

X-ray Radiation Damage Effects in Ps/Pbd Polymer Mixtures

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Introduction

Soft condensed matter organic-based materials are often susceptible to various kinds of damage upon prolonged exposure to high energy radiation beams, such as electron, γ -ray, or x-ray beams. This can be an important issue in X-ray Photon Correlation Spectroscopy (XPCS) studies of the dynamics of such materials. Often the effects of radiation damage are cumulative over time. This implies that there may be a maximum duration for an XPCS measurement at a particular position in a material. Very little information for x-ray radiation effects on organic materials exists in a form which can be directly useful in determining this maximum duration for an XPCS experiment. In this report, we describe such results for a polymer mixture of Polystyrene and Polybutadiene.

In XPCS experiments, one measures the low frequency dynamics of a material by determining the time autocorrelation function of the fluctuations in the speckle pattern, which modulates the scattering from the materials.[1] Speckle occurs when the sample is illuminated with a coherent x-ray beam. Transversely coherent x-ray beams are prepared by collimating the x-rays with an aperture whose dimensions are comparable to the transverse coherence lengths of the x-rays. At a typical beamline at the APS, the transverse coherence lengths, l_{tr} , are $\sim 5 \mu\text{m}$ in the horizontal and $30 \mu\text{m}$ in the vertical. The flux through this area is determined by the brightness of the source and the degree to which the beam is monochromatized. The longitudinal coherence length, l_l , is inversely proportional to the monochromaticity of the x-ray beam. The two most common arrangements are to either use the natural bandwidth of the undulator ($\Delta E/E \sim 2.5\%$), a so-called 'pink' beam with l_l of order 50 \AA , or that of either a Ge or Si monochromator, with l_l of order $1 \mu\text{m}$. Although l_l is rather small for a pink beam, it is nonetheless sufficient for coherent small angle x-ray scattering (SAXS) measurements. On the MHATT-CAT Sector 7 ID line, we typically produce coherent fluxes for XPCS experiments of $\sim 4 \times 10^8 \text{ ph/sec}/(5 \mu\text{m})^2$ with Ge resolution and $\sim 4 \times 10^{10} \text{ ph/sec}/(5 \mu\text{m})^2$ with a pink beam. Although these fluxes are not particularly large, they correspond to quite high intensities. As a result, they are capable of producing significant damage in organic materials.

In this report, we describe the effects of exposure of a polymer mixture, Polystyrene/Polybutadiene, to x-rays. We find that the SAXS changes dramatically upon irradiation and that the changes scale with radiation dose for widely varying dose rates. There also appears to be a threshold dose, below which no significant effects of damage are observable in the SAXS pattern.

Methods and Materials

This experiment was performed on the undulator beamline at sector 7 of the Advanced Photon Source, operated by MHATT-CAT. With the undulator fundamental set at 9.0 keV, the white beam was collimated with white beam slits to $100 \mu\text{m}$

by $100 \mu\text{m}$. In the experimental hutch 35 m from the source, two small Pt coated mirrors were used to produce a 'pink beam'. The doubly reflected beam had a bandpass of $\Delta E/E = 2.5\%$. The samples were illuminated with two different size x-ray beams, $(5 \mu\text{m})^2$ and $(50 \mu\text{m})^2$, with fluxes of $4 \times 10^{10} \text{ ph/sec}$ and $5 \times 10^{12} \text{ ph/sec}$, respectively, to check for any dependence on beam size. Attenuators were used to vary the incident flux for each beam size in order to check for any dependence on dose rate. The polymer studied was a 65% by weight mixture of 1000 MW polystyrene with 2000 MW polybutadiene. This mixture has an upper critical solution temperature of $\sim 34^\circ \text{C}$. Measurements were made for sample temperatures ranging from 80°C to 25°C , i.e., both above and below T_c . Time resolved SAXS patterns from the mixture were measured with a direct detection CCD camera as a function of time after the start of x-ray exposure.

Results

Fig. 1 shows the time dependence of the measured SAXS scattering rate a sample illuminated by an attenuated $(50 \mu\text{m})^2$ pink beam at a sample temperature of 40°C . At the earliest times, the SAXS is time invariant and is due to scattering from composition fluctuations in this critical mixture. This temperature dependent critical scattering will be reported separately. This initial 'quiescent' period is followed by a strong increase in scattering at wavevectors below $\sim 0.025 \text{ \AA}^{-1}$. Finally, in the late time behavior the scattering curve uniformly becomes smaller. We believe the initial increase in scattering at small wavevectors is due to the x-ray radiation induced formation of large cross-linked molecules. The eventual diminution of the scattering at late times is thought to be due to the growth in size of the cross-linked molecules, with their scattering moving to lower q , together with the reduction in scattering from composition fluctuations as the damaged material grows to fill the scattering volume being probed.

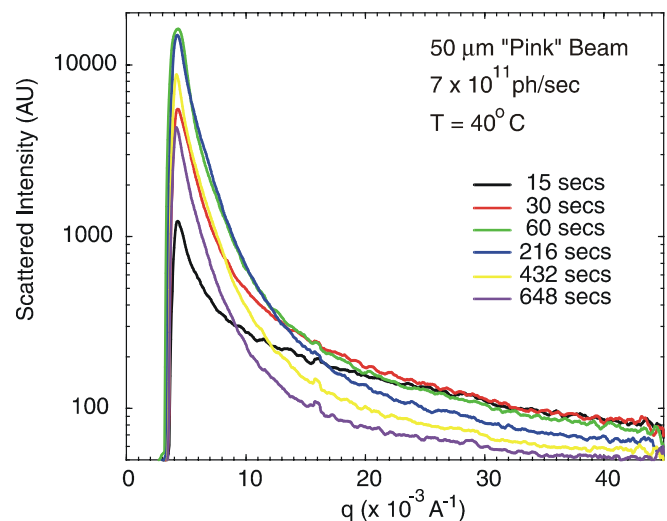


Figure 1. Time dependence SAXS from a Ps/Pbd mixture.

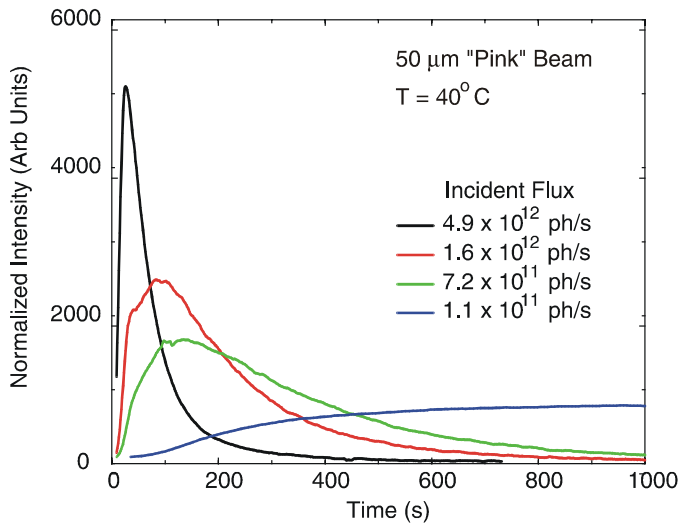


Figure 2. Time dependence of the scattering from the mixture at $q = 6.5 \times 10^{-3} \text{ \AA}^{-1}$ and a temperature of 40° C for various incident x-ray fluxes.

In Figure 2, the time dependence of the scattering rate at a wavevector of $q = 6.5 \times 10^{-3} \text{ \AA}^{-1}$ and a sample temperature of 40° C is shown for various incident fluxes obtained from a $(50 \text{ \mu m})^2$ pink beam by the use of attenuators. Again, we see three phases to the time dependence: a very early time-independent phase followed by an intermediate phase with a strong rise in scattering and a late phase with a strong decrease in scattering.

The large variation in times for the three phases in Figure 2 for different incident fluxes, with lower fluxes taking longer times to develop, suggests that the sample damage may be a function of accumulated dose. This relation is shown to be obeyed remarkably well in Figure 3, where the scattering intensity is normalized to 1 at its maximum and plotted versus radiation dose, expressed in kGy. The data follow a very similar curve

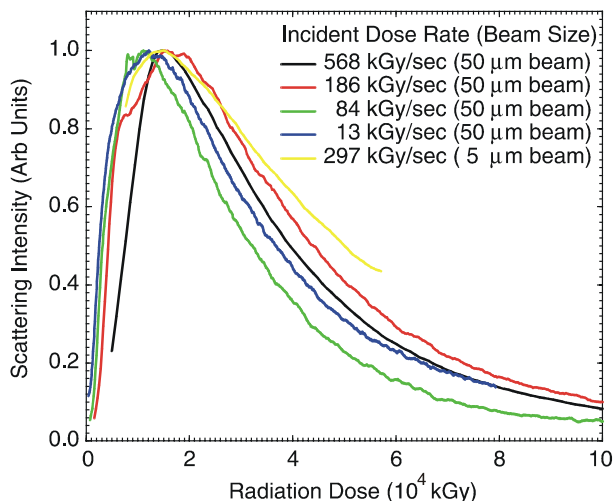


Figure 3. Scaling of the SAXS at $q = 6.5 \times 10^{-3} \text{ \AA}^{-1}$ with accumulated radiation dose, for various incident dose rates.

even though the dose rate varies by a factor of 43 and the incident beam size varies from $(5 \text{ \mu m})^2$ to $(50 \text{ \mu m})^2$.

Discussion

The results in Figure 1-3 show that x-ray radiation induced damage to this polymer mixture depends on accumulated dose and can result in dramatic changes in the polymer structure on relatively short time scales. Analysis of the data indicate that the first phase of irradiation, during which the structure and scattering are essentially unaffected by the irradiation lasts up to about 2000 kGy. This damage threshold can be used to estimate the approximate maximum duration of an XPCS experiment on this material for different incident coherent x-ray intensities. A pink beam with a flux of $4 \times 10^{10} \text{ ph/s}/(5 \text{ \mu m})^2$ results in a deposited dose rate of 180 kGy/sec. At this dose rate, the damage threshold dose would be reached in only 10 seconds. With a Ge resolution x-ray beam, the dose rate is lowered to 1.8 kGy/sec and the time to damage threshold increases to ~ 1000 seconds. In these mixtures, the relaxation time for concentration fluctuations can be as long as 1000 seconds. Thus, Ge resolution coherent beams are necessary. In addition, although the maximum measurement duration is of the order of the slowest relaxation time, ensemble averaging techniques utilizing a CCD detector are capable of determining the autocorrelation functions under those conditions. XPCS measurements of the temperature and wavevector dependence of critical dynamics of this mixture will be reported separately.

The damage threshold reported here for the Ps/Pbd mixture will surely vary for different materials, depending on their chemistry and viscosity. For example, in a recent XPCS study[2] of concentration fluctuations in the binary fluid mixture hexane/nitrobenzene, no observable radiation damage effects were observed even for much larger doses than the maximum doses studied here. This is likely due to a combination of the small molecules being more resistant to damage and the mixture having a very low viscosity, which allows any defect that are produced to diffuse out of the volume probed by the x-ray in much less than 1 second.

Finally, these results have implications for future experiments at a 4th generation x-ray sources, where the average brightness is expected to be several orders of magnitude greater than for the APS. Such large increases in dose rate at a 4th generation source may limit the ability to study *slow* fluctuations in many organic materials. On the other hand, such a large increase in flux would make it possible to study much faster fluctuations, which could be studied before the sample is destroyed.

Acknowledgments

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References

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