PHYSICAL REVIEW E **81**, 060801(R) (2010)

Large-scale dynamics of a single polymer chain under severe confinement

Karine Lagrené,[1] Jean-Marc Zanotti,[1,*] Mohamed Daoud,[2] Bela Farago,[3] and Patrick Judeinstein[4]
[1]*CEA/IRAMIS/Laboratoire Léon Brillouin, CEA-CNRS, CEA Saclay, 91191 Gif-sur-Yvette, France*
[2]*CEA/IRAMIS/Service de Physique de l'Etat Condensé, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*
[3]*Institut Laue Langevin, 38042 Grenoble Cedex, France*
[4]*ICMMO, UMR CNRS 8182, Université Paris-Sud, 91405 Orsay, France*

(Received 9 April 2010; published 24 June 2010)

We address the dynamical behavior of a single polymer chain under nanometric confinement. We show how neutron spin-echo, combined with contrast matching and zero average contrast, makes it possible to, all at once, (i) match the intense porous detrimental elastic small angle neutron scattering contribution to the total intermediate scattering function $I(Q,t)$ and (ii) measure the Q dependence of the dynamical modes of a single chain under confinement. The method presented here has a general relevance when probing the large scale dynamics of a system of large molecular mass under confinement.

DOI: 10.1103/PhysRevE.81.060801 PACS number(s): 61.25.hk, 78.70.Nx, 81.07.−b, 82.35.Lr

Depending on the time and length scales, a polymer chain experiences different dynamical regimes [1]. At short time and on a local scale (1 ns, 50 Å), the chain just experiences random entropic forces and freely fluctuates in an isotropic way. This is the Rouse regime. At larger scale and longer times (100 ns, 500 Å), the neighboring chains induce a topological constraint and the chain fluctuates alongside a fictive tube [2]: the reptation tube (regime of the local reptation). The tube diameter is similar to the distance between two entanglements i.e., around 50 Å. Then, at even longer times (1000 ns), in the so-called full reptation regime, the chain can finally escape the tube. Such a microscopic model is extremely useful and efficient, since with very few parameters such as a monomeric friction coefficient and the length of a chain segment, it is possible to bridge the local dynamics to macroscopic properties like, for example, the polymer viscosity.

In numerous scientific fields, reducing the dimensions of a physical system down to a scale that matches the characteristic sizes of its natural fluctuations in bulk, usually leads to unexpected and surprising new physical behaviors [3]. In soft matter, despite the key practical and industrial relevance of such situations, the peculiar properties of polymers in interfacial situations [4] or deep confinement [5] are far from being fully understood. Several theoretical approaches have addressed the issue of the polymer conformation when a melt is confined inside cylindrical pores [6]. It has been proposed that under confinement a modification of the monomer-monomer excluded volume interaction could lead to an increase of the longest polymer relaxation time and therefore of the confined polymer viscosity [7]. Recently, NMR relaxometry results have suggested [8] that the confinement of a polymer melt in a nanoscopic isotropic porous matrix leads to a chain dynamics that is dramatically different from the bulk behavior: the reptation tube diameter under confinement would be only few Angstroms i.e., one order of magnitude smaller than in the bulk. This would actually correspond to a situation where the chain experiences reptation alongside its own physical contour so that this phenomenon has been called the *corset effect* [8]. This effect has been observed at 373 K, on chains of high molecular mass Poly(Ethylene Oxide) (PEO, 10 kg mol^{-1}) confined by spinodal decomposition within the nanometric (100–200 Å) connected porous network of a Cross-Linked MethaCrylate (CLMC) matrix. At this temperature, the PEO is above its melting temperature (332 K) while the CLMC matrix is below its glass transition temperature. This is therefore a situation of so-called *hard confinement*. It should also be noted that at the nanometer scale, the structure of the cylindrical CLMC pores is highly anisotropic, but at the much larger scale probed by NMR relaxometry, the information is powder averaged.

In this paper, we challenge the existence of the *corset effect* by a neutron spin-echo (NSE) experiment at small scattering angles. To stay in tune with the conditions for which the *corset effect* has been observed, we consider a PEO melt with molecular mass 35 kg mol^{-1} i.e., above the critical entanglement mass $M_c \approx 3.5$ kg mol^{-1}. The chains

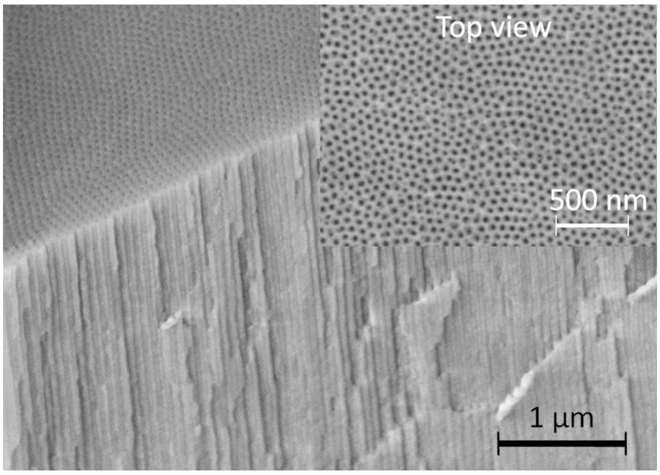

FIG. 1. Scanning electron microscope image of a typical LLB made AAO membrane. A highly oriented array of cylindrical pores goes from the top down to the bulk of the membrane. The imperfect hexagonal array of pores is clearly seen on the top of the membrane (inset).

---

[*] Corresponding author; jmzanotti@cea.fr

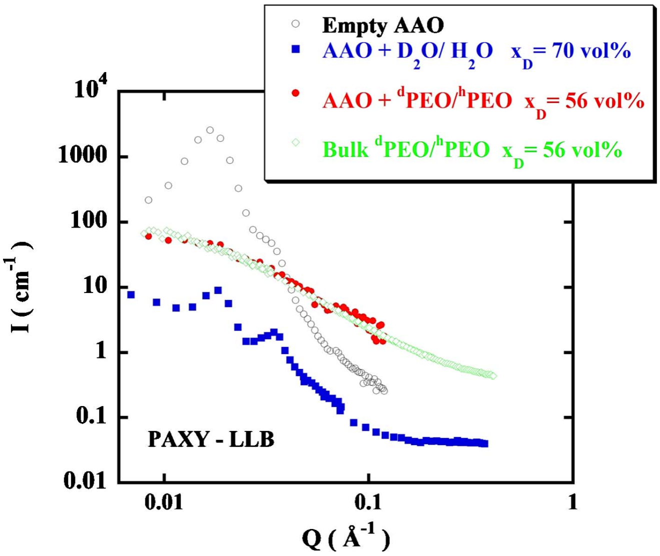

FIG. 2. (Color online) SANS spectrum of an empty AAO membrane. The extremely intense peak at 1.7 10^{-2} Å^{-1} is characteristic of the interpore distance, here $D_{Int}=370\pm40$ Å. The pore diameter is $D_P=180\pm20$ Å. The neat AAO membrane intense signal can be nearly perfectly *matched* [11] upon membrane impregnation by an isotopic mixture of water (x_D=70 vol %) or PEO (x_D=56 vol %). In the later case, the remaining contribution is the form factor of a single polymer chain. No large scale structural differences between the bulk and confined chain conformation are detected.

are long enough so that they can entangle and therefore lay in the reptation regime. The confining medium is membranes of anodic aluminum oxide (AAO, Fig. 1). Since porous materials are usually very good scatterers, small angle neutron scattering (SANS) is a key technique for accessing their structure. But this advantage turns to a strong handicap when it comes to access the dynamics under confinement in the SANS regime: the fraction of intensity scattered inelastically by the confined material is several orders of magnitude smaller than the elastic contribution due to the static confining matrix. Then within the typical statistics of a neutron experiment (few %) the dynamical information cannot be recovered. In this paper we detail a general way to lift this difficulty.

AAO membranes have been prepared following the two-step anodization process described by Masuda *et al.* [9]. After electropolishing, high purity aluminum has been anodized for 20 min in sulfuric acid (0.3 M) at −5 °C. After chemical leaching of the preformed porous anodic alumina film in a mixture of phosphoric acid (6 wt %) and chromic acid (1.8 wt %), the second and final anodization has been performed again, under the same conditions, for 24 h. The resulting porous membrane shows a hexagonal-like arrangement of fairly monodisperse pores with diameter $D_p=180\pm20$ Å. Ten such membranes of 10×10 mm^2 and 75 μm thick have been prepared. When placed in the neutron beam of a SANS spectrometer, in such a way that the pore axis is perfectly parallel to the incident beam, the scattered intensity is isotropic so that a radial grouping of the two-dimensional (2D) raw spectrum is possible (Fig. 2).

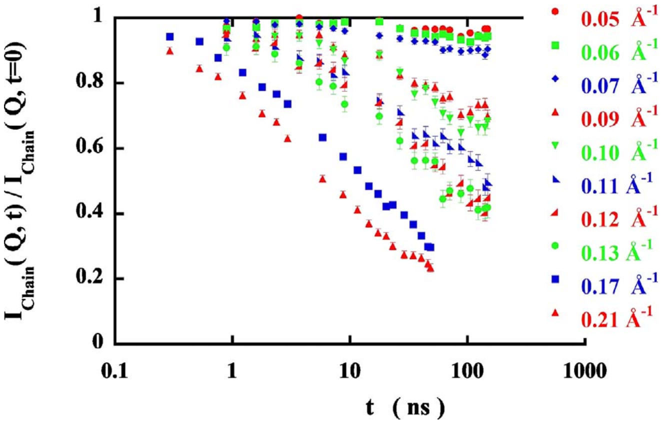

FIG. 3. (Color online) NSE intermediate scattering function of a single chain 35 kg mol^{-1} PEO confined within the porous network of an AAO membrane. The polymer is a mixture of deuterated (x_D=56 vol % chains) and hydrogenated PEO. This isotopic composition matching the AAO membrane, the intense elastic contribution due to the AAO membrane is canceled out and the scattered intensity is purely inelastic.

A detailed analysis of the scattering curve [10] shows that the extremely intense peak at $Q^*=1.7$ 10^{-2} Å^{-1} is characteristic of the interpore distance, here $D_{Int}=370\pm40$ Å.

A polymer mixture consisting of deuterated (d) (Polymer source: M_n=36.5 kg mol^{-1}, M_w=38 kg mol^{-1}, M_w/M_n=1.04) and hydrogenated (h) (polymer source: M_n=35 kg mol^{-1}, M_w=37.8 kg mol^{-1}, M_w/M_n=1.08) PEO with x_D=0.56 vol % deuterated fraction is prepared. It is then left melted, at 373 K under secondary vacuum, on top of the AAO membranes. After several hours, the polymer is confined within the AAO porous structure. The polymer excess is removed from the top of the membrane and is used as the bulk polymer sample. The bulk sample and the AAO+PEO membranes are sealed in a standard aluminum container. All samples have been measured at T=373 K, using three incident wavelengths (10, 14.5, and 22 Å) on the IN15 neutron spin-echo spectrometer (ILL, France) equipped with a 32×32 cm^2 2D detector. We probe the polymer dynamics on an extremely broad spacial [2.2 10^{-2} Å^{-1}, 0.2 Å^{-1}] and temporal [0.1 ns, 600 ns] ranges (Fig. 3). The melting point of the AAO confined PEO is 317 K [differential scanning calorimetry (DSC) thermograms not shown] compared to 332 K in bulk. This significant melting point depression is a purely thermodynamical so-called Gibbs-Thomson effect [12] and is clear evidence that the PEO chains are facing a confinement situation.

Lal, Sinha and Auvray [13] have successfully used the zero average contrast (ZAC) technique [14] to access the conformation of a polymer in semidilute solution, confined in the porous structure of Vycor. They have considered a solution of hydrogenated (H) and deuterated (D) polymer chains in a solvent (S) confined in a porous medium (Vycor) and show that, if the solvent scattering length densities matches the scattering length densities of the confining matrix, the SANS intensity $I(Q)$, can be written as a sum of only three partial structure factors

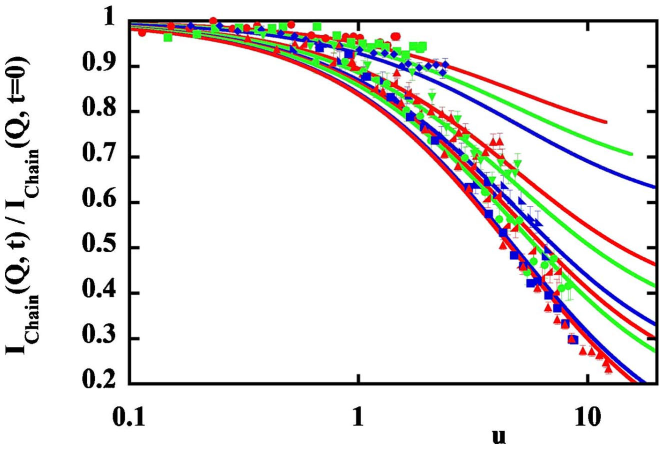

FIG. 4. (Color online) Same data as Fig. 3 plotted as a function of u (see text) showing the fit (full lines) to Eq. (4) with $W\sigma^4=1778\pm63$ Å^4 ns^{-1} and $d_{Rep}=67\pm3$ Å. The symbols used refer to the same Q values than on Fig. 3. The corresponding fit lines are in the same order, from top to bottom.

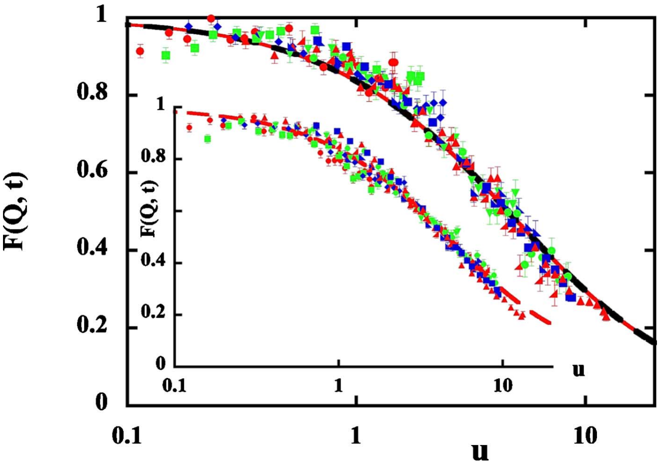

FIG. 5. (Color online) $[I_{Chain}(Q,t)/I_{Chain}(Q,t{=}0)-p(Q)]/[(1-p(Q)|$ for the confined and bulk polymer (inset). The symbols used refer to the same Q values than on Fig. 3. The full and dotted lines stand for the master curve $F(Q,t)$ (Eq. (4)) with the parameters fitted on the confined ($W\sigma^4=1778\pm63$ Å^4 ns^{-1}; $d_{Rep}=67\pm3$ Å.) and bulk ($W\sigma^4=2066\pm60$ Å^4 ns^{-1}; $d_{Rep}=65\pm2$ Å) polymer, respectively. The tenfold reduction of the reptation tube predicted by the *corset effect* is not observed.

$$I(Q)=(n_D-n_0)^2S_{DD}+(n_H-n_0)^2S_{HH}+2(n_D-n_0)(n_H-n_0)S_{HD}, \tag{1}$$

where, n_H, n_D, and n_0 are the neutron coherent scattering length densities of the hydrogenated polymer, deuterated polymer and the solvent, respectively. In our case, the solvent can be assimilated to the confining matrix. Each of these partial structure factors can be decomposed into an intrachain, $P(Q)$, and an interchain, $Q(Q)$, contribution. If one makes the assumption that the H and D polymer chains are identical (same polymerization index N, local structure and large scale conformation), Eq. (1) becomes

$$I(Q)=(n_D-n_H)^2x_D(1-x_D)v\Phi NP(Q)+[x_Dn_D+(1-x_D)n_H-n_0]^2[v\Phi NP(Q)+v\Phi^2Q(Q)], \tag{2}$$

where x_D is the proportion of deuterated chains, v the molecular volume of a monomer and Φ the polymer volume fraction. If x_D can be set to meet the condition

$$x_D\,.\,n_D+(1-x_D)n_H-n_0=0 \tag{3}$$

the second term of Eq. (2) vanishes so that $I(Q)$ is then only proportional to $P(Q)$, the form factor of a single chain.

As shown on Fig. 2, the intense AAO SANS signal can be *matched* [11] by full impregnation of the membrane by a 70 vol %D_2O of D_2O/H_2O mixture. The coherent scattering length density of an AAO membrane can then be derived: $\rho_{AAO}=4.21\ 10^{10}$ cm^{-2}. The coherent scattering length density of h and d PEO being $\rho_{hPEO}=6.20\ 10^{9}$ cm^{-2} and $\rho_{dPEO}=6.88\ 10^{10}$ cm^{-2}, respectively, the condition Eq. (3) is fulfilled for $x_D=0.56$. As shown on Fig. 2 by the perfect canceling out of the Q^* intense AAO peak, the h/d PEO mixture perfectly matches the AAO membrane. This is a direct experimental evidence that the polymer is fully and homogeneously confined within the AAO porous network. The remaining SANS signal is the form factor, $P(Q)$, of a single confined polymer chain. As shown by the strong similarity of the confined and bulk polymer chain form factor, no large scale significant structural change of the confined chain is detected by respect to its bulk analog. In particular, the radius of gyration $R_G=67\pm1$ Å is not affected by the confinement.

As far as the dynamical aspect is concerned, the reptation mechanism in a tube with diameter d_{Rep} leads to a transient localization of the chain. This is accounted for in $I_{Chain}(Q,t)$, the intermediate scattering function of a single polymer chain [15]:

$$\frac{I_{Chain}(Q,t)}{I_{Chain}(Q,t=0)}=[1-p(Q)]F(Q,t)+p(Q) \tag{4}$$

by $p(Q)=e^{-Q^2d_{Rep}^2/36}$, the form factor of the reptation tube, that shows as a Q dependent but time independent plateau. $F(Q,t)=e^{-u^2/36}\mathrm{erfc}(-\frac{u}{6})$, where $u=Q^2\sqrt{W\sigma^4t}$ is the Rouse variable, σ denotes the length of a chain segment and $W=3k_BT\zeta_0^{-1}\sigma^{-2}$ is the elemental Rouse rate. It is a function of ζ_0, the monomeric friction coefficient, k_B the Boltzmann constant and the temperature T. The NSE data of the bulk (not shown) and confined polymer (Fig. 4) follow the model Eq. (4). We estimate to only 70 mg the total amount of confined polymer in the neutron beam. It therefore should be stressed out that the quality of the data shown on Fig. 4 can be considered as exceptional. Next to the intrinsic quality of the IN15 instrument, this is partly due to the conjunction of two important factors: (i) the strong SANS scattering of the high molecular mass single chain (in SANS, the intensity at zero wave vector, $I(Q=0)$, is proportional to the molecular mass of the scattering objet) and (ii) the fact that the $x_D=0.56$ actual isotopic composition of the PEO mixture is very close to $x_D=0.5$ that maximizes the $x_D(1-x_D)$ term in

Eq. (2) and therefore the scattering intensity. To prevent any decomposition of the PEO, we avoided to measure the sample above 373 K, so that in the time range probed here, the reptation plateau (Fig. 4) is not fully visible. Nevertheless, a time and Q fitting of the whole $I_{Chain}(Q,t)$ data set provides a very precise determination of both the temporal and structural parameters of Eq. (4). As shown on Fig. 4, the description of the confined PEO data with the fitted parameters $W\sigma^4 = 1778 \pm 63$ Å^4 ns^{-1} and $d_{Rep} = 67 \pm 3$ Å is very satisfactory. The same data treatment applied to the signal of the bulk polymer (not shown) leads to $W\sigma^4 = 2066 \pm 60$ Å^4 ns^{-1} and $d_{Rep} = 65 \pm 2$ Å. As shown on Fig. 5, both the dynamics and the reptation diameter of the bulk and confined polymer are indistinguishable. We therefore do not observe any *corset effect*. If the confinement size, mobility of the confining matrix, temperature, nature, and molecular weight of the polymer are very similar, a key difference between the present experiment and the one by Fatkullin and Kimmich is the tortuosity of the porous network: while the pores of their CLMC sample has a correlation length in the hundreds of nanometer range, the AAO membrane pores are perfectly straight on about hundred micrometers.

We have combined SANS, contrast matching and ZAC with neutron spin-echo to experimentally probe the structure and dynamical behavior of a single polymer chain confined in a nanometric in diameter, micrometer long cylindrical pore of an AAO membrane. The confinement is quite severe since the pore diameter is only a factor three bigger than the natural reptation tube diameter. While the perfect SANS contrast matching of the AAO membrane evidences that the polymer is fully and homogeneously confined within the porous network, the ZAC condition makes it possible to relate the remaining SANS signal to the sole (statistically averaged) form factor of a single confined polymer chain. We do not detect any influence of confinement on the polymer chain conformation. A second advantage of working under perfect contrast matching of the porous network is that the intense static scattering of the confining matrix cancels out to leave only a pure inelastic scattering due to the confined polymer dynamics. By interpreting the data within the framework of the reptation theory, we show that confinement does not affect the dynamical property of the polymer chains nor the diameter of the reptation tube. If true, the *corset effect* is therefore not a general phenomenon.

A clear advantage of the method presented here, is the direct and simultaneous probe of correlation functions as a function of space and time, so that the Q dependance of the system characteristic time(s) can be measured. In the field of soft matter, it is particularly adapted to probe, in a nondestructive way, the rheology of any polymer under nanometric confinement, a situation where more classical experimental approaches are challenging. But the method has a general relevance when probing the large scale dynamics of a system of large molecular mass experiencing any type of confinement, a situation particularly relevant in the field of Biophysics [16].

---

[1] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[2] P.-G. de Gennes, J. Chem. Phys. **55**, 572 (1971).

[3] R. L. Jones, S. K. Kumar, D. L. Ho, R. M. Briber, and T. P. Russell, Nature (London) **400**, 146 (1999).

[4] H. Bodiguel and C. Fretigny, Phys. Rev. Lett. **97**, 266105 (2006).

[5] S. Sen, Y. Xie, S. Kumar *et al.*, Phys. Rev. Lett. **98**, 128302 (2007).

[6] F. Brochard and P.-G. de Gennes, J. Phys. (France) Lett. **40**, 399 (1979).

[7] A. N. Semenov, Phys. Rev. Lett. **80**, 1908 (1998).

[8] N. Fatkullin, E. Fischer, C. Mattea, U. Beginn, and R. Kimmich, ChemPhysChem **5**, 884 (2004).

[9] H. Masuda and K. Fukuda, Science **268**, 1466 (1995).

[10] K. Lagrené and J.-M. Zanotti, Eur. Phys. J. Spec. Top. **141**, 261 (2007).

[11] The SANS intensity of a porous material is controlled by a contrast term $(\rho - \rho_0)^2$ where ρ and ρ_0 are the coherent scattering length densities of the confined material and of the porous matrix. Setting $\rho = \rho_0$ cancels out any structural information related to the porous matrix.

[12] M. Alcoutlabi and G. B. McKenna, J. Phys.: Condens. Matter **17**, R461 (2005).

[13] J. Lal, S. K. Sinha, and L. Auvray, J. Phys. II **7**, 1597 (1997).

[14] M. Benmouna and B. Hammouda, Prog. Polym. Sci. **22**, 49 (1997).

[15] D. Richter, M. Monkenbusch, A. Arbe, and J. Colmenero, Adv. Polym. Sci. **174**, 1 (2005).

[16] B. Wang, J. Guan, S. M. Anthony, S. C. Bae, K. S. Schweizer, and S. Granick, Phys. Rev. Lett. **104**, 118301 (2010).