Mixing polymer cocktails: Diffusion and relaxation distributions of mixed and polydisperse poly (ethylene oxide) melts

K. Lindt[a], C. Mattea[a], S. Stapf[a] , S. Mailhiot[b]

[a]Dept of Technical Physics II, TU Ilmenau, 98684 Ilmenau, Germany

[b]Bruker BioSpin GmbH & Co. KG, Rudolf-Plank Str. 23, 76275 Ettlingen, Germany

Introduction: Theoretical predictions and experimental evidence for polymer melt dynamics date back for at least four decades, with NMR being a strong contributor by a combination of several techniques: whereas pulsed and constant field gradient diffusometry determines mean-squared displacements (MSD) within a rather narrow time interval from about 1 ms to 1 s, relaxometry of attached protons and other nuclei covers a much wider range of times but gives more indirect information that needs to be translated into MSD on the basis of available models. Common to the vast majority of studies is the restriction to ideal, monodisperse linear molecules with a well-defined length, a situation that can be approximated with some technical polymers but is never perfectly met. Important questions remain largely unanswered: how does an inherent distribution of molecular weights affect the measured quantities, and are diffusion and relaxation affected in different ways?

Methods: PEO melt samples with the narrowest available dispersity (typically 1.1) in bulk and in mixtures of 10% ^{1}H-containing in 90% ^{2}H-containing PEO were studied by PFG diffusometry, relaxometry and comparative echo analysis (e.g. Hahn, solid) and were compared to artificially broadened molecular weight distributions obtained from mixing defined samples with defined molecular weights. Measurements were predominantly carried out on the ^{1}H resonance, i.e. the minority component. Diffusion experiments were carried out with a Bruker Diffusion Observe Broadband Probe providing a maximum pulse gradient strength of 16.9 T/m at a resonance frequency of 500 MHz and at variable temperatures above the bulk melting point of PEO, between 343 and 373 K. Echo and relaxation dispersion data were obtained on a Bruker Avance III 7T spectrometer and a Stelar Spinmaster Relaxometer in the field range 0.2 mT to 0.5 T.

Results and Discussion: the essential questions considered the relative change of diffusion and relaxation properties of a component A in a matrix B, or of a defined mixture, considering the different theoretical predictions for melts below and above the critical molecular weight which is estimated at 5 kDa for PEO. For diffusion, the conditions of the majority matrix (90 vol%) dominate the minority component, i.e. short chains in a matrix of long chains are severely restricted in their mobility whereas long chains in a matrix of short chains show a significantly increased mobility compared to the homogeneous bulk. Relaxation qualitatively follows this trend and supports the concept of Rouse dynamics and chain reptation, respectively, as deuteration is sufficient to suppress intermolecular relaxation contributions. For these mixtures, both diffusion and relaxation are found to mostly behave exponentially. In protonated melts of narrow and broad weight distribution, however, multiexponential behavior is clearly identified in diffusion but absent in T_1 relaxation, making PFG diffusometry a possible tool for the quantification of polymer polydispersity.

Conclusion: Diffusion behavior of polymer melts with polydispersity as low as 1.1 can be identified as non-exponential, with average diffusivity values following the expected Mw dependence. Spin diffusion and cross-relaxation are much more efficient in averaging out relaxation properties so that it can be concluded that high-gradient PFG diffusometry can establish access to a quantitative assessment of polymer quality not only in solution, but also in the melt state.