## Effects of Self-Assembly on Diffusion Mechanisms of Triblock Copolymers in Aqueous Solution

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Molecular dynamics of self-assembling triblock copolymers in a mixture with water was explored using nuclear magnetic resonance (NMR) diffusometry with high-intensity field gradient pulses. With varying concentration, the diffusivities are found to cover 4 orders of magnitude. The dramatic changes in both the rates and patterns of polymer propagation can be attributed to their ordering in supermolecular formations and prove to be a sensitive means for probing structural and dynamic features of self-aggregation which only now, owing to recent progress in NMR diffusometry, have become accessible to direct observation.

DOI: 10.1103/PhysRevLett.102.037801

PACS numbers: 61.25.he, 82.35.Jk, 82.56.Lz, 83.80.Uv

Self-association of soft materials represents a subject of extensive interdisciplinary research [1-3]. It is central for a broad range of topics, from understanding selforganization of living systems [3] to establishing new synthesis routes in modern molecular engineering [4]. In spite of the progress achieved in the structure analysis of such systems, the dynamic properties of the involved molecules and their correlation with the underlying microstructure remain only poorly understood. At the same time, these properties are of crucial importance for the functionality of cell membranes, the rate of biochemical reactions, and the optimal properties of nanosensors and delivery devices.

Self-assembly on the mesoscopic length scale tends to impose severe internal constraints on molecular diffusion. These constraints act as *internal restrictions* on molecular propagation, analogously to the external *confinement* characteristic of typical host-guest systems [5]. Specific symmetry and connectivity properties of local molecular ordering tend to inhibit three-dimensional isotropy. The current work represents a study of the effect of supermolecular formation on diffusion in self-assembling block copolymers (BCP). BCP exhibit a rich variety of equilibrium symmetries (spherical, cylindrical and lamellar) which can be controlled by varying concentration, temperature, and block composition [6] and make them ideal candidates for this type of studies.

Up to now, diffusion studies of BCPs were essentially limited to the melts or liquid solutions of spherical micelles [7,8]. A few works dealt with cubic phases [9,10] and with multiblock copolymers in selected solvents [11]. Here, a deliberate selection of the BCP samples enabled us to perform self-diffusion study of the same molecules and at the same temperature, when the molecules are confined in four different supermolecular structures. They include micellar liquid and three liquid crystalline (micellar cubic, hexagonal, and lamellar) formations, schematically shown in Fig. 1. In our studies, supermolecular association is driven by the poor solubility of the PPO block in poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (PEO-PPO-PEO) in water [6], leading to their self-aggregation in dehydrated cores surrounded by a corona of hydrated PEO tails. This ambivalence ensures anchoring of the BCP molecules within the ordered structures and restrictions on the trajectories of molecular propagation as also sketched in Fig. 1.

The samples  $[(PEO)_{27} - (PPO)_{61} - (PEO)_{27}]$  (trade Pluronic P104, nominal molecular name mass  $\sim$ 5900 g mol<sup>-1</sup>) and  $(PEO)_{20} - (PPO)_{70} - (PEO)_{20}$ (P123, ~5750 g mol<sup>-1</sup>)] with a polydispersity P = $\bar{M}_{\rm w}/\bar{M}_{\rm n}$  of  $1.15 \le P \le 1.31$  were obtained as a gift from BASF Corp. and used without further purification. The phase diagrams of P104 and P123 are reported elsewhere [6]. A homopolymer PEO (~6000 g mol<sup>-1</sup>) with P = 1.38was purchased from Sigma-Aldrich and studied for a comparison as a water-soluble nonassembling counterpart. Polymer concentration c in the mixtures with water was varied from 3.8 to 100 wt %.

The self-diffusion coefficients *D* were measured by pulsed field gradient NMR [12–14] using the home-built diffusometer FEGRIS 400 (see [15], and references



FIG. 1 (color online). Schematics of Pluronic self-assemblages in water and of the associated diffusion paths with increasing concentration: micellar (a), cubic (b), hexagonal (c), and lamellar (d) structures.

therein) and the three-ninety-degree pulse sequence  $(\pi/2 - \tau_1 - \pi/2 - \tau_2 - \pi/2 - \tau_1$ —stimulated spin echo). In the simplest case of normal isotropic diffusion, the attenuation of the echo amplitude reads for  $\tau_1 \ll \tau_2$  [15–17]:

$$\Psi(q,t) = \exp(-q^2 t D), \tag{1}$$

with  $q = \gamma \delta g$ . Here,  $\gamma$  is the gyromagnetic ratio,  $\delta$  and g are duration and amplitude of the magnetic-field gradient pulses applied during the  $\tau_1$  intervals and separated by the time interval  $\Delta$ ;  $t = \Delta - \delta/3$  and denotes the observation time; in our experiments  $t \approx \tau_2$ . In each set of experiments, the values of  $\Delta$  and  $\delta$  were kept constant, while the gradient strength was varied. If not otherwise stated, the diffusivities were found to be independent of the observation time. Because of the occurrence of extremely low diffusivities, high-intensity gradients (up to 35 T m<sup>-1</sup>) had to be applied [15]. All diffusion measurements refer to polymer protons.

In the special cases of anisotropic diffusion in arrays of cylindrical symmetry, two coefficients  $D_{\parallel}$  and  $D_{\perp}$  (the principal elements of the diffusion tensor) have to be considered. They represent the diffusivities parallel and perpendicular to the axis of symmetry. For a "powder sample" Eq. (1) is replaced by [12,17]

$$\Psi(q,t) = \exp(-q^2 t D_{\perp}) \int_0^1 \exp[-q^2 t (D_{\parallel} - D_{\perp}) x^2)] dx,$$
(2)

implying integration over all axis orientations ( $x = \cos\theta$ ).

Monoexponential curves were only observed in Pluronic melts, micellar liquids, and PEO solutions. In these systems, (isotropic) diffusivities D could be determined by fitting Eq. (1) to the data points as shown in Fig. 2(a) for the micellar liquid with 24 wt % of P123 [see also inset in Fig. 2(b)]. Nonexponential attenuations were observed in all three liquid crystalline phases as also illustrated in Fig. 2(a) for P123 in the micellar cubic (28 wt %), hexagonal (50 wt %), and lamellar (70 wt %) phases. The departure from the monoexponential function was especially pronounced in the hexagonal phase.

In the micellar liquid, D was found to smoothly decrease with increasing concentration as shown in Fig. 3, regime I. Such a behavior is typical of polymer solutions and reflects growing efficiency of steric hindrances on molecular displacements [8,11]. The diffusivity of PEO molecules in water as a function of c is shown as an example. The absolute values are notably larger than in Pluronic systems at the same concentrations. This indicates that at given temperature of 23 °C Pluronic molecules tend to diffuse as micellar aggregates [Fig. 1(a)] rather than as individual molecules. At higher concentrations, beyond regime I in Fig. 3, diffusion behavior of Pluronic systems dramatically contrasts to that of PEO solutions. With increasing c the attenuation curves exhibit sharp changes in slope and shape. Figure 2(a) exemplifies the particular dramatic changes from 24 wt % (micellar liquid) to 28 wt % (cubic phase), and further to 50 wt % (hexagonal phase) and 70 wt % (lamellar phase). These conversions result in the most intriguing behavior of the Pluronic diffusivities with four distinctly different regimes as displayed in Fig. 3.

Regime II represents the cubic phase. As indicated by the solid line for P123 with 28 wt % in Fig. 2(a), the first points of the data sets were attributed to the contribution of a small fraction of "loose" micelles or molecules not attached to the crystalline lattice and left, therefore, out of consideration. For concentrations above 25 wt %, within a range of a few percents, the diffusivities drop by more than 2 orders of magnitude. This sharp decrease reflects phase transformation from micellar liquid to micellar cubic, as a variant of "hard-sphere crystallization." It is known to occur at well-defined, critical concentrations [18]. The diffusivities ( $<10^{-14}$  m<sup>2</sup> s<sup>-1</sup>) are even 20– 40 times smaller than in the pure Pluronic melts (i.e., with no water at all).

As part of the formed lattice [Fig. 1(b)], the micelles cannot move anymore freely in space, resulting in diffusion path ways dramatically reduced, from about 2  $\mu$ m in the micellar phase to about 100 nm (in each case t = 400 ms). These displacements are still much larger than the micelle dimensions (~5–10 nm [6,19]). Thus, our measurements refer to long-range diffusion rather than to interface diffusion within the individual micelle [as shown in Fig. 1(a)].



FIG. 2. PFG NMR attenuation plots of P123 in water for different concentrations at 23 °C (a) and for different temperatures for c = 29 wt % (b). Inset in Fig. 2(b), additionally, shows the plots for c = 24 wt % (23 °C) and 29 wt % (1 °C). The full lines represent best fits of Eqs. (1) [for 24 and 28 wt % (a) and for 29 wt % at 1 °C (b)] and (2) [for 50 and 70 wt % (a)].



FIG. 3. Diffusion coefficients of the polymers in aqueous solutions of P123, P104, and PEO as a function of polymer concentration at 23 °C. Also indicated are the different ranges of concentration giving rise to the various modes of Pluronic self-organization as illustrated by Fig. 1 [6].

This micellar crystallization onto the ordered lattice appears to strongly damp but not to completely stop the longrange diffusion. Diffusion most probably proceeds by "hopping" of individual molecules from micelle to micelle. Additional contributions may result from whole micelles, migrating along defects of the lattice structure.

With slopes (and hence diffusivities) increasing by 2–3 orders of magnitude with *decreasing* temperatures, the attenuation curves for P123 in Fig. 2(b) most impressively reveal the anomalous temperature behavior of the cubic phase. This is a consequence of the increasing solubilisation of the PO block below 15 °C which, being referred to as "inverse melting" [18], counteracts self-assemblage. In fact, yielding a diffusivity close to that of PEO in solution, the attenuation curve at 1 °C (inset) provides clear evidence that Pluronics diffusion now occurs by individually dissolved chains rather than by chain aggregations in micelles.

With further increasing concentration, at our principal measuring temperature of 23 °C (Fig. 3), the Pluronic molecules are known to form a hexagonal and, eventually, a lamellar phase [6]. Again, the phase transitions are found to be reflected by pronounced changes in the diffusion patterns as revealed by the PFG NMR signal attenuation curves [Fig. 2(a)]. They are in excellent agreement (full lines) with the dependency predicted by Eq. (2), with the fitting parameters  $D_{\parallel}$  and  $D_{\perp}$  given in Table I. Most importantly, with  $D_{\parallel} \gg D_{\perp}$  (essentially one-dimensional diffusion) in the hexagonal phase and  $D_{\parallel} \ll D_{\perp}$  (essentially two-dimensional diffusion) in the lamellar phase, the diffusivities impressively reflect the change in dimension-

ality. In Fig. 3, the anisotropic phases are represented by their dominating diffusivities:  $D_{\parallel}$  in the hexagonal phase (regime III) and  $D_{\perp}$  in the lamellar phases (regime IV).

Figure 3 demonstrates that Pluronic diffusion is not monotonically decreasing any more with increasing concentration as observed for nonassembling polymers like PEO (and for Pluronics within the concentration range of the micellar liquid phase) as a simple consequence of the increasing obstruction of the diffusion path ways [8,11].

As illustrated by Figs. 1(c) and 1(d), now, in the hexagonal and lamellar phases the molecules may diffuse over essentially unlimited distances within one and the same state of self-aggregation, namely, in axes direction in the hexagonal phase  $(D_{\parallel})$  and within each individual layer in the lamellar phase  $(D_{\perp})$ . The corresponding diffusivity values remain practically constant as the concentration increases within one phase (regimes III and IV) with essentially coinciding behavior of the two Pluronics considered. This, once again, emphasizes the dominance of microstructure in comparison with concentration, providing clear evidence that the main diffusion mechanism is along the boundary layer separating the segregated blocks. Long-range diffusion in directions perpendicular to the interface, leading to a departure from ideal one- and twodimensional diffusion in the hexagonal and lamellar phases and being the dominating mechanism of diffusion in the cubic phase, is strongly damped due to the energetic penalty associated with "pulling" the PPO block through the water-rich regions (coronas) [20].

The measured diffusivities in the hexagonal phase are found to be independent of varying observation times, corresponding to molecular displacements between 180 and 320 nm [see the perfect coincidence of the corresponding attenuation curves in Fig. 2(a)]. This finding indicates maintenance of an ideal homogeneous structure of selfaggregation over these spatial dimensions. In contrast, a slight decrease of the attenuation slopes with increasing observation time in the lamellar phase [Fig. 2(a)] has to be attributed to deviations from a uniform structural arrangement which become relevant for the longest displacements (of about 400 nm) considered in our experiments. The existence of defects and dislocations in the lamellar structure can facilitate diffusion in the perpendicular directions and may, therefore, be responsible for the fact that the diffusivity perpendicular to the lamellae  $(D_{\parallel})$  exceeds the diffusivity  $D_{\perp}$  perpendicular to the cylinder axis in the hexagonal phase by 1 order of magnitude; see Table I. Faster perpendicular diffusion across lamellae can also be facilitated due to smaller water concentration in the

TABLE I. The diffusion coefficients evaluated from the fits of Eq. (2) to the experimental data represented in Fig. 2(a) for the hexagonal (50 wt %) and lamellar (70 wt %) structure.

Morphology	$D_{\parallel}[m^2 s^{-1}]$	$D_{\perp}[\mathrm{m}^2 \mathrm{~s}^{-1}]$	$D_{\parallel}/D_{\perp}$	$D_\perp/D_\parallel$
Hexagonal	$(2.1 \pm 0.1) \times 10^{-13}$	$(1.7 \pm 0.4) \times 10^{-15}$	$124 \\ 8.8 \times 10^{-2}$	$8.1 \times 10^{-3}$
Lamellar	$(1.5 \pm 0.6) \times 10^{-14}$	$(1.7 \pm 0.1) \times 10^{-13}$		11

interface region reducing the overall penalty for pulling PPO blocks through this region.

In contrast to lamellar molecular arrangement with one preferential orientation perpendicularly to the lamellae, molecules in the hexagonal phase will assume all radial orientation with equal probabilities. In the extreme case of rodlike molecules, such a situation prohibits the mutual passage of adjacent molecules and gives rise to single-file confinement with vanishing diffusivity [21,22]. As a remarkable outcome of the present studies, the rates of molecular propagation by interface diffusion in the hexagonal phase ( $D_{\parallel}$  in regime III) and in the lamellar phase ( $D_{\perp}$  in regime IV) are found to coincide, irrespective of the differences in molecular orientations.

As a possible explanation, one might consider a mechanism similar to the "activated reptation" or "block retraction" suggested for entangled A - B diblock copolymers forming lamellar structures [23]. In entangled lamellar systems, lateral diffusion is hindered by a one-dimensional "tube" formed by the entanglements and oriented, in average, perpendicular to the interface. Propagation anticipates diffusion by retracting of A-block through the entanglements into the B-rich area (or merely into the interfacial zone) with following reextension into a new configuration. In this way, molecular propagation in lateral direction becomes possible.

Even if, in the investigated triblock copolymers, block shortness makes conventional entanglements unlikely, similar constraints are imposed by the localization of distant junction points in the spatially separated interfacial areas. The thus arising "bridge"- and "loop"-like configurations would strongly hinder lateral diffusion. So, unless all the chains adopt the "folded" loop configurations with the end blocks very close to each other, the propagation should occur as a sequence of molecular curling and dilation of the end blocks through the interface (or core) areas. Such a mechanism may be expected to lead to comparable propagation rates in lamellar and hexagonal phases as observed in our experiments.

High-intensity pulsed field gradient NMR diffusometry has been shown to provide unprecedented insight into the internal dynamics in self-assembling BCPs and its correlation with the underlying microstructure. The rates of molecular propagation are subject to dramatic structureinduced changes which have become accessible by direct observation owing to recent progress in NMR diffusometry. With the exception of the initial (micellar fluid) phase, internal constraints by supermolecular ordering on a mesoscopic length scale rather than mere obstruction effects, otherwise typical of polymer solutions, are found to dominate the diffusion behavior with increasing concentration. The observed diffusion patterns clearly reveal the dimensionality of the molecular arrangements. The remarkable coincidence of the diffusivities along the interfaces of the lamellar and hexagonal phases might be explained by a propagation mechanism consisting of block retraction (curling) and reextension (dilation). Molecular aggregates in the hexagonal and lamellar phases are large enough to encompass the diffusion paths as directly recorded by PFG NMR. The necessity of interaggregate hopping in the cubic phase is found to lead to a dramatic retardation of molecular propagation, reflecting the thermodynamic penalty of pulling the hydrophobic blocks through a water-rich environment. "Inverse melting" of the cubic lattice with decreasing temperature restores diffusion of the molecules as individual units, with a diffusivity typical of polymer solutions.

Financial support by Deutsche Forschungsgemeinschaft (IRTG "Diffusion in Porous Materials") and European Community (NoE "INSIDE-PORES") is gratefully acknowledged.

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