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Cooperative polymer dynamics under nanoscopic pore confinements probed by field-cycling NMR relaxometry

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Abstract

Reptational dynamics of bulk polymer chains on a time scale between the Rouse mode relaxation time and the so-called disengagement time is not compatible with the basic thermodynamic law of fluctuations of the number of segments in a given volume. On the other hand, experimental field-cycling NMR relaxometry data of perfluoropolyether melts confined in Vycor, a porous silica glass of nominal pore dimension of 4 nm, closely display the predicted signatures for the molecular weight and frequency dependences of the spin-lattice relaxation time in this particular limit, namely $T_1 \propto M^{-1.2}$. It is shown that this contradiction is an apparent one. In this paper a formalism is developed suggesting cooperative chain dynamics under nanoscopic pore confinements. The result is a cooperative reptational displacement phenomenon reducing the root-mean-squared displacement rate correspondingly but showing the same characteristic dependences as the ordinary reptation model. The tube diameter effective for cooperative reptation is estimated on this basis for the sample system under consideration and is found to be of the same order of magnitude as the nominal pore diameter of Vycor. © 2007 American Institute of Physics.

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