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## Equilibrium and non-equilibrium dynamics of polymers confined in nanopores

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The nonequilibrium dynamics of linear and star-shaped *cis*-1,4 polyisoprenes confined within nanoporous alumina was explored as a function of pore size,  $d$ , molar mass and functionality ( $f = 2, 6, 64$ ).<sup>1,2</sup> Two thermal protocols were tested; one resembling a quasi-static process (I), and another involving fast cooling followed by annealing (II). Although both protocols give identical equilibrium times, it is through protocol I that it is easier to extract the equilibrium times.<sup>2</sup> Both thermal protocols establish the existence of a critical temperature below which nonequilibrium effects set-in. The critical temperature depends on the degree of confinement,  $2Rg/d$ , and on molecular architecture. Strikingly, establishing equilibrium dynamics at all temperatures above the bulk  $T_g$  requires  $2Rg/d > 0.02$ , i.e., pore diameters that are much larger than the chain dimensions. The non-equilibrium phenomena in pores reflects the nonequilibrium configurations of the adsorbed layer that extend away from the pore walls.<sup>3</sup> The equilibrium times depend strongly on temperature, pore size and functionality. In general, star-shaped polymers require longer times to reach equilibrium because of the higher tendency for adsorption.

Subsequently, we studied the adsorption kinetics of PI by following the evolution of the dielectrically active longest normal mode with *in situ* nanodielectric spectroscopy.<sup>4,5</sup> For a given pore diameter the characteristic adsorption times are some 8 orders of magnitude slower than the terminal relaxation times and more than 12 orders of magnitude slower than the segmental times. The extremely slow kinetics reflect the fact that exchanging chains with the pore surface have to pass through several unfavorable configurations (e.g trains, loops). The molar mass dependence of the characteristic adsorption times was in good agreement with a scaling theory proposed by de Gennes and later refined by Semenov and Joanny. The results from *in situ* nanodielectric spectroscopy demonstrate the capacity of the technique to provide the imbibition length, the adsorption kinetics and, at the same time, the chain dynamics.

- (1) Kardasis, P. et al., Effect of Star Architecture on the Dynamics of 1,4-*cis*-Polyisoprene under Nanometer Confinement. *Macromolecules* **2021**, 54, 11392-11403.
- (2) Kardasis, P. et al., Nonequilibrium Effects of Polymer Dynamics under Nanometer Confinement: Effects of Architecture and Molar Mass. *The Journal of Physical Chemistry B* **2022**, 126, 5570-5581.
- (3) Krutyeva, M. et al., Effect of Nanoconfinement on Polymer Dynamics: Surface Layers and Interphases. *Phys. Rev. Lett.* **2013**, 110, 108303.
- (4) Tu, C. H. et al. Interfacial Interactions During *in situ* Polymer Imbibition in Nanopores. *Phys. Rev. Lett.* **2020**, 125, 127802.
- (5) Tu, C.-H. et al., Adsorption Kinetics of *cis*-1,4-Polyisoprene in Nanopores by *In Situ* Nanodielectric Spectroscopy. *Macromolecules* **2021**, 54, 13, 6267-6274.

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