Field-cycling NMR relaxometry of polymers confined to artificial tubes: verification of the exponent 3/4 in the spin–lattice relaxation dispersion predicted by the reptation model

Rainer Kimmich [a,*], Ralf-Oliver Seitter [a], Uwe Beginn [b], Martin Möller [b], Nail Fatkullin [c]

[a] *Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany*
[b] *Universität Ulm, Abteilung Makromolekulare Chemie, 89069 Ulm, Germany*
[c] *Kazan State University, Department of Molecular Physics, 420008 Kazan, Tatarstan, Russia*

Received 1 April 1999

Abstract

^{2}H field-cycling NMR relaxometry was applied to deuterated linear polyethyleneoxide (PEO) of different chain lengths confined in a porous matrix of cross-linked polyhydroxyethylmethacrylate (PHEMA). The PHEMA pore diameter was of the order of 10 nm, i.e. smaller than or similar to the dimension which the PEO coils would have in the unconfined melt. The frequency and molecular weight dependences of the spin–lattice relaxation time predicted by de Gennes as $T_1 \propto M^0 \omega^{3/4}$ on a timescale short compared with the Rouse relaxation time are well reproduced experimentally. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In his famous 1971 paper [1], de Gennes treated the frequency (ω) and molecular mass (M) dependences of the spin–lattice relaxation time T_1 of polymer chains ''in the presence of fixed obstacles''. On a timescale which is short compared with the so-called Rouse relaxation time τ_R the prediction was

$$T_1 \propto M^0 \omega^{3/4}. \tag{1}$$

Later the 'reptation/tube' model [2] was worked out in more detail, leading to a set of limiting power laws summarized in Table 1. This concept, which was originally developed for the model situation mentioned before is now widely considered for the description of 'entangled dynamics' in polymer fluids with chain lengths above the critical value. However, despite many attempts, the combined frequency dispersion and (absent) molecular mass dependence given in Eq. (1) was never found under such conditions [3–8].

In the present Letter, we report on the experimental verification of the law given in Eq. (1). Flexible linear polymer chains were incorporated in a porous medium in order to have 'obstacles' in the form of pore walls, in analogy to those assumed by de Gennes. There have been a number of earlier attempts to study the confinement effects of organic

---

* Corresponding author. Fax: +49 731 502 3150; e-mail: rainer.kimmich@physik.uni-ulm.de