

6.3 Dynamic Properties of the Ester Methyl Group Rotation in PMMA {Poly(methyl methacrylate)} as Studied by Deuteron NMR

(St. Pfändler and R. Kind)

In the previous annual report we have described the deuteron spin–lattice relaxation study on poly(methyl-methacrylate) (PMMA) deuterated on the ester methyl group. The relaxation mechanism was found to be essentially of quadrupolar nature due to the rotational motion of the CD₃ groups around their individual C₃ axes. The non-exponential decay of the magnetization was explained by a temperature independent Gaussian distribution of activation energies centered around 58 meV with a standard deviation of 21 meV. This was confirmed by the analysis of the line-shape transition from the motionally narrowed Pake pattern to the normal one which is broader by a factor of three. From the signal shape, which is a superposition of the two Pake patterns, the relative intensities can be determined. There is a very good agreement between measured and calculated fractions (calculated from the Gaussian distribution of activation energies), except for temperatures below 30 K where tunneling motion seems to become important.

However, the magnetization recovery curves can be explained by the above mentioned distribution of activation energies only from room temperature down to 80 K. Below this temperature the relaxation is much faster than the pure hopping over the rotational barriers would yield. This could be due to the onset of librational motions to the first excited state and to tunneling at higher frequencies where the line shape is not affected. Very recently another mechanism unexpectedly was shown to be effective in deuteron Pake patterns: Spin diffusion. It affects the long time side of the recovery curve. In view of these additional effects we have tried to calculate the influence of the mentioned mechanisms on the recovery curves. Reasonable fits can be obtained for each temperature but the fit parameters are strongly temperature dependent, so that considerable doubts about the used models arise. In order to clarify the situation a diploma work was started where deuteron 2D exchange spectroscopy should give more information on the rotational motion of the CD₃ groups in PMMA.