

Electronic Supplementary Information

Self-assembly of 1,4-*cis*-polybutadiene and an aromatic host to fabricate nanostructured crystals by CH \cdots π interactions

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Materials

TPP was synthesized by our group following the procedure previously reported.¹ The 1,4-*cis* polybutadiene rubber (Europrene NEOCIS BR 60: Polimeri Europa S.p.A.-Milano; 98% *cis*, average $M_w = 300,000$) has been purified from stabilizers by dissolution in chloroform and precipitation in methanol. The crystalline TPP/1,4-*cis*-PB materials were prepared both from solution and by mechanochemical method with variable amount of rubber. The TPP/PB crystals (Sample 3: PB molar fraction = 0.53) were obtained by crystallization from a benzene solution containing TPP combined with a chloroform solution of the rubber, maintaining the solution under stirring for two hours. At the end of the process the crystals were dried under vacuum for removing the solvents. The TPP/PB materials (Sample 1: PB molar fraction = 0.70; Sample 2: PB molar fraction = 0.62) were obtained by compounding the polybutadiene rubber and the crystalline TPP powder in a mortar at a temperature of about 50°C.

X-ray Powder Diffraction.

Powder X-ray diffraction experiments were performed using a Bruker D8 diffractometer in the Bragg-Brentano geometry. The radiation wavelength λ of the incident X-rays was 1.5406 Å and a 2θ range from 5° to 60° was investigated. The unit cell parameters were refined using the GSAS program A. C. Larson, R. D. Von Dreele Los Alamos National Laboratory Report LAUR 86-748 (2004).

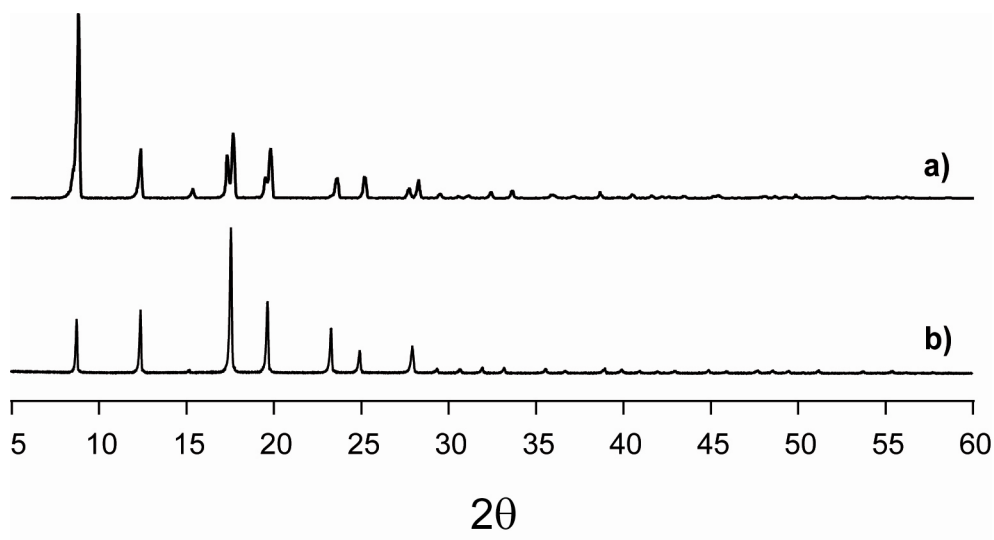


Figure S1. Powder X-ray diffraction patterns of: a) guest-free TPP crystals (space group $P6_3/m$, $a = b = 11.454(5)$ Å; $c = 10.160(5)$ Å; $V = 1154.4(9)$ Å³); b) TPP/1,4-*cis*-PB supramolecular crystals obtained from solution crystallization (Sample **3**) (space group $P6_3/m$, $a = b = 11.6562(8)$ Å; $c = 10.0782(13)$ Å; $V = 1185.85(13)$ Å³).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) traces were performed on Mettler Toledo Star^e Thermal Analysis System equipped with N₂ low-temperature apparatus. The experiments were run under nitrogen atmosphere Al-crucibles. The samples were heated from 25 °C to 350 °C at 10 °C/min. The sample weights for the DSC measurements were about 3 ÷ 5 mg and were measured to an accuracy of 0.05 mg.

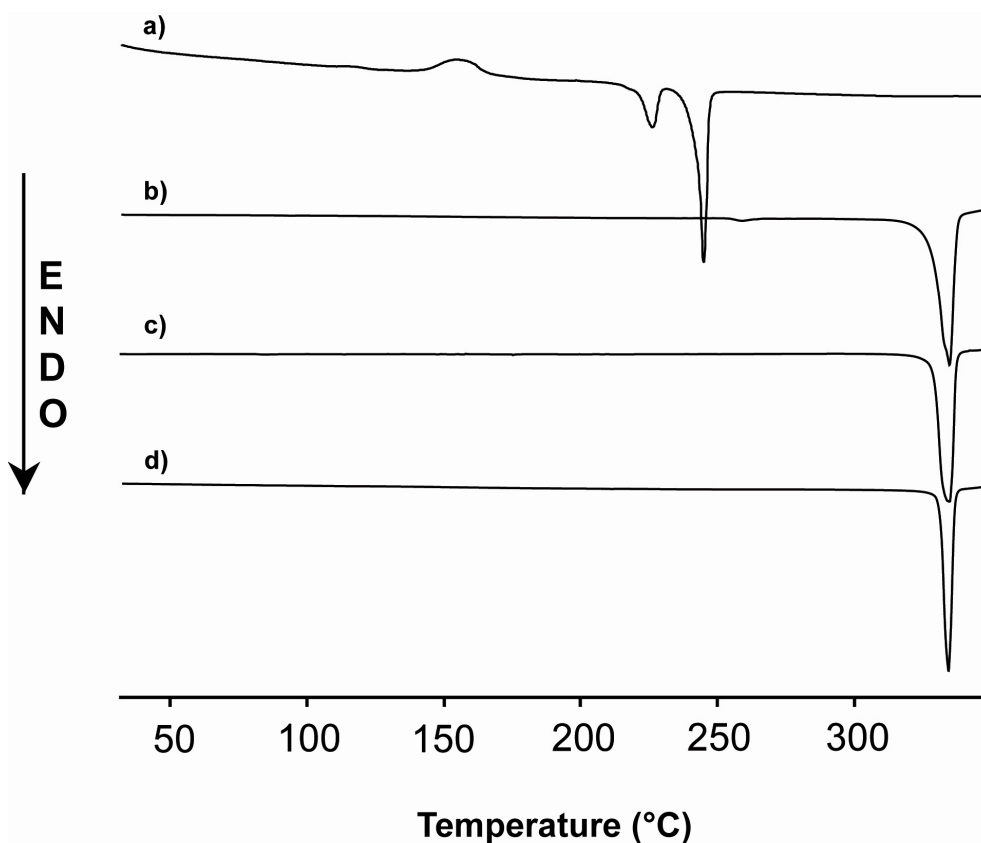


Figure S2. Differential scanning calorimetry traces of: a) guest-free TPP crystals; b) sample 1 c) sample 2; d) sample 3. Melting temperatures of the composite materials are stable at 333°C and the melting enthalpies are respectively - 122 j/g, - 120 j/g and - 112 j/g for the sample 3, sample 2 and sample 1.

Solid State NMR

Quantitative ^1H MAS NMR measurements have been performed on a Bruker Avance III 600 MHz instrument operating at 14.1 T, by using a recycle delay of 20 s. A MAS Bruker probe head was used with 2.5 mm ZrO_2 rotors spinning at the speed of 35 kHz.

Phase-Modulated Lee-Goldburg (PMLG) heteronuclear (^1H - ^{13}C) and (^1H - ^{31}P) correlation (HETCOR) spectra were run at 75.5 MHz, on a Bruker Avance 300 MHz instrument operating at a static field of 7.04 T. A MAS Bruker probe head was used with 4 mm ZrO_2 rotors spinning at the speed of 15 kHz. 90° pulse for proton was 2.9 μs . LG period was usually 18.9 μs . Quadrature detection in t_1 was achieved using TPPI method. RAMP-CP³ is obtained changing the strength of the proton rf from 80 kHz at the beginning of the contact time to a value of 40 kHz at the end of the cross polarization period in 100 steps. Cross-polarization times of 0.5 ms and 5 ms were applied on each sample. Carbon and phosphorous signals (t_2) are acquired under proton decoupling, applying two pulse phase modulation scheme (TPPM)⁴. Particular care must be paid when the chemical shift values in F1 dimension are taken into account, since the chemical shift dispersion is scaled by a factor of $1/\sqrt{3}$ compared to what obtained in a directly detected ^1H spectrum. A mismatch of the Lee-Goldburg condition might lead to a different scaling. Therefore, the chemical shifts were confirmed by the performance of 1D ^1H spectra.

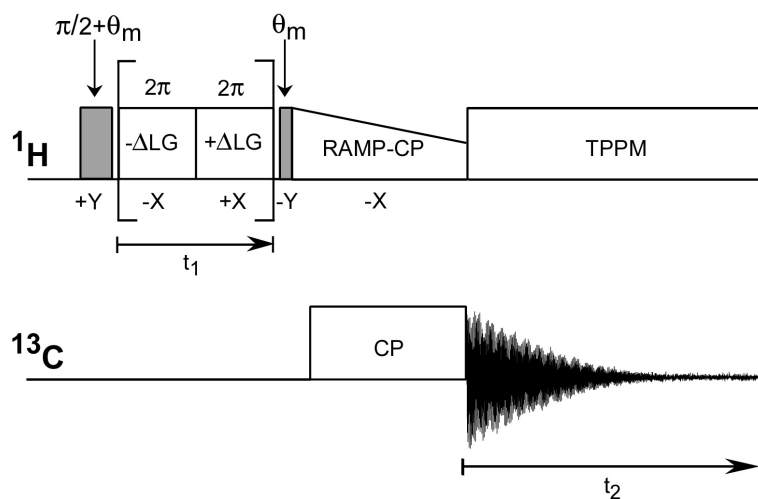


Figure S3. Pulse sequence used for 2D PMLG-HETCOR NMR experiments. A $(\pi/2 + \theta_m)_y$ preparation pulse reorients the ^1H polarization perpendicular to z axis of the effective field in the tilted rotating frame, during t_1 a PMLG irradiation sequence is applied. At the end of t_1 a θ_m pulse brings back the magnetization into the xy plane. In order to have an efficient transfer of magnetization to the carbon nuclei under fast MAS during the contact time a RAMP-CP is applied, this procedure restores a broader matching profile between proton and carbon nuclei. During acquisition TPPM heteronuclear decoupling is applied.

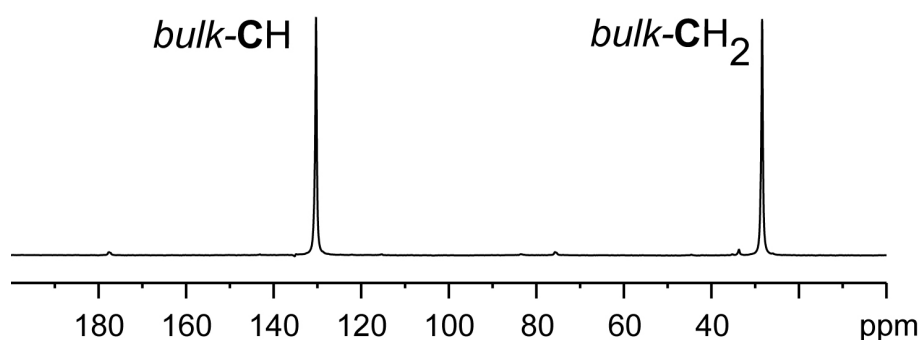


Figure S4. ^{13}C MAS spectrum of the bulk polymer performed at 300MHz by using a spinning speed of 3.5 kHz and a recycle delay of 10 s. The *bulk-CH* and *bulk-CH₂* species resonate at 130.3 ppm and 28.3 ppm, respectively.

Table S1. ^1H and ^{13}C NMR Chemical Shifts (δ/ppm) TPP/PB materials as detected in the ^1H fast-MAS NMR, 2D PMLG HETCOR NMR and ^{13}C CP MAS spectra, independently recorded.

	<i>cry-CH</i>	<i>cry-CH₂</i>	<i>bulk-CH</i>	<i>bulk-CH₂</i>	<i>i-CH</i>	<i>i-CH₂</i>	TPP
^1H	3.5	0.1	5.2	1.9	5.7	2.4	H ₁ : 6.5 H ₂ : 7.3
^{13}C	128.2	26.1	130.3	28.3	-	-	C ₁ : 113.3 C ₂ : 124.9 C _{quat} : 144.8

References

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