

s8.m28.o4 **Morphological Changes in Isotactic Polypropylene Evaluated by Saxs Analysis: a Comparison between Polymer Samples Obtained by Different Ziegler-Natta Catalysts.** E. Ferracini^a, R. Goergl^b and A. Mazzavillani^a, ^aChemistry Dpt. "G. Ciamician" - Università di Bologna, Bologna, Italy, ^bMaterials Center Leoben, Leoben, Austria. E-mail: elena.ferracini@unibo.it

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The morphologic and structural behaviour of isotactic polypropylene (i-PP) has been studied by a numbers of authors, as well as in our lab since more than thirty years [1] (the references reported in [1] include also the most of our previous papers). A remarkable feature of i-PP is its transition from the quenched form to the well-crystallized one by annealing; the quenched form has been obtained by a rapid cooling of the molten polymer in a mixture of dry ice and acetone (-78°C); the annealing of the quenched and cold-stretched samples (fibers) has been carried out isometrically, at different temperatures till 155°C. The morphology of the quenched (mesomorphic) form as well as of the annealed samples has been studied through the analysis of the respective SAXS patterns; the SAXS patterns showed, for all the samples, a meridional interference peak, indicating a coherent macroreticular sequence in the fiber axis direction; the analysis of the meridional spots was performed two-dimensionally, according to the paracrystal theory. The equatorial intensity profiles are continuous-like and have been analyzed by Guinier-Warren approximation.

Three kinds of i-PP have been studied and compared, obtained by different Ziegler-Natta catalysts: first-generation catalyst, high-yield heterogeneous MgCl₂ supported catalyst and Zr-cene based catalyst, respectively.

Meaningful results come from SAXS analysis: the mesomorphic form of i-PP represents an interesting case of an apparently amorphouslike state; the annealing treatment allowed us to follow the reorganization of the amorphouslike state with increasing temperature; the number of morphologic parameters determined, both in the quenched samples and over the transition, allowed us to put in evidence differences in the behaviour of the samples.

[1] E.Ferracini, R.Goergl, V.Malta, A.Mazzavillani and B.Moretti "Saxs Analysis of the Transition Induced by Annealing Quenched Isotactic Polypropylene", *J. Macromol. Sci.-Physics*, **B40**(6), 1193-1216 (2001).

s8.m28.o5 **Structural and Spectroscopic Properties in the (CH₃NH₃)₂Mn_{1-x}M_xCl₄ (0≤x≤1) System with M=Co or Cu.** P.Durand and S.Techert, *Structural Dynamics of (Bio)chemical Systems - Max-Planck Institut für Biophysikalische Chemie, Am Faßberg 11, 37077 Göttingen.* E-mail: pdurand@gwdg.de

For (CH₃NH₃)₂MnCl₄ (MAMnCl) and the related Cobalt (MACoCl) and Copper compounds (MACuCl) several structural phase transitions between monoclinic, tetragonal and orthorhombic modifications were previously found and are related to the ordering of the methylammonium ions and are therefore of special interest from a crystallographic point of view.¹ For MaMnCl the sequence of phase transitions is as follows: Tetragonal (Tc=393.8K) ↔ Orthorhombic ↔ (Tc=256.5-256.9K) ↔ Tetragonal (Tc=93.7-95.1K) ↔ Monoclinic

From a spectroscopic approach MaMnCl also attracts the attention. The faint pink (001) crystals have strong luminescence properties, similarly to (TMA)₂MnCl₄² and (TMA)MnCl₃³ (TMA⁺=N(CH₃)₄⁺). The MaMnCl crystals are fluorescent and exhibit a significant fluorescence quantum yield. If Cu²⁺ or Co²⁺ impurities are introduced at the Mn²⁺ sites, the luminescence properties are drastically altered and fluorescence disappears. Very small amount of copper (x≤0.1%) induces a deep red colour of these crystals. 4 Attempts to introduce cobalt in the structure results in a phase segregation although quenching of the fluorescence is observed, meaning a partial substitution of Mn²⁺ by Co²⁺. The analysis of both the charge transfer and crystal field spectra due to the Jahn Teller Cu²⁺ (d⁹) will be discussed, and low to room temperature spectroscopic measurements using optical absorption and emission methods will be presented.

Additionally, substitution of Mn²⁺ by Co²⁺ or Cu²⁺ is investigated by Powder X-ray diffraction. Results concerning structural phase transitions and evolution of cell parameters with doping will be discussed.

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