	Experiment title: Investigating the molecular mechanism of aging in polymeric materials	**Experiment number**: 26-02 545
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Shifts: 6	**Local contact(s)**: Dr. G. Portale	

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Report:

In this experiment, we have investigated the effect of molecular structure and processing conditions on aging of polystyrene (PS), a model polymer system. The hypothesis is that a glassy polymer has a heterogeneous structure with some domains denser than the matrix. As discussed by Roe and Curro (Macromolecules 1983, 16, 428-434), heterogeneities can be studied by SAXS. In particular, because of the presence of heterogeneities, the SAXS intensity can be described by:

$$I(q) = I(0)\exp(b \cdot q^2) \qquad (1.1)$$

where q is the magnitude of the scattering vector, I(0) the intensity extrapolated at zero angle and b the characteristic length scale of the heterogeneities.

I(0) is proportional to the number density of heterogeneities. Its value as a function of temperature during heating at 10°C/min is shown in Figure 1 for aPS specimens with various thermo-mechanical histories. Apparently, at room temperature, the thermally rejuvenated specimen exhibits the smallest number of heterogeneities while the mechanical rejuvenated the largest. When temperature exceeds Tg, frozen-in heterogeneities dissolve and the dynamic heterogeneities control I(0).

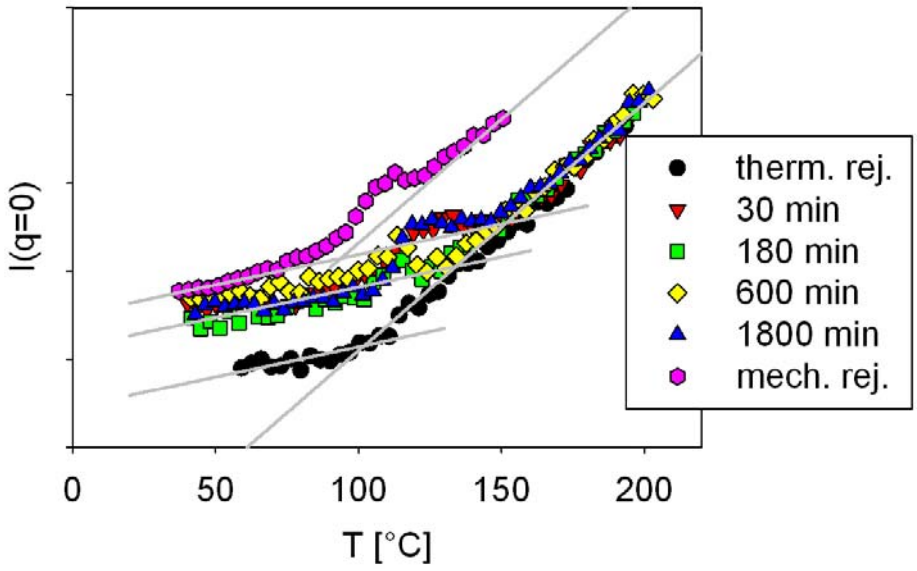

Figure 1: I(0) as a function of temperature during heating at 10C/min for thermally and mechanically rejuvenated specimens and for specimens annealed at 85C for varying times.

The transition to dynamic heterogeneities is visible in the characteristic length scale (b) as well, see Figure 2. Moreover, Figure 2 shows that the mechanical rejuvenated specimen exhibit heterogeneities with the smallest length scale.

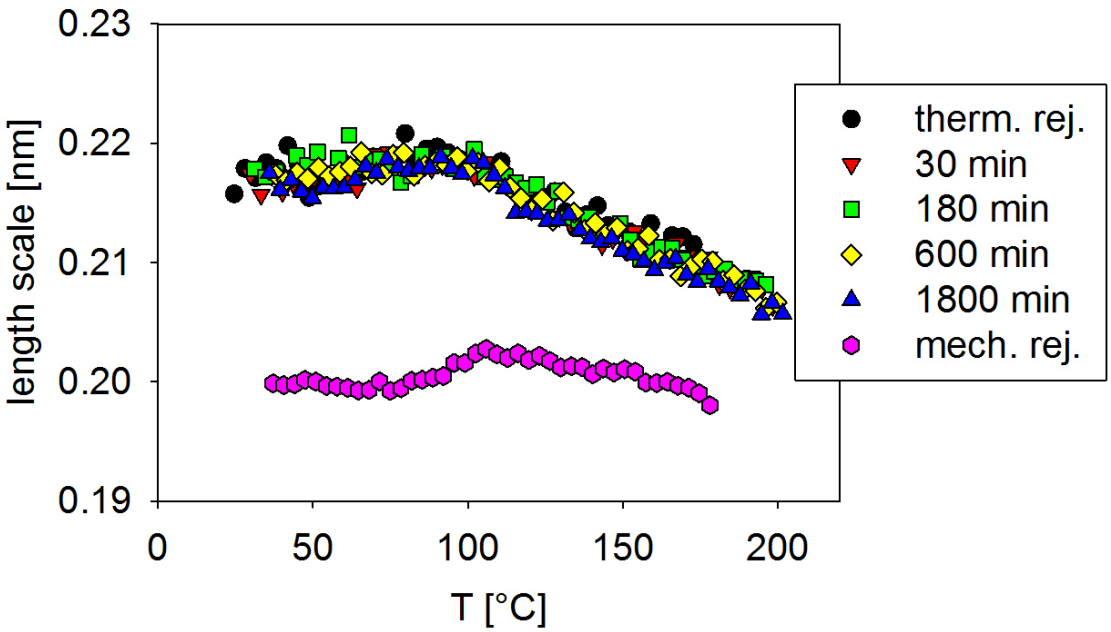

Figure 2: b as a function of temperature during heating at 10C/min for thermally and mechanically rejuvenated specimens and for specimens annealed at 85C for varying times.

Together with SAXS, with our scattering setup, we could access simultaneously also the WAXD region. During the heating experiments we observe the intensity of the first amorphous halo of aPS increasing whereas the intensity of the second amorphous halo decreases, see Figure 3. These features are associated to changes of the molecular configuration occurring at scales smaller than 1nm.

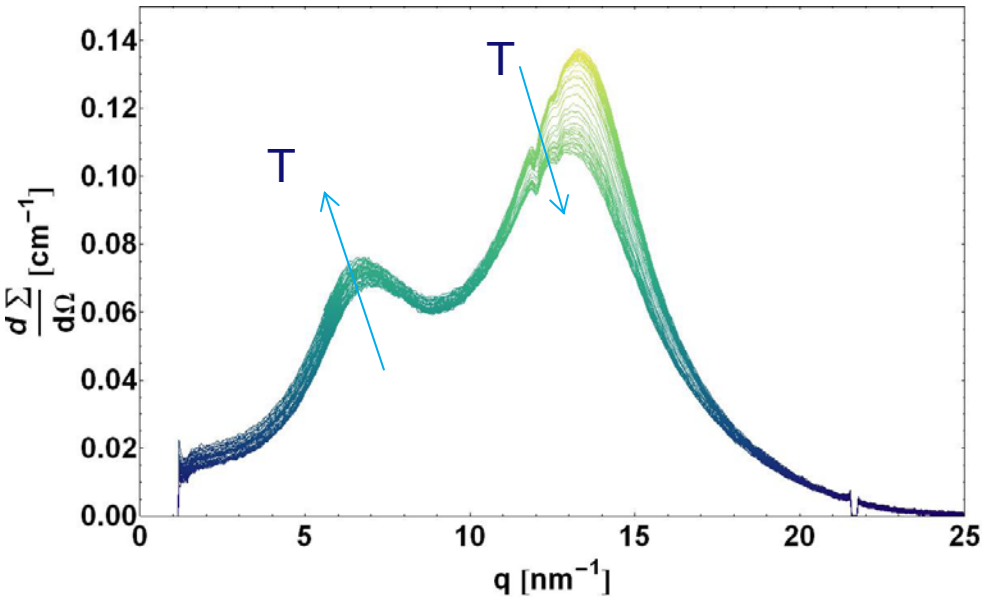

Figure 3: WAXD intensity as a function of temperature during heating at 10C/min for thermally rejuvenated aPS.