Molecular cooperativity against locality at glass transition onset in poly(n butyl methacrylate)

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Abstract. Dynamic dielectric and mechanical responses in the splitting region of PnBMA are analysed with the help of two Havriliak–Negami-function fits. The α and β processes in the Arrhenius diagram are parallel to each other over a wide temperature range, and do not merge.

The glass transition is interesting because of the underlying equilibrium dispersion zones at different time scales (Creta 1991, Alicante 1994). In an Arrhenius diagram, a linear activated β and a strongly curved α relaxation (main transition) are often observed for glass-forming substances. The molecular cooperativity of the main transition is a general and unresolved problem in condensed matter physics. The interrelation between α and the local β relaxation can help (Johari and Goldstein 1970) to explore the cooperativity. Usually there is a splitting region S from a high-temperature regime to separate α and β relaxations (Johari and Goldstein 1970, McCrum *et al* 1991), see figure 1. A true merging (figure 1(a)) is often assumed. However, a separate onset of the α zone was also suggested (figure 1(b)) based on the concept of a minimal cooperativity necessary for it (Donth 1991, Schulz and Donth 1994). A third splitting topology (figure 1(c)) is expected if the α cooperativity, in
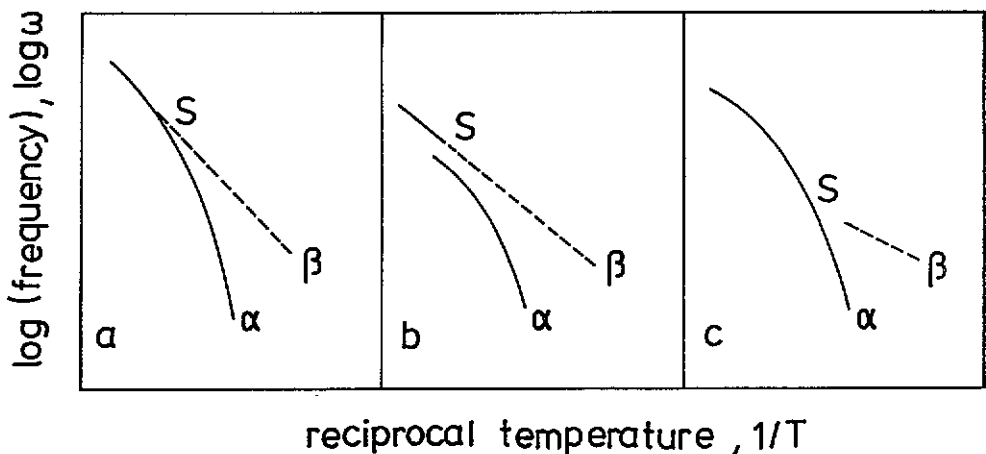

Figure 1. Three alternatives for the $\alpha\beta$ splitting in the Arrhenius diagram. (a) True merging of the cooperative α and the local β relaxation to a high-temperature process. (b) Separate onset of the α transition. (c) Classical β process stimulated by the development of the α process. S: splitting region.

a certain stage of development, is a precondition for β. Here we show that both dielectric and shear response in the S region of poly(n butyl methacrylate) indicate a separate α onset according to the topology of figure 1(b). The difference with the β relaxation is about one frequency decade, i.e. a factor of ten. The separate onset means that there is no smooth extrapolation of the α cooperativity to β locality, in accordance with minimal cooperativity. The lower α onset frequency suggests that the α cooperativity has a larger typical mode length than the local β process.
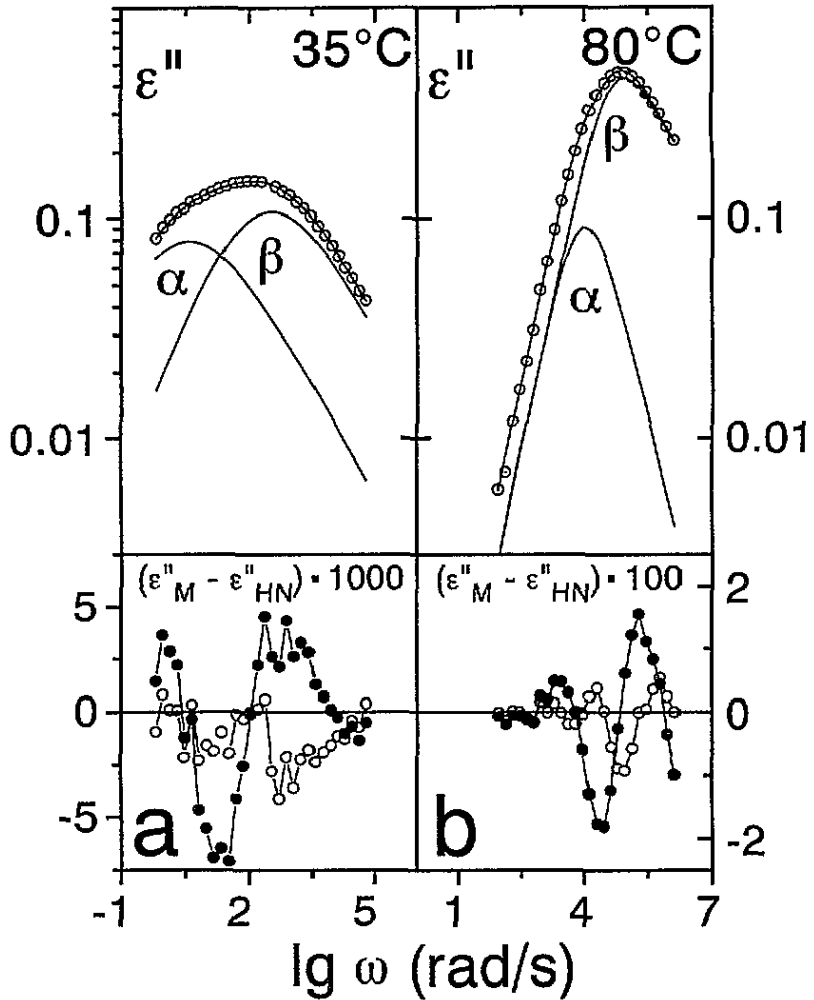

Figure 2. Two HN fits (simultaneously for ϵ' and ϵ'') illustrated for the dielectric loss curve $\log \epsilon''$ at $T = 35\,°C$ (a) and $T = 80\,°C$. The deviation plots at the bottom are for two HN fits (o) and for comparative one HN fit (•).

There are only a few substances where the splitting S is in the frequency region ($\omega = 10^{-3} \ldots 10^{+2}\,\mathrm{rad\,s^{-1}}$) accessible for precise shear experiments (Heijboer 1965, Kovacs *et al* 1963, Gomez Ribelles and Diaz Calleja 1985, Beiner *et al* 1993). An advantage for the splitting analysis in poly(n butyl methacrylate) (PnBMA) are the comparable dielectric
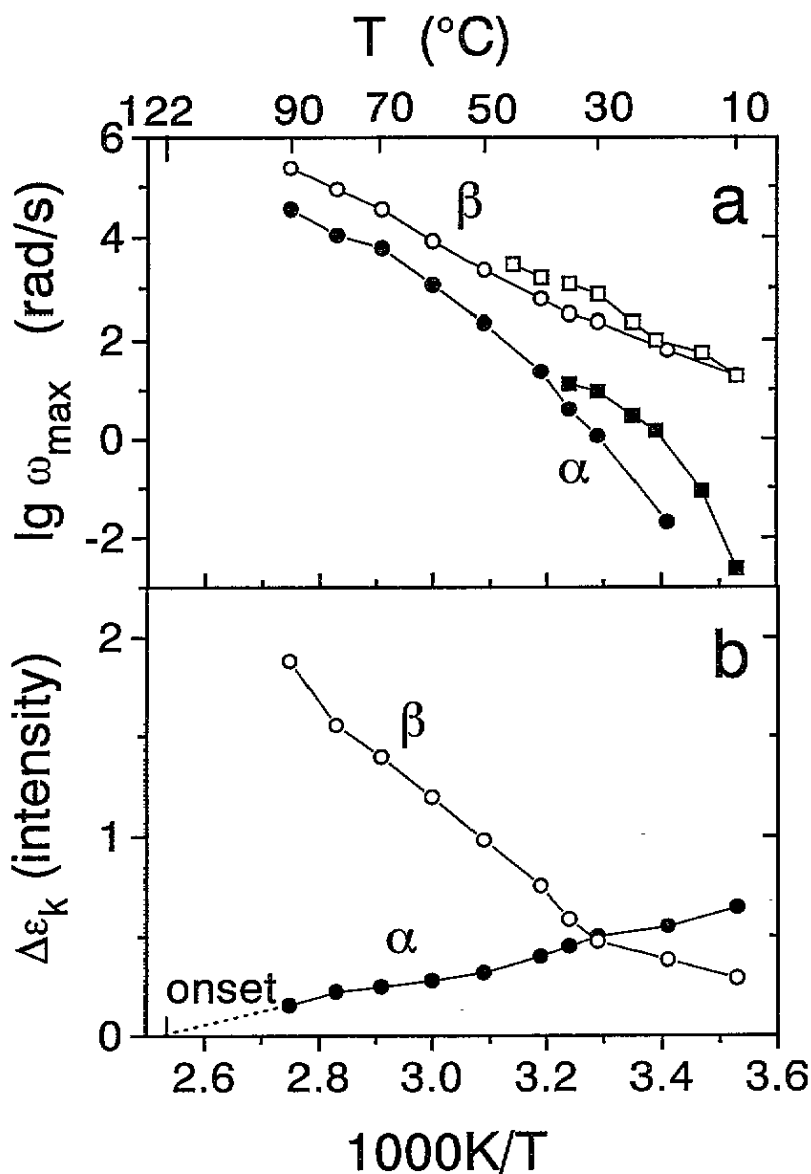
Figure 3. (*a*) Arrhenius diagram for α (full points) and β (open symbols) loss maxima from the two HN fits. •, ○: dielectric; ■, □: shear. This plot demonstrates the separate α onset of dielectric and the separate appearance of shear response, and also some difference between shear and dielectric activity. (*b*) Dielectric intensities $\Delta\epsilon_k$ for α and β as functions of temperature. The onset temperature, $T_{on}^\epsilon = 122\,°\text{C}$, is linearly extrapolated from the α intensity, $\Delta\epsilon_\alpha \to 0$.

activities of the α and β processes. The details of sample characterization (78±4% syndio tactic, $\overline{M_w} = 330 \pm 8\,\text{kg}\,\text{mol}^{-1}$, $\overline{M_w}/\overline{M_n} = 2.35$, $T_g(\text{DSC}) = 20°\text{C}$), of dielectric (Schönhals *et al* 1991) and shear measurements (Garwe *et al* 1994), and of long-time aging experiments (Beiner *et al* 1994) for equilibrating the sample up to probing frequencies of $10^{-3}\,\text{rad}\,\text{s}^{-1}$ are published elsewhere.
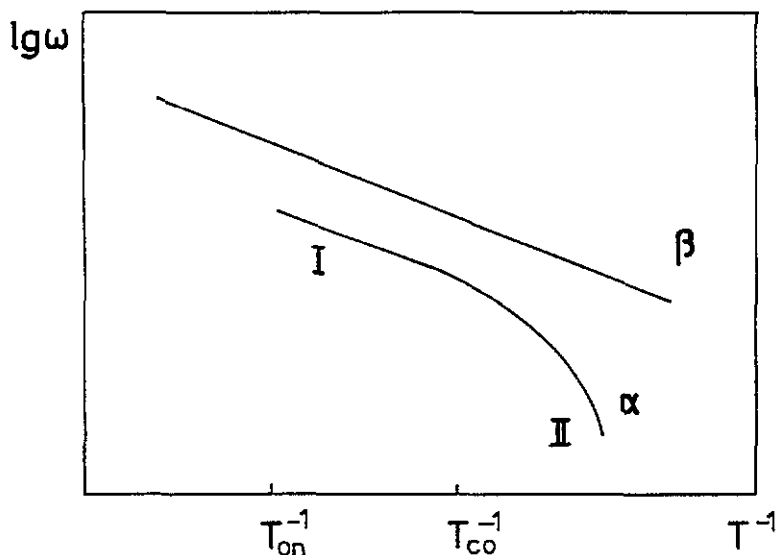
Figure 4. Suggested scenario for the splitting region according to the topology of figure 1(*b*). The symbols are explained in the text.

The fit procedure in the splitting region is crucial for the decision between the three topologies of figures 1(*a*)–(*c*). Two models are used. (i) Two logarithmic Gaussian functions for the imaginary part of the shear modulus and (ii) two Havriliak–Negami (HN) (Havriliak and Negami 1966, Schlosser *et al* 1993) functions:

$$\Delta\epsilon^* \equiv \epsilon' - \epsilon_\infty - i\epsilon'' = \sum_k \Delta\epsilon_k \left[1 + \left(\frac{i\omega}{\omega_{ck}} \right)^{\alpha_k} \right]^{-\gamma_k}$$

or

$$\Delta G^* = G' - G_\infty + iG'' = \sum_k \Delta G_k \left[1 + \left(-i\frac{\omega'_{ck}}{\omega} \right)^{\alpha'_k} \right]^{-\gamma'_k}$$

where $k = 1$ for the α relaxation and $k = 2$ for the β relaxation, simultaneously used for both the real and imaginary parts of the dielectric compliance ϵ, or of the shear modulus G, respectively. Each isothermal data set was fitted separately. Two examples for the dielectric adjustments are shown in figure 2, for ϵ'' at $T = 35\,°C$ (*a*) and $T = 80\,°C$ (*b*). As shown by the deviation plots, comparative fits with only one HN function show larger and more systematic deviations from the experimental points.

The results of the fits are converted to maximum frequencies of the loss parts shown in the Arrhenius diagram figure 3(*a*). For shear both models give practically the same points. The topology obtained is those of figure 1(*b*). From the linear extrapolation (Schulz and Donth 1994) of the dielectric α loss intensities to zero (figure 3(*b*)), we find the α onset at $T_{on}^\epsilon = 122 \pm 10\,°C$ and $\log\omega_{on}^\epsilon(\text{rad s}^{-1}) \approx 5.5$. The α shear activity appears (from linear extrapolation, too) at approximately $T^s = 55 \pm 15\,°C$ and $\log\omega^s = 2 \pm 1$. Both the dielectric onset and the shear appearance are well below the β line. The long parallelism of the dielectric α and β traces in figure 3(*a*) proves the fit stability for the small α/β

intensity ratios at high temperatures. A bend of the α curves in the direction of β is not very probable in the onset region.

The results will be discussed on the assumption that there is a common dispersion law for α and β. Modes with a larger length are slower. The merging topology of figure 1(a) would mean that the α cooperativity can be smoothly extrapolated to the locality of the classical β relaxation. Our experiments show that such an extrapolation is not possible for PnBMA. There must be some minimal cooperativity, estimated (Donth 1991) to involve $N_a^{\min} = 10 \ldots 30$ particles (repeating units of the polymer chains here), that cannot be diminished in the α regime.

Two stages of the α regime are suggested by figures 3(a) and (b), and are summarized in figure 4. (Region I) The long parallelism of α and β at higher temperature, and the linear α intensity increase with $1/T$ there, is interpreted as caused by an increasing number of regions with minimal cooperativity. The α activation energy therefore remains constant and is equal to the β activation energy (Kulik *et al* 1994). (Region I $\leftrightarrow$ II) In the crossover range, $T_{co} \approx 30 \ldots 50\,^{\circ}\mathrm{C}$ and $\log \omega_{co}(\mathrm{rad\,s^{-1}}) = 1 \ldots 2$, the liquid bulk volume is assumed to be fully occupied by the minimal-cooperativity regions. This suggestion is supported by the appearance of the α shear loss peak, because the isolated cooperativity regions in I cannot be very shear active. (Region II) Below this crossover we have a specific increase of cooperativity with lower temperatures, $N_a(T)$, leading (Adam and Gibbs 1965, Donth 1992) to a large curvature of the α trace in the Arrhenius diagram.

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