The "Corset Effect" of Spin-Lattice Relaxation in Polymer Melts Confined in Nanoporous Media

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Abstract. Linear polyethylene oxides with molecular weights $M_c$ of 1665 and 10170 confined in pores with variable diameters in a solid methacrylate matrix were studied by proton field-cycling nuclear magnetic resonance relaxometry. The pore diameter was varied in the range of 9-57 nm. In all cases, the spin-lattice relaxation time shows a frequency dependence close to $T_1 \propto \nu^{-0.4}$ in the range of $\nu = 3 \cdot 10^{-1}-2 \cdot 10^1$ MHz as predicted by the tube-reptation model. This proton $T_1$ dispersion essentially reproduces that found in a previous deuteron study (R. Kimmich, R.-O. Seitter, U. Beginn, M. Möller, N. Fatkullin: Chem. Phys. Lett. 307, 147, 1999). As a feature particularly characteristic for reptation, this finding suggests that reptation is the dominating chain dynamics mechanism under pore confinement in the corresponding time range. The absolute values of the spin-lattice relaxation times indicate that the diameter of the effective tubes in which reptation occurs is much smaller than the pore diameters on the time scale of spin-lattice relaxation experiments. An estimation leads to a value $d' \sim 0.5$ nm. The impenetrability of the solid pore walls, the uncrossability of polymer chains ("excluded volume") and the low value of the compressibility in polymer melts create the "corset effect" which reduces the lateral motions of polymer chains to a microscopic scale of only a few tenths of a nanometer.

1 Introduction

In previous papers [1-3] it was shown that polymer melts confined in porous media are subject to chain dynamics considerably deviating from the behavior in bulk. These studies were performed by field-cycling nuclear magnetic resonance (NMR) relaxometry and field-gradient NMR diffusometry in the fringe-field variant [4, 5]. It turned out that the dynamical limits predicted for the tube-reptation model [6, 7] can be well reproduced with experiments in polymer melts confined in nanoporous solid matrices. The motivation of the present work is the attempt to detect experimentally the crossover from confined to bulk behavior by varying the pore diameter, or more precisely, to probe the length scale
on which pores give rise to confined chain dynamics. A theoretical treatment and a Monte Carlo simulation of this sort of phenomenon was recently published in ref. 8. A further objective of this article is to estimate theoretically the diameter of the “tube” (in contrast to that of the pores) effective under confinement conditions on the time scale of spin-lattice relaxation experiments.

2 Samples and Techniques

The nanoporous methacrylate samples were prepared as semi-interpenetrating networks from a variable mixture of hydroxyethyl-methacrylate, dodecyl-methacrylate and 1,2-ethyleneglycol-dimethacrylate in which linear polyethylene oxide (PEO) was incorporated in pores. The experiments refer to mainly two almost monodisperse PEO fractions purchased from Aldrich and characterized by gel permeation chromatography in our laboratory. The molecular weights were $M_w = 1665$ and $10170$, the polydispersity was $M_p/M_w \approx 1.08$ and $M_p/M_w \approx 1.07$, respectively. The bulk value of the critical molecular weight of PEO is reported to be in the range $M_c = 3600-5900$ [9, 10]. That is, polymer dynamics was examined below as well above $M_c$.

The preparation method is similar to that published in refs. 11 and 12. A more detailed description and additional sample characterization experiments were reported in ref. 13. Figure 1 shows typical electron micrographs visualizing the pore channels in which the PEO chains are free to move. The pore diameters can be estimated crudely from the electron micrographs and more precisely by fitting the theoretical spin echo attenuation curves to field-gradient NMR diffusometry data [13]. Values between 9 and 57 nm were found, depending on the composition of the matrix. The samples were evacuated over night in order to remove any volatile constituents.

![Fig. 1. Typical freeze-fracture electron micrographs of semi-interpenetrating networks formed of cross-linked methacrylate and linear PEO ($M_w = 6000$). The “worm-like” structures represent PEO that was contained in pores with a diameter of about 10 nm.](image-url)