STRUCTURE AND DYNAMICS OF SOLID POLYMERS FROM 2D-NMR

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Two-dimensional solid state NMR offers new possibilities for the investigation of structure and dynamics of solid polymers (1). This holds in particular for the detection of ultraslow motions with correlation times longer than 1ms. **Well-defined** rotational motions in the crystalline regions of semicrystalline polymers lead to well-defined geometrical ridge-patterns in the 2D spectrum (2-4). As an example Fig. 1 shows the ^{13}C-exchange spectrum of polyoxymethylene (POM). The exchange pattern results from the rotation of the helical polymer around the helix-axis by discrete steps of $\pm 200^{o}$ (3). This result can, likewise, be obtained from high resolution solid state NMR on a drawn sample in a magic angle spinning (MAS) experiment, which correlates molecular order and dynamics (5,6). This helical jump motion is responsible for the pronounced α-relaxation in the mechanical spectrum of this material. In amorphous polymers the rotational motions are ill-defined leading to distributions of rotational angles. These can, likewise be extracted from the resulting 2D-exchange spectra (7-9). Ultraslow motions then occur either due to local processes, e.g. phenyl flips, or due to chain motions above the glass transition. There the motional mechanism involves small step rotational diffusion, which in a polymer chain can only be visualized as a cooperative process involving many monomer units. It is, therefore not surprising that the correlation times extracted

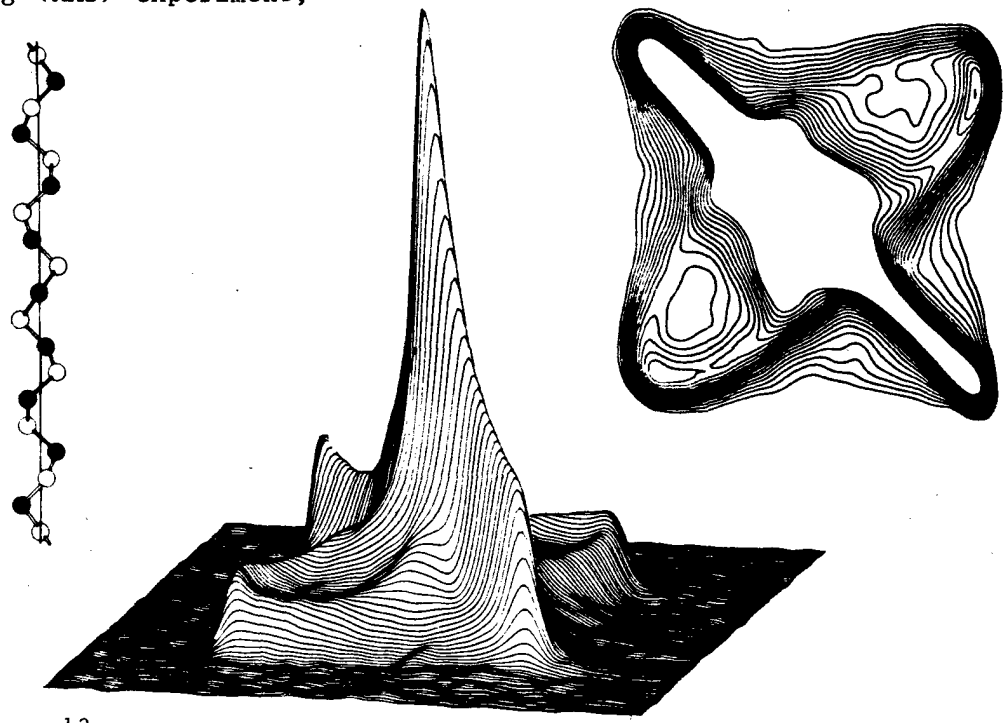

Fig.1: ^{13}C-2D exchange NMR spectrum (center) and contour plot of POM at 360 K and a mixing time of 2 s.

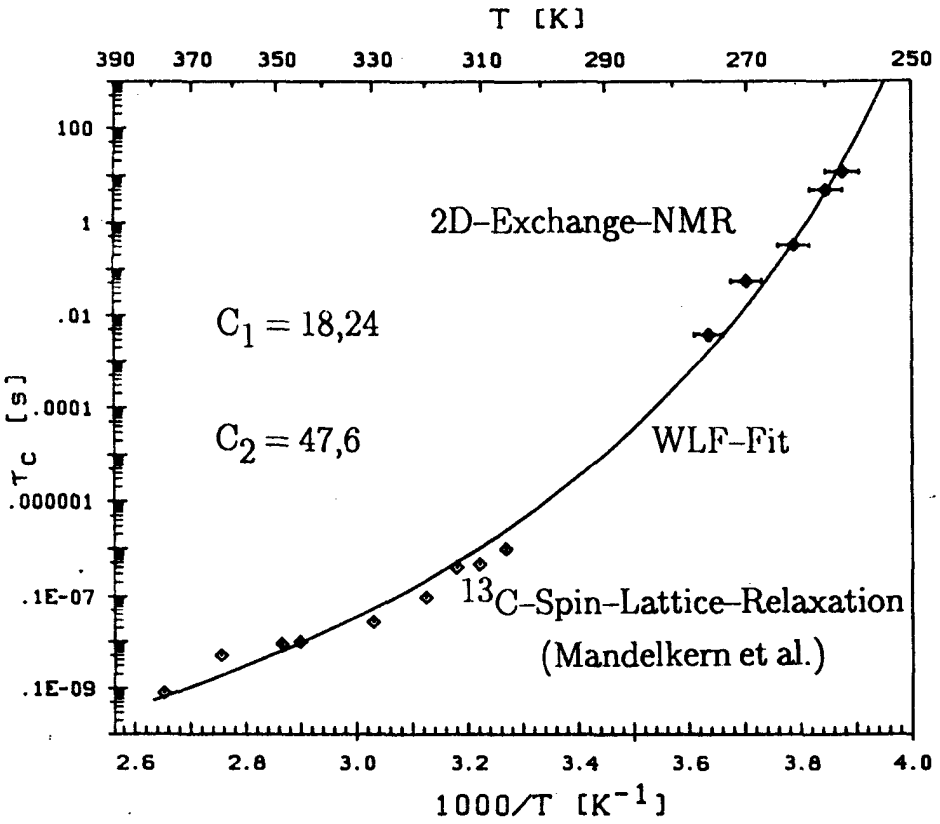

Fig.2: Correlation times of atactic polypropylene above Tg.

from 2D-NMR can be fitted by the WLF-equation with parameters known from mechanical measurements (4,9). As an illustrative example Fig. 2 shows an activation diagram of polypropylene.

References

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