

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

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The non-exponential deuteron magnetization recovery curves $M(t)$ of the ester methyl group in PMMA are caused by a spatial distribution of relaxation rates $\rho(W) = \rho(1/T_1)$. The corresponding $M(t)$ is given by

$$M(t) = M_0 \cdot [1 - 2 \cdot \langle \exp(-W \cdot t) \rangle] , \text{ where } \langle \exp(-W \cdot t) \rangle = \int_0^{\infty} \rho(W) \exp(-W \cdot t) dW$$

is the average over the sample and is obtained by numerical integration. Using a log-Gaussian distribution of W the measured $M(t)$ curves in PMMA can be fitted directly from room temperature to 80K. The standard deviation of this distribution was found to be indirectly proportional to the temperature. This indicates that we have a temperature independent Gaussian distribution of activation energies centered around 58 meV with a standard deviation of 21 meV.

A second possibility to measure the distribution function of E_a is the observation of the line-shape transition. At room temperature the Pake pattern is motionally narrowed by a factor of three due to the fast rotation of the CD_3 groups. The line-shape transition to the normal Pake pattern occurs when the jump-rate of the rotation becomes lower than the quadrupolar line splitting. Because of the extremely broad distribution of local auto-correlation times this transition extends from 80 K down to 10 K. Furthermore only very few CD_3 groups are in the transition region, so that the DMR spectrum consists of only two superimposed Pake patterns. The relative weight of the two patterns measures the fractions of CD_3 groups in the fast and in the slow motion regime, respectively as a function of temperature. Using the distribution function of E_a obtained from the T_1 measurements we have calculated the temperature dependence of these fractions. There is a very good agreement between measured and calculated fractions, except for temperatures below 30 K where tunneling motion seems to become important.