

# Studies of Dynamic Critical Behavior of Polymer Mixtures Using X-ray Photon Correlation Spectroscopy

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## Introduction

X-ray photon correlation spectroscopy (XPCS) is an extension of the well-known and widely used photon correlation spectroscopy (PCS), sometimes also called intensity fluctuation spectroscopy. Probing the matter with coherent x-rays, instead of coherent visible light, allows probing the sample dynamic properties in a region of relaxation times ( $1 \mu\text{s} - 1000 \text{s}$ ), and wave vectors  $q$  ( $0.004 - 2 \text{ \AA}^{-1}$ ) that are inaccessible to light scattering techniques. XPCS capabilities were tested at the 7-ID beamline with studies of the critical concentration fluctuations in the simple binary fluid mixture of hexane-nitrobenzene.<sup>1</sup> All the previously reported studies applied XPCS to studying aggregate systems, where the intrinsic sample structure enhances the scattering. These systems included colloids,<sup>2-5</sup> polymer micelles,<sup>6</sup> borosilicate glass,<sup>7</sup> and metal alloys.<sup>8-9</sup>

Recently we conducted studies of the dynamic critical behavior of binary polymer mixture of polystyrene/polybutadiene using XPCS.<sup>10</sup> Here we provide a short report of these studies. Static and dynamic properties of the polystyrene/polybutadiene mixture at the critical composition were measured. Effects of the damage caused by synchrotron radiation to the sample and sample components were extensively studied.<sup>10</sup> The damage caused by radiation affects the scattering, as well as the relaxation time, of the sample.

## Methods and Materials

The studies were conducted on the undulator beamline at sector 7 of the Advanced Photon Source, operated by MHATT-CAT. Because polybutadiene proved to be quite susceptible to x-ray radiation damage, it was necessary to use a monochromatic, rather than a pink, beam in the x-ray measurements of both the statics and the dynamics. A flux of  $6.6 \times 10^8 \text{ ph/sec}/(100 \text{ mA})$  of  $9.0 \text{ keV}$  x-rays, monochromated by the combination of a single bounce mirror filter and Ge monochromator, and determined by  $5 \times 10 \text{ mm}^2$  coherence slits was incident on the sample. This resulted in about 100 times less incident x-ray flux than in the hexane/nitrobenzene experiments.<sup>1</sup> A CCD area detector was used to measure the static x-ray scattering from the sample. It was also possible to use the CCD detector in XPCS measurements of the dynamics of concentration fluctuations in the mixtures, since the relaxations are quite slow due to the relatively high viscosity of the polymers.

The polystyrene/polybutadiene (PS/PB) polymer samples were mixed in air by weighing the components directly into the sample cell. Sample cell had a 3-mm-long scattering volume with the entrance and exit windows covered by Be foils. The sample temperature was stable to within 1 mK during all measurements.

## Results

The dynamic data were collected in a sequence of 6000 exposures of the CCD. The exposure time for each frame was 0.15 seconds and the frame-to-frame time was 0.33 seconds. The total time for which the sample was exposed to x-rays during the

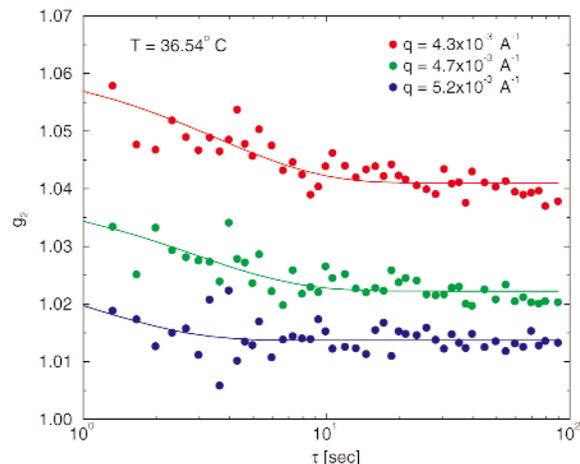


FIG. 1. Correlation functions for a  $\phi_{PS}=0.557$  PS/PB mixture at  $T=36.54^\circ\text{C}$  and three different wave vectors, as indicated. Solid lines are fits of a single exponential relaxation.

sequence acquisition was around 900 seconds. During this time the sample was exposed to a radiation level of about 2000 kGy, which was below the x-ray radiation damage threshold experimentally determined for this sample.<sup>10</sup> The x-ray scattering was collected over a CCD area of  $180 \times 180$  pixels. At the detector-to-sample distance of 0.70 m, the pixel resolution was  $q=5.839 \times 10^{-5} \text{ \AA}^{-1}/\text{pixel}$ , and the speckle size was  $\sim 9 \mu\text{m}$  in detector plane, or about the pixel size. The CCD was offset from the  $q=0$  position so that the  $q$  range covered was from  $\sim 3.5 \times 10^{-3} \text{ \AA}^{-1}$  to  $\sim 1.8 \times 10^{-2} \text{ \AA}^{-1}$ . The data were collected and then analyzed offline using the custom written multitau correlation software, with 8 quasi-logarithmic correlators with 16 channels per correlator. Resulting correlation functions are shown in Fig. 1, where the solid lines represent single exponential fits. Several correlation functions were extracted for a few values of wave vector  $q$  and temperatures near the critical point. The contrast of the correlation functions,  $\beta$ , was between 1 and 3%, similar to the values we found for the measurements on the hexane/nitrobenzene mixtures made using a single channel detector and a hardware correlator.<sup>1</sup>

## Discussion

The fit values of the relaxation rates are plotted versus  $q$  for all three temperatures in Fig. 2. The manner in which the relaxation rate scales with wave vector depends on the conditions of the sample and the manner in which we probe it. These conditions can be characterized by the values of  $q$ , correlation length  $\xi$ , and the radius of gyration  $R_g$ , in terms of the values of  $1/qR_g$ ,  $q$ , and  $q/R_g$ . The average value of the wave vector in our experiment was  $5 \times 10^{-3} \text{ \AA}^{-1}$ . The reduced temperatures range from  $9.1 \times 10^{-4}$  to  $1.6 \times 10^{-3}$ . For this range of reduced temperature,  $\xi$  is about  $400 \text{ \AA}$ , as determined by fits of the scaling behavior of the amplitude and correlation length in our static scattering. An average value for  $R_g$  of the sample mixture is  $9.2 \text{ \AA}$ .  $N^{0.5}$  equals 4.4. Hence, the rele-

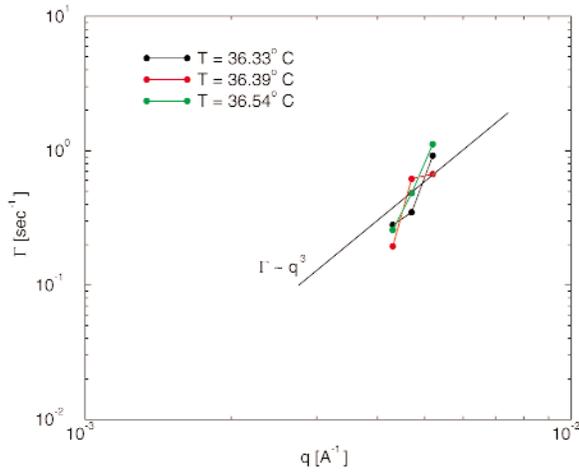


FIG. 2. Relaxation rate versus  $q$ . A straight line is a guide to the eye showing a  $q^3$  scaling of  $\Gamma$ .

vant physical regime is determined by the values  $1/qR_g=21.7 > N^{0.5}$ ,  $\xi/R_g=43.5 > N^{0.5}$ , and  $q\xi=2 > 1$ . This puts us in the so-called "critical nondiffusive" regime, where mode coupling corrections dominate and the relaxation rate should scale with wave vector as  $\Gamma \sim q^3$  and should be temperature independent, apart from the temperature dependence of the viscosity. A guide to the eye, which shows a  $q^3$  dependence of  $\Gamma$  on  $q$ , is also shown in Fig. 2. While the measured values of  $\Gamma$  do increase with wave vector, they appear to increase much more quickly than  $q^3$ . Within the evident large scatter, the results for  $\Gamma$  are also approximately temperature independent.<sup>10</sup>

Unfortunately the dynamic data we have been able to collect so far are not extensive enough nor of sufficient quality to warrant drawing broader conclusions at this time. Nevertheless, we have demonstrated the ability to use XPCS to measure the relaxation

rate from this polymer mixture, and our work has identified a number of opportunities for enhancing the signal quality. Hence, there is good reason to expect that much better quality data, covering a more extensive range of reduced temperatures and wave vectors, can be obtained in the near future and the tantalizing results shown in Fig. 2 further pursued.

## Acknowledgments

This work was partially supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, under grant ACS-PRF#32105-AC7. The MHATT-CAT facility located at the APS was built with grants from NSF and DOE as well as contributions from the University of Michigan, Bell Laboratories-Lucent Technologies, and Howard University. Its current operation is supported by DOE grant DE-FG02-99ER45743. The APS is supported by the U.S. Department of Energy under contract No. W-31-109-ENG-38.

## References

- <sup>1</sup> E. Dufresne et al., APS User Activity Report 2000 (ANL-00/5). Available at <http://www.aps.anl.gov/xfd/communicator/user2000/dufresnee1.pdf>
- <sup>2</sup> S. Dierker et al., Phys. Rev. Lett. **75**, 499 (1995).
- <sup>3</sup> T. Thurn-Albrecht et al., Phys. Rev. Lett. **77**, 5437 (1996).
- <sup>4</sup> O. Tsui et al., Phys. Rev. E **56**, 2030 (1998).
- <sup>5</sup> T. Thurn-Albrecht et al., Phys. Rev. E **59**, 642 (1999)
- <sup>6</sup> S. Mochrie et al., Phys. Rev. Lett. **78**, 1275 (1997).
- <sup>7</sup> A. Malik et al., Phys. Rev. Lett. **81**, 5832 (1998).
- <sup>8</sup> S. Brauer et al., Phys. Rev. Lett. **74**, 2010 (1995).
- <sup>9</sup> J. Mainville et al., J. Appl. Crystallogr. **30**, 828 (1997).
- <sup>10</sup> T. S. Nurushev, Ph.D. Thesis, University of Michigan (2000).