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**Electrical and Nuclear Magnetic Resonance (NMR)**  
**Properties of Linear Polymers**

By

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## Abstract

Broadband dielectric spectroscopy (DS) and fast field cycling  $^1\text{H}$  NMR relaxometry (FFC NMR) are employed to investigate the molecular dynamics of linear polymers, namely, bulk cis-1,4-polyisoprene (PI) and polypropylene oxide (PPO).

Dielectric measurements are carried out on polyisoprenes (PI) with various molecular weights ( $M$  in g/mol) from  $652 \leq M \leq 436000$ . The dielectric normal mode relaxation due to fluctuations of the end-to-end vector and the segmental relaxation related to the glass transition of the polymer are observed. The contribution to the dielectric normal mode relaxation is determined by subtracting the segmental relaxation. This yields the full spectrum including its high-frequency cut-off. Regarding the Rouse regime ( $1040 < M < 9910 \cong M_c \cong 2M_e$ ), the normal mode relaxation is broader than that predicted by the Rouse model. Introducing a weak stretching ( $\beta_K = 0.8$ ) of the correlation function for each normal mode provides a significant improvement of interpolating the experimental spectra. In the low- $M$  limit ( $M < 1040$ ) the normal mode relaxation cannot any longer be clearly identified. In the entanglement regime ( $M > M_c$ ), the normal mode spectrum exhibits a power-law behavior  $\varepsilon'' \propto \nu^{-\gamma}$  at high frequencies with an exponent continuously changing until it saturates around  $M_{\text{rep}} \approx 100000$ , with  $\gamma = 0.26 \pm 0.01$ . Moreover, the  $M$  dependence of the ratio  $\tau_n / \tau_\alpha$  changes from  $M^4$  at  $M_c < M < M_{\text{rep}}$  to  $M^3$  at  $M > M_{\text{rep}}$ . The latter exponent is that of pure tube-reptation; yet, the exponent  $\gamma = 0.26$  is not compatible with the reptation model. Nevertheless, both findings are taken as evidence for another characteristic molecular weight, namely,  $M_{\text{rep}} \cong 20 M_e$ , beyond which entanglement dynamics are fully established.

The relaxation time  $\tau_n(T)$  for the normal mode and  $\tau_\alpha(T)$  for the segmental mode conform to the Vogel-Fulcher-Tammann equation. The ratio of  $\tau_n / \tau_\alpha$  is constant at high  $T$ , whereas, it decreases as temperature approaches the glass transition temperatures  $T_g$ . At high  $T$ , the frequency-temperature-superposition principle (FTS) works for the whole loss curve including both the normal and segmental mode processes.

Analyzing the strength of the normal mode relaxation as a function of  $M$  yields Gaussian statistics of the chains at  $M > 2000$ , i.e., well below  $M_c$ .

Fast field cycling  $^1\text{H}$  NMR is applied to study segmental reorientation dynamics in melts of linear 1,4-polyisoprene with different  $M$  and polypropylene oxide with  $M=18200$ . Dispersion data of the spin-lattice relaxation time  $T_1(\omega)$  are analyzed in terms of the susceptibility  $\chi''(\omega) = \omega/T_1(\omega)$ . FTS is applied to construct the master curves  $\chi''(\omega\tau_\alpha)$  which reflect spectral contributions from glassy as well as polymer specific dynamics. The analysis of spectra yields the molecular weight of a Rouse unit  $M_R \approx 1200$ , and the entanglement weight  $M_c = 2M_e \approx 10000$ . Characteristic polymer dynamics are separated from the total spectrum dominated by the contribution of the glassy dynamics. The polymer dynamics show typical Rouse relaxation features for which Rouse modes grow with  $M$  up to  $M_c \approx 10000$  and saturate when entanglement sets in.

Comparing the  $T_1$  dispersion of fully protonated as well as partially deuterated polyisoprene PI and polybutadiene PB reveals that the polymer spectra are not universal unless the spectral contribution from the glassy dynamics is taking into account but rather depends on the orientation of the inter-nuclear vectors with respect to the contour of the chain present in the particular monomer. After extracting the polymer specific contributions from the overall susceptibility spectra, the universal polymer spectra of entangled polymers show two power-law regimes reflecting the free Rouse

dynamics at low frequencies and the entanglement dynamics at the lowest frequencies.

A comparison of the dielectric and NMR master curves shows that the dielectric segmental relaxation is much broader than that probed by NMR, particularly toward low frequency,  $\omega\tau_\alpha < 1$ . Dielectric and NMR relaxation times  $\tau_\alpha(T)$  agree well and they can be interpolated by a VFT equation.

In the susceptibility representation, indication of the terminal relaxation is recognized at low frequency which is very close to the peak maximum of the normal mode relaxation.