

Confinement of Gases and Polymers in Van Der Waals Crystals

Piero Sozzani, Department of Materials Science, University of Milano-Bicocca, Milan, Italy. E-mail: piero.sozzani@mater.unimib.it

The exploitation of weak interactions for the fabrication of binary adducts by self-assembly is receiving a great interest. We could obtain high-melting crystalline materials with macromolecules by simple mechanical mixing and grinding of D_3 and D_{3h} molecules with linear polyethylene or several polyconjugated oligomers [1]. A number of weak $CH\cdots\pi$ and $\pi\cdots\pi$ interactions cooperatively promote the stabilization of the architecture as recognized by solid state 2D MAS NMR. In particular, tris-(*o*-phenylenedioxy)cyclotriphosphazene (TPP) organizes the aromatic paddles parallel to the nanochannels encasing the elongated molecules. The guest hydrogens are subjected to the strong magnetic susceptibility of the surrounding aromatic groups that demonstrate the topology of the guest hydrogen above the π -system. The favorable intermolecular interactions compensate the loss of entropy necessary for constraining the macromolecules to the stretched geometry. However, 2H NMR and $^{13}C(T_1)$ show diffusional fast spinning motion ($\tau_c \approx 10^{-10}s$) about the polymer axis. The exceptional mobility of the polymer chains in the fully aromatic environment creates unique examples of molecular rotors and gyroscopes stabilized up to 350°C by soft interactions. The anisotropic alignment of polyconjugated molecules is suitable for growing crystal for electronic applications. The same kind of driving forces determine effective enclathration of light molecules and gases and promote absorption properties from the gas phase [2].

[1] Sozzani P., Comotti A., Bracco S., Simonutti R., *Angew. Chem. Int. Ed.*, 2004, **43**, 2811. [2] Sozzani P. et al., *Angew. Chem. Int. Ed.*, 2005, **44**, 2.

Keywords: self-assembly, weak interactions, gas storage