Experiment title:	Experiment number:
Relations between Molecular Mobility and Density Fluctuations in Amorphous Polymers	SC-197

Beamline:	Date of Experiment:	Date of Report:
D2-D2AM	from: 01 -Feb-96 7:00 to: 04-Feb-96 7:00	28-02-96
Shifts: 6	Local contact(s): Erik Geissler.	*Received at ESRF:* 1 MAR

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Report:

Objectives.
The aim of this work is to study the electronic density fluctuations in glassy materials, such as amorphous polymers and molecular glasses. The density nanofluctuations are believed to play central role in the physics of amorphous solids, because the presence of disorder (static fluctuations) is likely to affect the molecular mobility, and reciprocally, the mobility is likely to induce the presence of (dynamic) density fluctuations. Static and dynamic density fluctuations scatter X rays, and the question was to determine the evolution of these fluctuations as a function of temperature and microstructural state. A variety of amorphous materials were studied, namely:
Polymers: Polymethyl methacrylate, Polyhydroxyethyl methacrylate, Polystyrene, Polycarbonate of diallyl glycol, Polycarbonate of bisphenol A, a Polytetrafluoroethylene amorphous copolymer, Polyaryl ether sulfone, polyaryl ether ether ketone. Molecular glass: Maltitol. The case of PMMA was specially investigated as a function of rnicrostructural state. Deformed, annealed and quenched samples were to be compared so as to detect any difference in density fluctuations.

Methodology.
The elastically scattered intensity have been recorded in the diffusion vector range $q=4\pi \mathrm{Sin}(\theta)/\lambda$ from 5.10-3 to 1 $Å^{-1}$. The measurements were performed in the temperature range from -80°C to 300°C by means of a cryostat built by us for the existing beamline D2AM. The experiments thus consisted in the collection of spectra series during heating at 3 or 4 K/min.

Results

The density fluctuations that scatter X-rays are of two origins:

-Static fluctuations.

-Dynamic fluctuations.

The amount of density fluctuations can be estimated by the extrapolation of scattered intensity at zero angle Io using standard procedures (2). Below Tg, the value of Io is a slowly increasing function with temperature. Above Tg, there is a classic increase in Io, revealing an increase of density fluctuations. The nature (either static or dynamic feature) of these fluctuations can be determined by the study of Io as a function of the microstructural state. We studied the contribution to scattering of static fluctuations by comparing the scattering spectra of an annealed and quenched sample as the thermal histories were chosen to induce the most different static contributions (fig. 1).

The modeling of the scattering spectra as a function of temperature is on going, on the basis of the different chemical structures investigated, in relation with the dynamic behavior as revealed by other techniques.

Experimental Problems

The experimental problems encountered during this experiment were the following:

-It was not possible to digitalize and write the temperature in the data files as well as the values of reflected intensities before and after the sample, because of a software problem. Thus, we' deduced the temperature and PM detection values from handwriting notes taken during the experiment, when it was possible.

-The response of the detector in front of a radioactive source was not available. The corresponding correction of raw spectra could not be made. We observed important oscillations (#l 0%) of the incident beam intensity. This reveals a problem in the optic hutch. The necessary correction was performed thanks to the manual procedure described above, but some files could not be corrected.

-We did not have time to study the influence of deformation on the scattering properties of PMMA, as 12 hours were necessary to produce a satisfactory beam.

References

(1) Frick, B.; *Progr.* ***Colloid Polymer Sci, 1989,80, 164***

(2) Tanabe, Y.; Muller, N.; Fisher, E. W.; ***Polym. J.*** 1984,16,445