers[5-8]. The main ideas will be concisely presented in this paper.

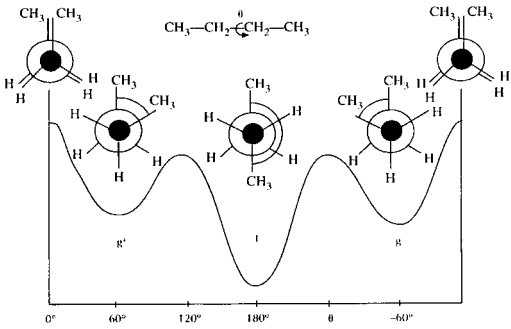


Figure 2. The internal energy for the rotation around the central bond in n-butane.

Internal viscosity

The rotational propagation is controlled by *internal viscosity*, i.e., the dissipation effect produced by the energy barriers hindering the rotations.

In the Langevin equation of motion, each chain atom experiences (at least) three forces, namely

1) the elastic force

$$K\left[\boldsymbol{R}(k+1,t)-2\boldsymbol{R}(k,t)+\boldsymbol{R}(k-1,t)\right]\cong K\frac{\partial^2\boldsymbol{R}(k,t)}{\partial k^2}; \qquad \left(K=\frac{3k_BT}{C_\infty l^2}\right)$$

where C_∞ is the polymer characteristic ratio, l is the C-C bond length, k_B Boltzmann's constant, T the temperature and $\boldsymbol{R}(k,t)$ the position vector of the k-th chain atom (k=1,2...N) at time t (see Fig.3);

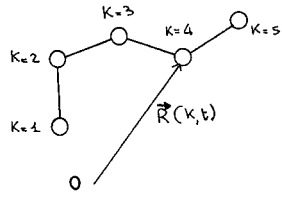


Figure 3. Vector representation of the chain atoms.

2) the friction force

$$-\zeta \frac{\partial \boldsymbol{R}(k,t)}{\partial t}$$

3) the Brownian force $\boldsymbol{X}(k,t)$, purely stochastic.

The polymer *internal viscosity* may be identified with an additional force (4th force) proportional to

$$K\tau_0 \frac{\partial^2 \boldsymbol{R}(k,t)}{\partial k \partial t}; \qquad \left(K = \frac{3k_B T}{C_\infty l^2}\right)$$

The sign ambiguity is related with the direction of propagation of the deformation. The rotational characteristic time τ_0 is

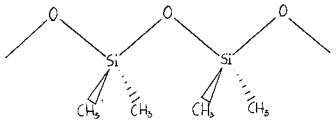
$$\tau_0 = A \cdot \exp\left(\frac{\Delta E}{k_B T}\right)$$

(ΔE is the average rotational barrier, see Fig.2)

Recent experimental investigations

Recently D. Richter, A.Arbe and coworkers[2-4] carried out careful neutron spin-echo investigations on the dynamics of monodisperse chains with a similar length of PDMS (a polymer with a small value of τ_0) and of PIB in toluene solution. They also studied PIB melts with the same technique.

The classical Rouse-Zimm theory, with no internal viscosity, accounts satisfactorily for the data from PDMS. Conversely, the results from PIB could only be interpreted after adding the internal-viscosity, according to the approach proposed by Allegra and Ganazzoli[5-8].



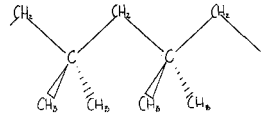


Figure 4. PDMS PIB

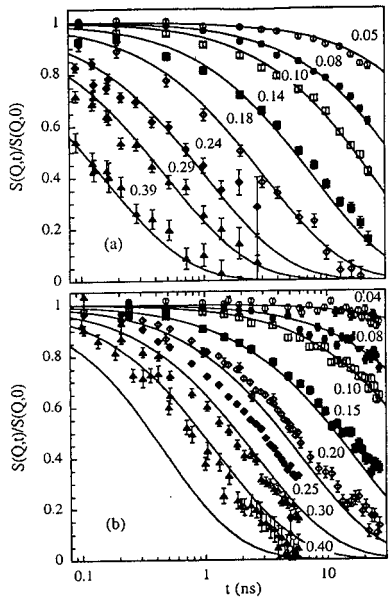


Figure 5. Chain dynamic structure factor of (a) PDMS at 373 K and (b) PIB at 417 K measured in the melt[2]. Each symbol corresponds to the same or very close values of $Q=4\pi \sin\theta / \lambda$ for both polymers, which are indicated in the figures. Solid lines show the Rouse prediction.

In the case of PIB in a toluene dilute solution, the numerical results for τ_0 were ($30<T<100$°C)

$$\tau_0 = 1.27 \times 10^{-12} \, exp\left[\frac{3.1}{RT}\right] [\mathrm{s}] \qquad (RT \text{ in kcal/mol}).$$

The result for ΔE (=3.1 kcal/mol) is in a reasonable agreement with the current value of the rotational barrier for alkyl polymers. The pre-factor is consistent with the rotational frequency around C-C bonds, in one of the limiting cases considered by Kramers, 1940[9] (i.e., the natural oscillation frequency, whereby the medium viscosity produces a negligible friction, but is sufficient to provide the Brownian energy at constant temperature; see Figs. 5-7).

In the case of PIB in the melt the theoretical interpretation is qualitatively similar but the value of ΔE is much larger (~10 kcal/mol instead of ~3 kcal/mol, in the temperature range 100-200°C).

It is reasonable to assume that in the molten state the skeletal rotations of adjacent chains are strongly coupled.

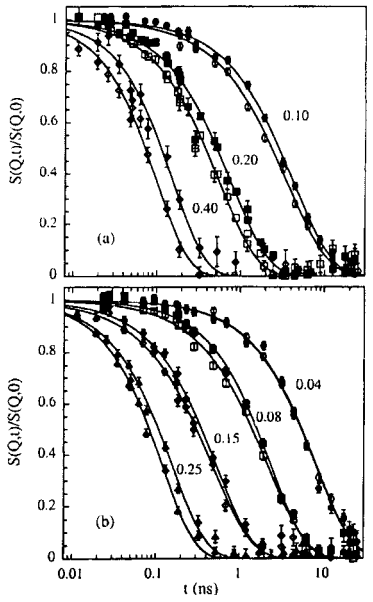


Figure 6. Chain dynamic structure factor of PDMS (empty symbols) and PIB (full symbol) in toluene solution at 300 K (a) and 378 K (b)[4]. the corresponding Q values are indicated. Lines through the points are guides to eye.

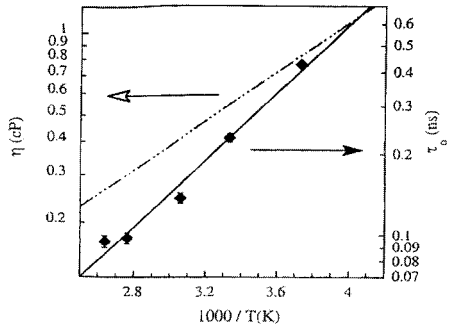


Figure 7. *T*-dependence of the solvent viscosity (dashed line) and the characteristic time τ_0 deduced for the conformational transitions in PIB (diamonds). The solid line through the points corresponds to the fit to an Arrhenius law [4].

Steric hindrance to rotational propagation

a) Isotactic Polystyrene[10]

With isotactic polymers, left- and right-handed chain strands with a threefold helical conformation follow one another with alternating types of conformational inversions (see Fig.8).

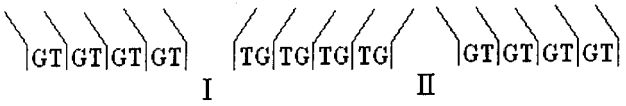


Figure 8

While in the first type side groups of adjacent monomer units point away from the inversion point, in the second group they point towards the inversion point. With the latter type of inversion a significant steric hindrance arises from interactions between 4-th and 5-th neighbouring phenyl rings (see Fig.9). As it may be seen in Fig.10, skeletal rotations around five consecutive chain bonds were driven together in the search for the lowest-energy path that shifts transition point I by one monomer unit (see also Figures 8 and 9). The energy barrier is about 15 kcal/mol; it effectively increases the natural barrier producing τ_0.

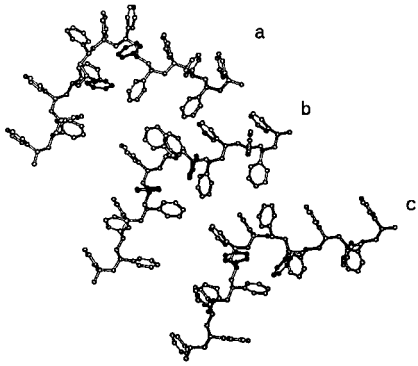


Figure 9. Molecular models of i-PS involved in a conformational transition shifting the inversion point (I in Fig.8) by one monomer unit. The starting point is (a), the final model is (c), the intermediate model (b) is recorded near the energy maximum.

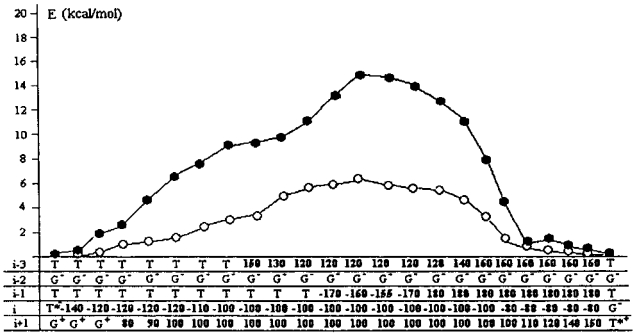


Figure 10. Energy (black circles) as a function of the conformational path in transition II (step 1) for i-PS, see Fig.9. Open circles represent the torsional contribution to the total energy. Bold numbers indicate torsion angles imposed as strong restraints; T, G and A symbols indicate the corresponding trans, ± gauche and ± anticlinal states but allow for wide deviations from standard values.

b). Syndiotactic Polystyrene[10]

In this case the transition shown in Fig.11 was investigated. The transition does not involve strong conflicts among side groups, and it was performed by driving four chain bonds one at a time without co-operative changes of other bonds.

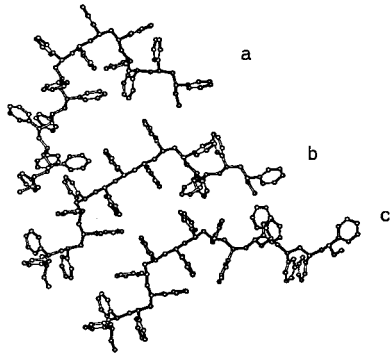


Figure 11. Molecular models of s-Ps: the starting model (a), the final model (c) and an intermediate model (b) recorded at the relative minimum corresponding to eight consecutive *trans* states.

The resulting energy plot is given in Figure 12. The energy barrier is in the vicinity of 6 kcal/mol.

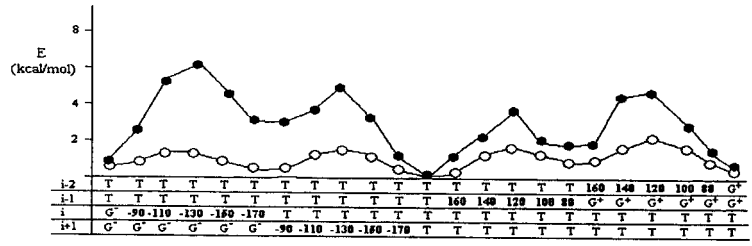


Figure 12. Energy as a function of the conformational path for s-PS, see Fig.11. Open circles represent the rotational contribution to the total energy. Bold numbers indicate torsion angles imposed as strong restraints. T and G symbols indicate the standard trans and ±gauche states but allow for wide deviations from standard values. Note that bonds are driven one at a time.

Some concluding remarks on internal viscosity

The polymer crystallisation rate is controlled by strain-rate propagation. It is interesting that isotactic polystyrene (i-PS) crystallises more slowly and to a lower degree than s-PS, in qualitative agreement with the results reported. In a polymer chain in a low-viscosity solvent, strain propagation takes place via rotational rearrangements and its velocity cannot exceed the limiting value τ_{eff}(bonds/s along the chain contour), where τ_{eff} is the characteristic time of the *effective* rotational barriers. In a polymer like PIB, with a small steric hindrance to skeletal rotations, $\tau_{eff} = \tau_0$, or the characteristic time due to the *intrinsic* energy barrier (mainly due to electron-pair interactions). The resulting linear rate is around 1 cm/s, for a coiled chain with N=104 skeletal atoms at 300K. The same limiting rate of strain propagation should hold in a highly swollen polymer network.

In the presence of steric hindrance as with i-PS the rate may be approximately expressed as τ^{-1}_{eff} ($<\tau^{-1}_0$), where $\tau_{eff} = \tau_0 + \Delta\tau_{steric}$.

These considerations suggest new possible experimental verifications of internal viscosity in highly swollen polymer networks. At lower temperatures, in the bulk polymer the effective energy barrier ΔE increases, as an increasing number of adjacent chains tend to couple their skeletal rotations, with a sort of steric effect. At the glass temperature *Tg* the effective barrier ΔEeff goes to very large values.

Polymer friction against a hard surface

a) The problem

Friction of a bulk polymer on a hard surface bearing stochastic steps (see Fig.13).

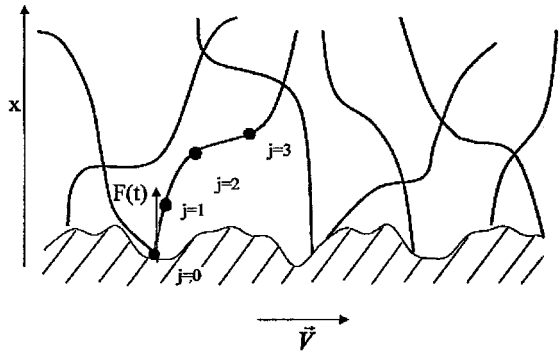


Figure 13. A stochastic model of an un-crosslinked polymer moving against a hard surface (shaded) at a velocity V.

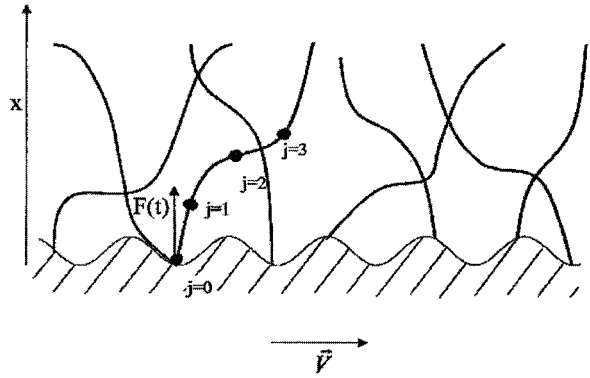


Figure 14. Same as in Fig. 13 but only one Fourier component of the surface roughness is considered. The sinusoidal wavelenght is λ.

Equation of motion of the terminal chain bead (j=0, see Figure 14)The equation of motion of the j-th chain atom is

$$x(j=0,t)=A\cdot exp(i\omega t)\ , \qquad \omega=\frac{2\pi V}{\lambda}$$

$$K\frac{\partial^2 x(j,t)}{\partial j^2}-\zeta\frac{\partial x(j,t)}{\partial t}+K\tau_0\left[\frac{\partial^2 x(j,t)}{\partial j\partial t}+\frac{\partial^3 x(j,t)}{\partial j^2\partial t}\right]-\zeta\tau_0\frac{\partial^2 x(j,t)}{\partial t^2}=0$$

$K=\frac{3k_BT}{C_\infty l^2}$; $l=$(chain bond length); $\zeta=$(monom. friction coeff.); $C_\infty=$(characteristic ratio)

The equation represents a travelling strain wave. Its solution yields ($\omega\tau_0<1$):

$$x(j,t)=A\cdot exp[i(\omega t-qj)-Qj]\ ;$$

Q and q depend on the pure number $\Omega=\tau_0^2\omega K/$

$$W_{diss}=\int_0^\infty dj\cdot\zeta\left\langle\frac{\partial x(j,t)}{\partial t}\cdot\frac{\partial x^*(j,t)}{\partial t}\right\rangle_t=\frac{\zeta}{Q}\cdot\left(\frac{2\pi VA}{\lambda}\right)^2;$$

(and by definition) $W_{diss}=\zeta_{eff}\cdot V^2;$

(by comparison)

ζ_{eff}(friction coeff. per chain end) $=\frac{\zeta}{Q}\left(\frac{2\pi A}{\lambda}\right)^2$

b) 1st case: $\Omega=(\omega\tau_0^2K/\zeta)\to 0$, $(K=3kBT/C_\infty l^2)$

$$Q\cong\sqrt{\frac{\pi V\zeta}{K\lambda}}\cong q;\qquad \zeta_{eff}=4A^2\left(\frac{\pi}{\lambda}\right)^{3/2}\sqrt{\frac{K\zeta}{V}}\propto V^{-1/2}$$

$v=$ strain velocity along the chain

$$v=\frac{\omega}{q}\cong\frac{2\pi V}{\lambda q}=2\sqrt{\frac{\pi KV}{\lambda\zeta}}$$

c) 2nd case: $\Omega=(\omega\tau_0^2K/\zeta)>>1$ $\quad(\omega\tau_0<1,\ \tau_0K/\zeta>>1)$

$$Q\cong\left(\frac{2\pi V\tau_0}{\lambda}\right)^2\cong q^2;\quad \zeta_{eff}=\frac{\zeta A^2}{V^2\tau_0^2}\propto V^{-2};\quad v(\text{strain velocity})=\frac{\omega}{q}=\frac{2\pi V}{\lambda}\cdot\frac{1}{\sqrt{Q}}\cong\frac{1}{\tau_0}\quad(\cong\text{constant})$$

d) The network case

Suppose that for n chain bonds there is one junction with a functionality degree f. Based on simple assumptions we evaluate

$$\zeta_{eff,network} = \frac{1}{\frac{1}{\zeta_{eff}} + \frac{\ln(f-1)}{n \cdot \zeta}}$$

e) Semi-quantitative comparison with experiment

Data from PS and from PVBC (polyvinyl benzyl chloride) show that the friction coefficient $z_{eff}=F$(friction force)/V(sliding speed) decreases indeed more quickly at larger values of V (see Figure 3).Also, force results after crosslinking appear to be much lower than before.

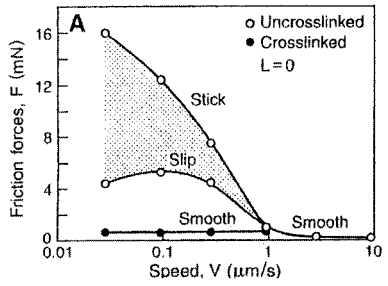


Figure 15. Preliminary data from double-strain experiments on filled rubbers appear to give a qualitative support to the theory (see Figure 15[11]).

The higher-frequency results depend on the assumption $\tau_0 K/\zeta >> 1$ (in addition to $\omega\tau_0 < 1$), which may not be true for PDMS, or similar polymers with very low rotational barriers.

Concluding remarks

Chain internal viscosity and steric hindrance to skeletal rotations produced by side groups are important factors controlling chain dynamics at the local scale as well as polymer crystallisation kinetics.

Their joint effect is instrumental to determine polymer friction against a hard surface.

Acknowledgements

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