Crystalline Structure of Polyamide 12 as Revealed by Solid State NMR and Synchrotron WAXS and SAXS

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The experimental data on polyamide 12 (PA12) polymorphism available up to now are scarce and not very well outlined. Here a report is presented on the crystalline structure and phase transitions in PA12 samples based on the same polymer grade, as a function of their thermal history and orientation. For the purpose, a combination of solid state ¹³C NMR and synchrotron WAXS and SAXS techniques was used. This allowed to extract additional and more reliable information from the WAXS and SAXS patterns¹.

Three different PA12 samples were investigated. The first one comprises as-supplied granules with no initial mechanical or heat treatment. The second sample was prepared by melting of the granules in a melt flow index apparatus followed by drawing of the resulting cables until undergoing neck formation. Some oriented PA12 cables were annealed with free ends at various temperatures.

Solid state NMR measurements were performed in a Bruker MSL300P spectrometer using Magic-Angle Spinning, high-power ¹H Dipolar Decoupling, and ¹H-¹³C Cross-Polarization combined techniques. Experimental spectra were fitted by individual Gaussian peaks. Synchrotron radiation generated at the Soft Condensed Matter Beamline (A2) of HASYLAB, Hamburg, Germany was employed. The first setup used allowed consecutive two 2D SAXS and 1D WAXS measurements. The PA12 granules were heated in the 30-175ºC range taking patterns at certain temperatures employing a heating rate of 20ºC/min. Similar heating was applied in the PA12 oriented cable followed, however, by two cooling cycles: the first after reaching 170ºC (i.e., before melting), and the second one – after 200ºC, i.e., after melting and isotropization of the sample. All X-ray patterns of the PA12 annealed oriented samples were obtained at 30ºC after performing the annealing at the respective temperature.

Isotropic and oriented PA12 showed different NMR spectra ascribed to γ- (Fig. 1a) and γ’-(Fig. 1b) crystalline modifications.

Figure 1: ¹³C CP MAS NMR spectra of PA12 samples: (a) isotropic granules (γ-form); (b) oriented cable (γ’-form). Spectra obtained at 21ºC.

Based on the position of the first diffraction peak, the isotropic γ-form and the oriented γ’-form were shown to be with hexagonal crystalline lattice at room temperature. When heated, the two PA12 polymorphs demonstrated different behaviour. Above 140ºC, the isotropic γ-PA12 partially transformed into α-modification (Fig. 2 a). Such transition was not observed with the oriented γ’-
PA12 phase even after annealing at temperatures close to melting (Fig. 2 b). A $\gamma'$-to-$\gamma$ transition was observed here only after isotropization by melting.

\[ \gamma' \rightarrow \gamma \]

Figure 2: 1D WAXS profiles of (a) PA12 isotropic granules and (b) oriented cable obtained after keeping the corresponding samples for 30 s at the respective temperatures. The arrows indicate the position of the $\alpha$-phase peak in Fig. 1a. No such peak is present in Fig. 1b.

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**References**