

# Unusual Wavevector Dependence of the Relaxation Rate of Giant Copolymer Micelles

P. Falus, M. A. Borthwick, D. Lumma, L. B. Lurio, S. G. J. Mochrie

Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

## Introduction

Block copolymers are all around us, found for example in adhesive tape, upholstery foam, and asphalt additives. These macromolecules are produced by joining two or more chemically distinct polymer blocks—each a linear series of identical monomers—that may be chemically incompatible. Polymer incompatibility is the driving force that gives rise to a wide variety of structures [1]. In a solvent that is a good solvent for one block (block A) and a bad solvent for block B, the interfacial energy between block B and the solvent tends to lead to complete phase separation, while the chemical links between the blocks allow only micro phase separation. As a result, micelles form at low block copolymer concentration as the B-blocks aggregate into spherical or cylindrical clusters.

If the length of the cylindrical micelles exceeds a characteristic length scale known as the persistence length, they may flex and thus resemble giant polymer molecules. However, departure from ordinary polymer behavior is caused by the self-assembling nature of micelles. The rupture and recombination of chains in equilibrium leads to a very broad size distribution. In the so-called “fast breaking” case the breaking has a profound effect on dynamics. The micelle breaks many times before it can finish its reptative relaxation, causing important difference between the dynamics of these wormlike micelles and polymers [2]. Wormlike micelles have been extensively studied with rheology [2], static and dynamic light scattering [2], and neutron scattering [3]. None of these methods, however, could directly probe the relaxation of micelles on molecular length scales. Hence we have initiated studies of micelle motion using small angle x-ray scattering and the emerging technique of x-ray photon correlation spectroscopy [4].

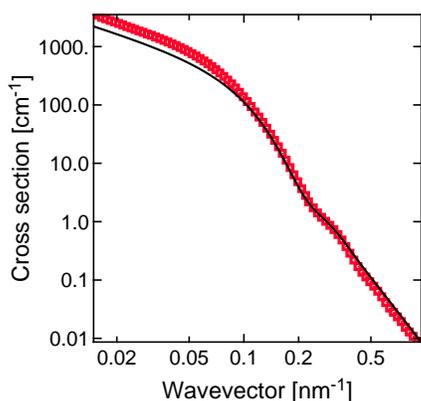


FIG. 1. Cross-section for  $\phi = 0.03$  Kraton in PS. The solid line is a fit to a rigid cylinder cross section with cylinder radius of 15 nm.

## Methods and Materials

To prepare the samples, poly-styrene ( $M_n = 3270$ ,  $M_w/M_n = 1.09$ ) was obtained from Polymer Source

(Québec, QC) and Kraton G1651 (poly-ethylene-butylene block copolymer,  $M_n = 240,000$ ,  $M_w/M_n = 1.04$ ) was obtained from Shell Chemical. Known weights of the polymers were thoroughly mixed in toluene. Then they were precipitated in isopropyl alcohol and dried under vacuum. Samples were manufactured with nominal weight fractions  $\phi = 0.01, 0.03, 0.05, 0.08,$  and  $0.15$ . For the x-ray experiments, samples were mounted in an evacuated, temperature-controlled sample chamber.

The measurements were carried out at beamline 8-ID at the Advanced Photon Source (APS). We employed x-rays of energy 7.66 keV produced by a 72-pole undulator. A silicon mirror and germanium monochromator selected a relative energy bandwidth of  $3 \times 10^{-4}$  full-width-at-half-maximum. Subsequently, a pair of precision crossed slits, 55 m from the undulator source and 40 cm upstream of the sample selected a  $20 \mu\text{m}$  horizontal by  $50 \mu\text{m}$  vertical portion of the beam. The resulting flux on the sample was  $\sim 10^{10}$  photons per second. Scattered x-rays were detected 4.85 m further downstream using a CCD detector.

## Results

The time- and circularly-averaged x-ray scattering cross-sections are displayed in Fig. 1. for wavevectors from  $QR = .2$  to  $QR = 15$ . The solid line is a fit to the scattering cross-section of rigid, polydisperse rods. The fitted value of the micelle radius is  $R = 15 \pm 1$  nm. The curves fit well at high wavenumbers confirming that locally the micelles look like rigid cylinders. At low wavenumbers the curves deviate, indicating that the micelles are not rigid rather they are worm like. The characteristic micelle length and persistence length were larger than measurable with our x-ray setup. Future light scattering studies can supply this information.

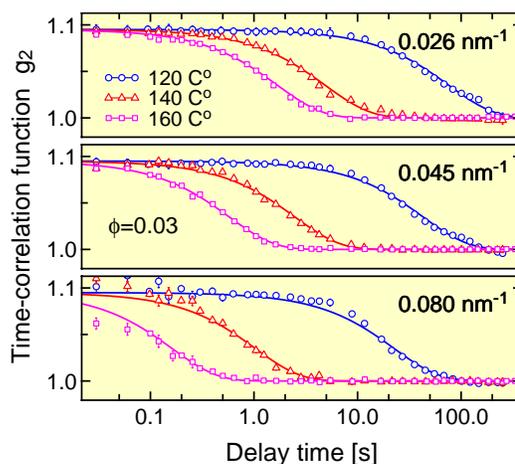


FIG. 2. Time-correlation functions for  $\phi = 0.03$  Kraton in PS. The solid lines are fits of single exponential decays. Note that the time axis spans four orders of magnitude!

The technique of XPCS [4] applies the well-known principles of dynamic light scattering to X-rays. Briefly, a sample is illuminated by partially coherent light that gives rise to a time varying speckle pattern. The speckle images are recorded by a CCD detector. Time autocorrelation of the images yields the characteristic relaxation times of the sample. The result of the analysis, the intensity-intensity time auto correlation functions, are shown on Fig. 2.

### Discussion

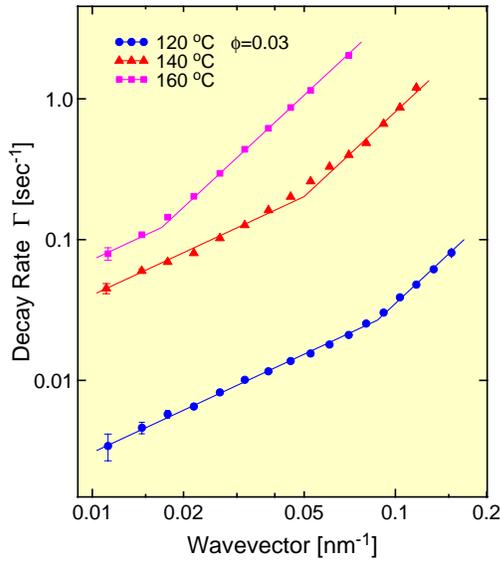


FIG. 3. Decay rates versus wavenumber derived from the fits on Fig. 2. The solid lines are power law functions of  $Q^1$  and  $Q^2$

The first surprising result of this measurement is that the correlation functions are single exponentials in spite of polydispersity. However single exponential decays are expected as a result of fast scissoring, as was noted in previous light scattering studies [2].

It is also interesting to note the wavevector dependence of the decay rates which is shown in Fig. 3. Diffusion of particles in a dilute solution would lead to  $Q^2$  scaling of the decay rates. It can be seen that the  $Q^2$  dependence applies only at high wavenumbers. It is interesting to compare the temperature dependence of the decay rate to the temperature dependence of the solvent viscosity (Fig 4). Evidently their temperature dependence is similar, suggesting that the observed decay rate corresponds to diffusion. Interestingly the ratio of the viscosity to the decay rate corresponds to hydrodynamic radius of  $15 \pm 5$  nm comparable to the cylinder radius obtained

by SAXS.

At intermediate wavenumbers the decay rate has linear dependence on Fig 3. This behavior is very unusual; further theoretical and experimental investigation are necessary.

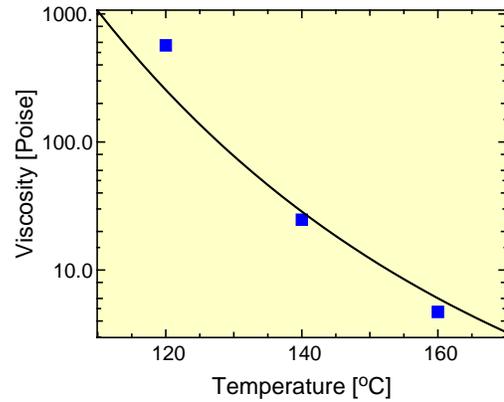


FIG. 4. Viscosity of  $M_n = 3270$  poly-Styrene (solid line). The symbols are the viscosities calculated from the  $Q^2$  fit of Fig 3. using hydrodynamic radius of 15 nm.

### Acknowledgements

8-ID was developed with support from the NSF Instrumentation for Materials Research Program (DMR 9312543), from the DOE Facilities Initiative Program (DE-FG02-96ER45593), and from NSERC. Work at MIT was also supported by the NSF MRSEC Program (DMR 9808941). D. L. acknowledges the JSEP for support. The APS is supported by the DOE under contract No. W-31-109-Eng-38. We thank Harold Gibson for his invaluable assistance. We are also indebted to Gerry Swislow for his help.

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