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Study of Molecular Dynamics of poly(ethylene glycol) inside Intercalated Nanocomposites by ^{13}C Solid-State NMR

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Abstract – CP/MAS, 2D Exchange, Centerband-Only Detection of Exchange (CODEX), and Separated-Local-Field (SLF) NMR experiments were used for studying the molecular dynamics of poly(ethylene glycol) (PEG) inside Hectorite/PEG intercalation compounds in both single- and double-layer configurations. The results show that in single-layer configuration the overall amplitude of the PEG chain motions is considerably smaller than that observed for double-layer intercalation. This indicates that the effect of having the polymer chain interacting with both clay platelets is to produce a substantial decreasing in the motional amplitudes of those chains.

In the present work we used Exchange [1] and Separated-Local-Field [2] NMR experiments in order get additional understanding about dynamical and conformational aspects of poly(ethylene glycol)/Na$^+$-Hectorite intercalation compounds in both single- and double-layer configurations. Nanocomposites were obtained by the stoichiometric addition of PEG and Na$^+$-clays in acetonitrile. Two reaction stoichiometries were used for the preparation of layered nanocomposites: R = 0.1 and 0.4 (R = g PEG/g clay), in order to obtain uniform gallery expansions of 0.4 and 0.8 nm, associated to the formation of single and double PEO layers, respectively [3].

Figures 1a and c show the experimental 2D Exchange spectra for samples 10k-(0.71) and 10k-(0.46) at temperatures 20 and 100 °C, respectively. The absence of well-defined elliptical ridges in the spectrum shows that the motion does not occur between well-defined sites, which can be interpreted as a direct consequence of the conformational disorder along the polymer chains. Additionally, due to the spatial hindrance induced by the intercalation in the clay galleries, a two-dimensional dynamics is expected for the PEO chains. Figure 2a shows the t_m-dependences of the normalized pure-exchange CODEX intensities for the samples 10k-(0.46) and 10k-(0.71). Both curves were fit using stretched exponential functions. Note that the parameter τ_c and the stretching parameters b obtained from the t_m-dependence are very similar for both samples. This confirms that choosing the temperatures such that the line widths are motion narrowed to similar values, the dynamics of the chains in both samples occurs with similar correlation times, i.e., they are occurring in comparable motional regimes. Figure 2b shows the Nt_r-dependences for the samples 10k-(0.46) and 10k-(0.71) as well as the corresponding simulations. For both samples the agreements between the experimental and simulated curves are very good.

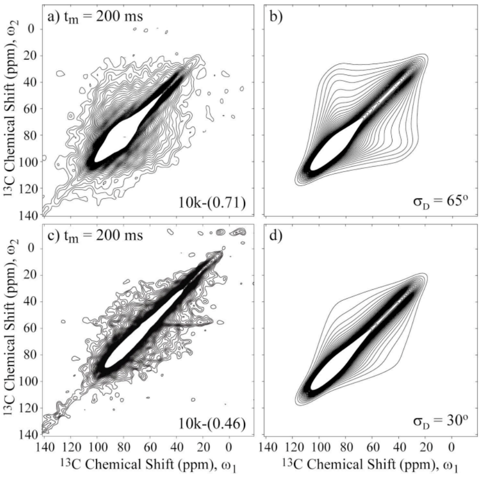

Figure 1: Experimental and simulated 2D Exchange spectra for samples a,b) 10k-(0.71) at T = 20 °C, and c,d) 10k-(0.46) at T = 100 °C.

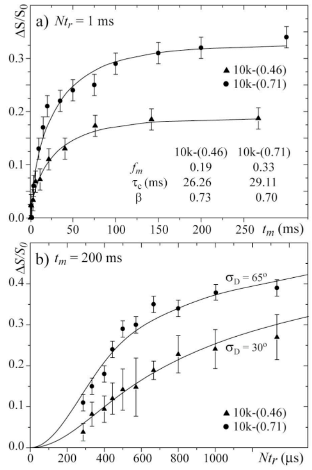

Figure 2: a) Mixing time t_m- and b) evolution time Nt_r-dependences of CODEX normalized intensities for the samples 10k-(0.71) at T = 20 °C and 10k-(0.46) at T = 100 °C.

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