Magnetic-Field-Induced Order of Polymer-Grafted Biomembrane Mimetic Gels

M. A. Firestone,[1] D. Teide,[2] S. Seifert[2]

[1] *Materials Science and* [2] *Chemistry Divisions, Argonne National Laboratory, Argonne, IL, U.S.A.*

Introduction

A major area of current research interest in the field of materials chemistry is the development of hierarchically organized complex systems to produce materials with novel structure or properties. One approach involves the use of self-assembly. The harnessing of self-assembly to produce functional aggregates (and ultimately, self-constructing devices) poses a significant challenge, since frequently it leads to polymicrodomain structures, limiting the utility of these materials. Although much effort has been directed at the study of the design principles of self-organizing molecular assemblies, considerably less attention has focused on the use of post-assembly processing as a means of converting poorly organized materials, such as complex fluids, into useful/functional materials of well-defined structure. In this report, we examine the magnetic-field-induced alignment of a recently developed polymer-grafted lipid mesophase (i.e., complex fluid)[1-3] using synchrotron small angle x-ray diffraction.

Materials and Methods

Ex situ magnetic field studies were carried out on samples in 1.5 mm quartz capillaries that were then inserted into a 5 mm NMR tube. Magnetic field alignment of the sample was achieved in the superconducting magnet (7.05 Tesla) of a GE Omega 300 NMR spectrometer. The sample temperature was controlled via dry-ice-cooled N_2 gas flow. In the presence of the field, the sample was cooled to 2°C and held for 1 h, then gradually(over a 30 min period) warmed to 25°C, held an additional 1 h, and then removed from the magnet. Aligned samples were stored at room temperature until taken for x-ray studies. Synchrotron small angle x-ray diffraction measurements were performed at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) undulator beamline (12-ID) of the Advanced Photon Source at Argonne National Laboratory. The scattering profiles were recorded with a mosaic detector composed of 9 CCD chips with an imaging area of 15 x 15 cm, with 1536 x 1536 pixel resolution. The area detector images were corrected for background scattering of water by subtracting from the recorded images an area detector image of a water sample obtained with the same total exposure time as for the liquid crystalline sample (5 s). The collected low-angle scattering data were calibrated based upon the known positions of silver behenate powder Bragg reflections.

Results and Discussion

We have established that persistent structural changes/enhanced asymmetry can be induced in the gel phase of the complex fluid by modest exposure to a magnetic field.[4] This effect is observed by comparing the two-dimensional (2-D) small angle x-ray scattering patterns of the unaligned and aligned gels (Fig. 1A and B, respectively). The isotropic 2-D intensity pattern observed for the gel phase prior to magnetic field processing indicates that it is a mosaic structure consisting of lamellar microdomains in which all spatial orientations are present (Fig. 1A). After magnetic field alignment below the phase transition temperature followed by warming in the presence of the field, a strong anisotropic 2-D scattering pattern is observed (Fig. 1B), indicating long-range ordering of the lamellar domains. The anisotropy about the equatorial axis indicates that the lamellae preferentially orient perpendicular to the magnetic field direction.

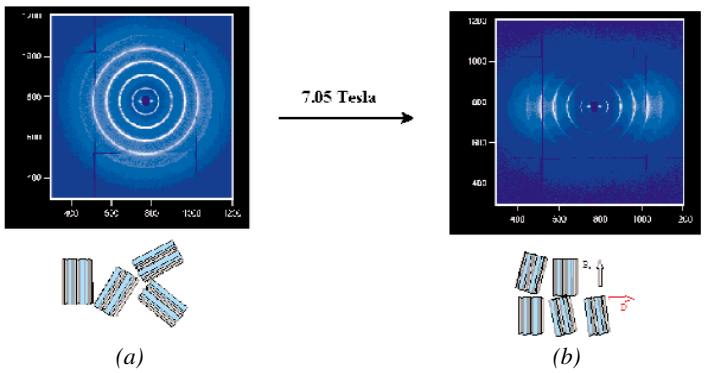

FIG. 1. (A) Two-dimensional small-angle x-ray scattering patterns from the unoriented gel phase sample. (B) 2-D SAXS image obtained after alignment in a 7.05 T magnetic field.

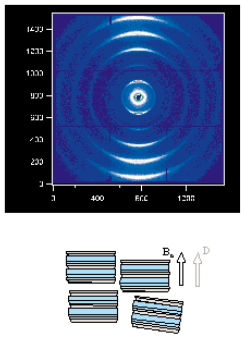

FIG. 2. 2-D SAXS pattern collected after magnetic field processing of a gel phase containing Eu^{3+}.

Relevant to both structure-function studies of biomolecules and to the development of biomolecule-based composite materials for device applications is the ability to design and produce anisotropic media that can be oriented both perpendicular and parallel to the applied field direction. To this end, we have examined the effect of the addition of lanthanide ions ($EuCl_3$) to the composition prior to magnetic field exposure. The effect was monitored by comparing the 2-D small-angle x-ray scattering patterns of an unaligned lanthanide-doped sample to one that had been subjected to moderate magnetic field exposure (Fig. 2). The results indicate that the alignment of the lamellar domains can be switched/flipped 90° (lamellae oriented parallel to the applied field direction) by introduction of these agents.

In summary, a polymer-grafted biomembrane-mimetic hydrogel has been shown to be oriented by application of a moderate magnetic field. The field-induced anisotropy of the gel phase persists even after removal from the field. These results, together with previously established physicochemical properties of the complex fluid (e.g., excellent optical transparency and the ability to encapsulate a wide range of molecules, including membrane proteins) suggest that this material offers enormous poten-

tial as a medium for the study of a range of biomolecules by magnetic resonance, optical spectroscopy, and small-angle diffraction.

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