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# Investigations of polymer dynamics in nanoporous media by field cycling NMR relaxometry and the dipolar correlation effect

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**Abstract**

The chain dynamics of short-chain perfluoropolyether melts confined in Vycor nanoporous media has been characterized by field cycling nuclear magnetic resonance relaxometry and the dipolar correlation effect. The slowdown of motions under confinement, leading to larger residual dipolar couplings, has been probed by looking at the quotient of stimulated and primary echoes. Using field cycling relaxometry, it has been shown that there is strong evidence of reptation-like motion, even for such short-chain polymers as shown by the frequency and molecular weight dependences of the spin–lattice relaxation time.


*Keywords:* Reptation; Confined polymer; Dipolar correlation effect; Field cycling relaxometry

## 1. Introduction

The predominant mechanism by which long-chain polymers are expected to undergo translational motion is reptation. De Gennes [1] originally suggested the reptation model for polymer segment displacements, assuming a three-dimensional network of fixed obstacles in which polymers are trapped. In this study, we have taken melts of short polymers that are subject to Rouse dynamics under bulk conditions [2] and have investigated them for signatures of reptation under confinement in nanoporous Vycor glass. Thus, instead of the fictitious tube anticipated in the reptation model, we have the polymer now confined in real artificial tubes. We have been able to show that such a situation is close to the scenario wherein the reptation theory is valid.

Field cycling nuclear magnetic resonance (NMR) relaxometry [3] probing a time scale of $10^{-9}$–$10^{-4}$ s has proven to be an excellent technique for studying polymer dynamics in both bulk and confined systems. NMR signatures of the Rouse model and the Doi/Edwards tube/reptation model [4] involving frequency and molecular weight relationships with respect to spin–lattice relaxation time can be investigated with this method [5]. Moreover, the time window investigated by this technique covers the most interesting chain mode regime of polymer dynamics.

The dipolar correlation effect (DCE) on the stimulated echo has earlier been shown to be an ideal tool for probing ultraslow fluctuations of long-chain polymers [6] or liquid crystals under confinement [7]. We have used this technique in our work to investigate the slowdown of motions, which is induced by the geometry of the confining system.

## 2. Theory

The Doi/Edwards tube/reptation model has various regions corresponding to specific time limits concerning the dynamics of polymers [5,8–10]. In our experimental window, we have found the time scale to correspond to that between disengagement time and the terminal Rouse relaxation time of confined polymer species. The reptation model suggests for this limit $\tau_d^{-1} \ll \omega \ll \tau_R^{-1}$ (Doi/Edwards Limit III):

$$\frac{1}{T_1^{\mathrm{rep,III}}} \approx \tilde{M}_2 \tau_s \frac{2\pi^{1/2} 3^{1/2} \Gamma(1/2)\cos(\pi/4)}{(\omega\tau_s)^{1/2}} \times \frac{(1+2^{3/2}) N^{1/2} b^3 \tilde{l}}{d_{\mathrm{HRPT}}^4}. \quad (1)$$

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