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Cooperation of multiple CH···π interactions to stabilize polymers in aromatic nanochannels as indicated by 2D solid state NMR†

Piero Sozzani,* Angiolina Comotti, Silvia Bracco and Roberto Simonutti
Department of Materials Science, University of Milano Bicocca, Via R. Cozzi 53, Milan, Italy.
E-mail: piero.sozzani@unimib.it; Fax: 02 6448 5400; Tel: 02 6448 5124

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Advanced 2D solid state NMR techniques reveal weak intermolecular interactions that cooperatively sustain nanostructures of high molecular mass aliphatic polymers entrapped as guests in channels formed by an aromatic host.

Weak interactions are pivotal for shaping cooperatively complex supramolecular architectures. Wide implications have been recognized for the construction of high-performance and functional materials and for the self-organization of biological structures.[1] In particular, hydrophobic interactions between benzene rings and hydrocarbon molecules are weak (2–8.5 kJ mol^{-1}) and mildly directional forces.[2] Their strengths are 20% that of the hydrogen bonds formed between water molecules, nevertheless they must be invoked for understanding molecular recognition and packing modes in crystals. Macromolecular and supramolecular assemblies exploit cooperative non-covalent interactions to build up high-melting nanostructured materials and nanocomposites.[3] Decrease of the overall energy drives the stabilization of complex architectures and wins out over unfavorable loss of macromolecular conformational entropy. However, the contribution of soft and diffuse interactions is somehow hidden and not easily recognizable. Here we observe for the first time by advanced NMR techniques organized interaction of π-systems with flexible synthetic high-polymers, that are forced to align in crystalline nanochannels. By our work it is shown that soft CH···π interactions can support unusual arrangements where aromatic rings surround the linear chains to form robust nanocomposite structures, melting at temperatures some 200 K higher than the bulk polymer. Contrasting the tendency of the polymer to explore multiple conformations, CH···π interactions induce a single macromolecule to fit nanocylinders adopting the entropically unfavorable extended-chain conformation. The dramatic morphology changes due to self-assembly are driven by a dense network of CH-aromatic hydrogen bonds, unique to examples of synthetic polymers. This study is a contribution to the enormous amount of evidence coming up on the importance of CH···π interactions to chemical and biological assemblies, but rarely highlighted in high polymers.[1]

Tris-(*o*-phenylenedioxy)spirocyclotriphosphazene (TPP) can easily assemble with or absorb substances of high and low molecular mass to form nanostructured materials showing a hexagonal lattice (Fig. 1, a and b).[4] The adduct we obtained with polyethylene (PE) (M_w = 10^5) shows a congruent melting temperature as high as 350 °C. XRD of single crystals with oligomers (M_w = 10^3) gives the crystal structure (space group $P6_3/m$) but cannot recognize the polymer inside the channels because the structure is incommensurate.[5] Previous characterization of the polymer conformation was based on 1D carbon MAS NMR.[4] To probe through-space host–guest interactions proton NMR is a most sensitive technique and a major challenge of modern solid state NMR spectroscopy is to obtain high resolution in the hydrogen domain.[6] Our approach allowed us to obtain very high resolution both in the hydrogen and the carbon domain by integrating Phase Modulated Lee–Goldburg (PMLG) homonuclear decoupling and fast Magic Angle Spinning (15 kHz) in a 2D (^{1}H–^{13}C) HETCOR experiment (Supporting Information).

The PMLG (^{1}H–^{13}C) 2D HETCOR spectra of a TPP/PE adduct, also containing an excess of PE, are presented in Fig. 2. Cross-polarization time rules the communication between the specific spins in the 2D experiment and the cross peak intensities measure the distances according to the scaling law of $1/d^6$. For short contact times (1 ms) (Fig. 2a) we observe polarization transfer to carbons only from covalently bonded protons at less than 1.5 Å. Two signals for PE in both hydrogen and carbon dimensions are assigned, through relative peak intensities and carbon chemical shifts, to PE included in the aromatic nanochannels (CH$_2$-in, upfield) and to the

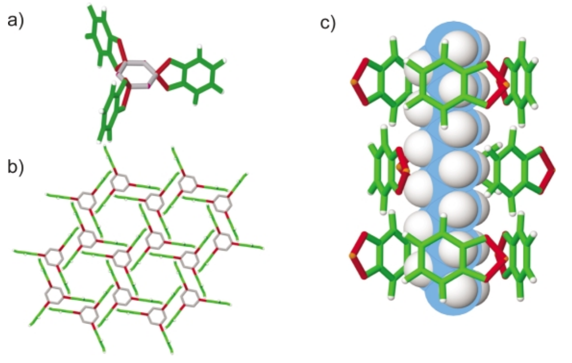

Fig. 1 a) Skeletal representation of TPP molecule. b) Organization of TPP molecules in the hexagonal lattice typical of the adducts, where guests are omitted for clarity. c) Extended conformation of –(CH$_2$)$_n$– chain wrapped by the TPP paddles that form a 0.5 nm aromatic nanochannel (C: green, H: white, O: red, P: orange; guest C: blue).

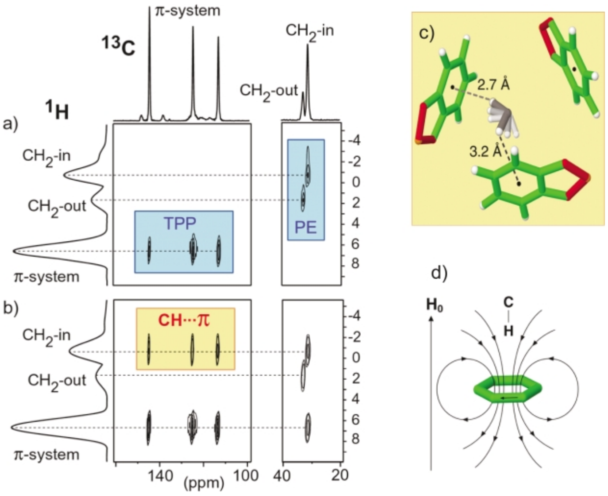

Fig. 2 PMLG (^{1}H–^{13}C) HETCOR NMR spectra of TPP/PE adduct: contact times of 1 ms (a) and 5 ms (b). The CH···π interaction between the –(CH$_2$)$_n$– of PE and the π-system of TPP is highlighted. CH$_2$-in indicates the PE chains included in TPP nanochannels, CH$_2$-out indicates excess PE. c) Modeling of on-plane rotation of a single –CH$_2$– group of PE in the nanochannel. d) Topology of guest hydrogens located at 2.5–2.7 Å above the plane of the benzene rings: the ring currents generate an upfield shift of 2.2 ppm.

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† Electronic supplementary information (ESI) available: details on the samples and on the NMR experiments, 2D NMR spectra of TPP/PTHF and ^{2}H NMR spectrum of TPP/PE-d$_4$. See http://www.rsc.org/suppdata/cc/b3/b316855g/

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excess PE (CH_2-out, downfield) in the orthorhombic phase. The PMLG (^1H–^{13}C) HETCOR spectrum with long contact times (Fig. 2b) revealed correlations at larger distances, and intense cross-peaks between the aromatic and aliphatic atoms (yellow shaded area) provided evidence of strong and numerous magnetization interactions of the polymer chains included in the aromatic nanochannel. A single spin-system defines a single extended phase constituted by PE chains in close contact with the aromatic groups. The nuclei of the excess polymer (CH_2-out) far from the aromatic surfaces do not participate in the same phase and remain an isolated spin-system. In the ^{13}C projection the $\Delta = -1.60$ ppm shift originating from the aromatic groups near the included polymer (CH_2-in) can be directly appreciated. The polymer protons interacting with the aromatic carbons resonate even at negative values to TMS ($\delta_H = -0.6$ ppm), exceptionally upfield ($\Delta = -2.2$ ppm shift) compared to those belonging to the bulk polymer phase and to the polymer included in saturated hosts.[7] The upfield shift can be explained by the TPP/PE nanostructured architecture, where a fully aromatic tubular space contains the polymer chain that experiences intensely the aromatic ring currents, as depicted in Fig. 1c. The polymer chain aligns itself in parallel with the aromatic TPP paddles, and the methylenes are perpendicular to the π-system.

It is possible to model the interactions by a rigid body rotation of the chain bearing methylenes (virtually no torsion is allowed due to tight fit), calculating guest-proton/TPP-aromatic distances. The close 2.5–2.7 Å contact between the aromatic ring and the methylene hydrogens pushes the latter under the influence of strong anisotropic diamagnetic susceptibility, generating the upfield shifts (Fig. 2, c and d). We have observed large upfield shifts also in 2D spectra of other linear polymers containing methylene groups when confined to TPP, confirming the generality of our findings (Table 1 and Supporting Information).

Rare observations have been reported showing strong shifts due to intermolecular aromatic ring currents, particularly in solids.[8] Proton resonances shifted 2 ppm upfield indicate the exact topology of the guest hydrogens above the plane of benzene rings at a distance of 2.5 Å, as calculated by nucleus-independent chemical-shift maps.[8] This datum combined with the PMLG 2D HETCOR evidence of the proton proximity to aromatic carbons shows that the hydrogens are in a critical position to establish favorable energetic interactions with the π-system. The spatial arrangement (2.5–2.7 Å above the benzene ring) is typical of the structures where CH···π hydrogen-bonds of about 8.5 kJ mol^{-1} are described.[1] The attraction forces are mainly due to dispersive interactions, as calculated for the ethane–benzene complex when ethane approaches along the benzene 6-fold axis.[2] In our case, favorable interactions between a multiplicity of aliphatic protons and the aromatic counterpart contribute cooperatively to a considerable ΔH gain for the self-assembly process (-140 J g^{-1}), overcoming the loss of entropy necessary for constraining the macromolecules to the elongated geometry. However, motion is not hindered because the density of aromatic rings lining the nanochannel is high (three per cross-section) and permits the guest protons to pass smoothly from the influence of one ring to the next. Thus, intriguingly, rotations and librations are allowed because a spinning polymer chain never falls into a deep energy minimum. Solid-echo deuterium NMR confirms the occurrence of diffusional reorientation about the polymer axis (60 kHz between the singularities: Supporting Information), modeled as complete averaging for fast ($\tau_c < 10^{-6}$ s) on-plane rotations or librations. ^{13}C T_1 of 12 s, in the extreme narrowing limit typical of liquids, suggests an even faster spinning of the large segments of the polymethylene chains ($\tau_c < 10^{-10}$ s). The exceptional mobility of the polymer chains in the fully aromatic environment creates a unique example of a molecular rotor stabilized by soft interactions.

Table 1 ^1H and ^{13}C NMR chemical shifts (δ/ppm) of polymers in the presence of CH···π interactions within the aromatic nanochannels, as detected in the 2D PMLG HETCOR NMR spectra

	PE	TPP/ PE	PEO[a]	TPP/ PEO	PTHF[b]	TPP/ PTHF
^1H	1.6	−0.6	3.5	1.6	1.6 3.3	−0.8 1.1
^{13}C	32.80	31.20	71.00[c]	68.45	27.37[c] 71.10[c]	25.18 70.63

[a] PEO: polyethylene oxide. [b] PTHF: polytetrahydrofuran. [c] Chemical shifts measured in the amorphous phase.

In conclusion, we have recognized by multinuclear solid-state NMR the role of CH···π interactions cooperating to fabricate polymer nanostructured materials that shape exceptionally stable aromatic nanochannels. The recognition of weak interactions in supramolecular assemblies of synthetic polymers can bring significant consequences to the study of polymers at the interfaces and promote projects for obtaining innovative heterogeneous materials and nanocomposites.

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