Synthesis, Characterization and Structure Properties of Biobased Hybrid Copolymers Consisting of Polydiene and Polypeptide Segments

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Supporting Information
The following data are given in the Supporting Information:
(A) SEC chromatographs of polydiene precursors, functionalized intermediate products and final biobased hybrid copolymers.
(B) Magnified spectra of amide III, IV, V, VI as well as IR characteristic wavenumbers for specific chemical groups of all hybrid materials (Table S1).
(C) ^{1}H-NMR & ^{13}C-NMR chemical shifts corresponding to all different chemical groups of the hybrid materials (Table S2, Table S3).
(D) 3D AFM images and the corresponding characteristic surface roughness profiles for $PB_{1,4}$-*b*-P(o-Bn-L-Tyr), $PB_{1,2}$-*b*-P(o-Bn-L-Tyr) and $PI_{1,4}$-*b*-P(o-Bn-L-Tyr) samples.

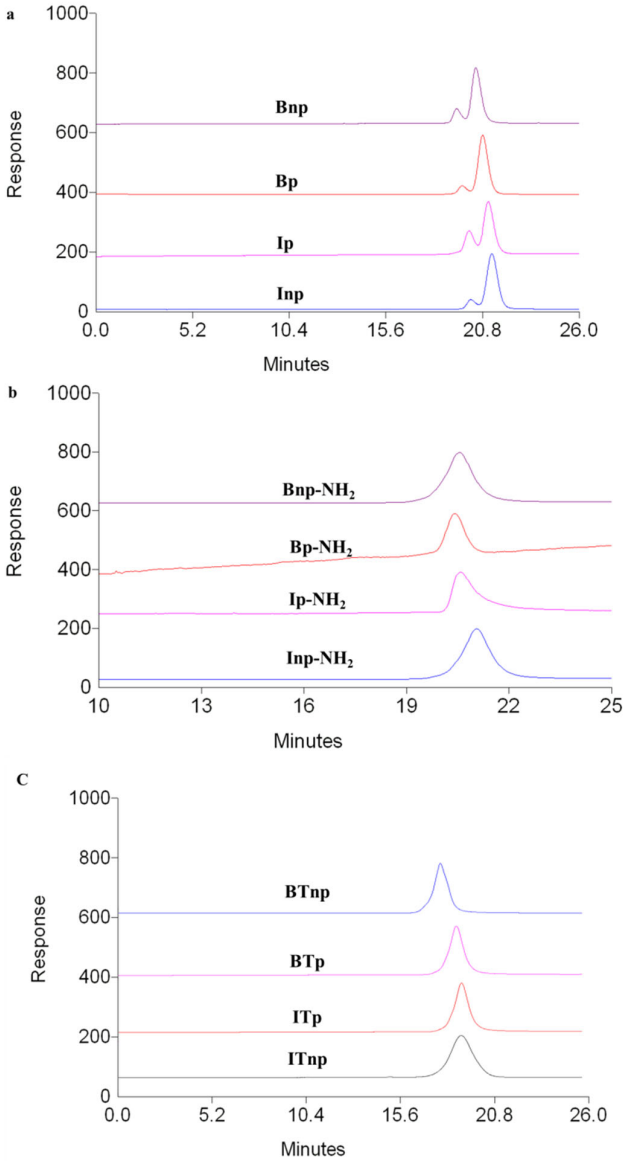

Figure S1: SEC chromatographs corresponding to: a. polydiene precursors, b. functionalized intermediate products and c. all final biobased hybrid copolymers.

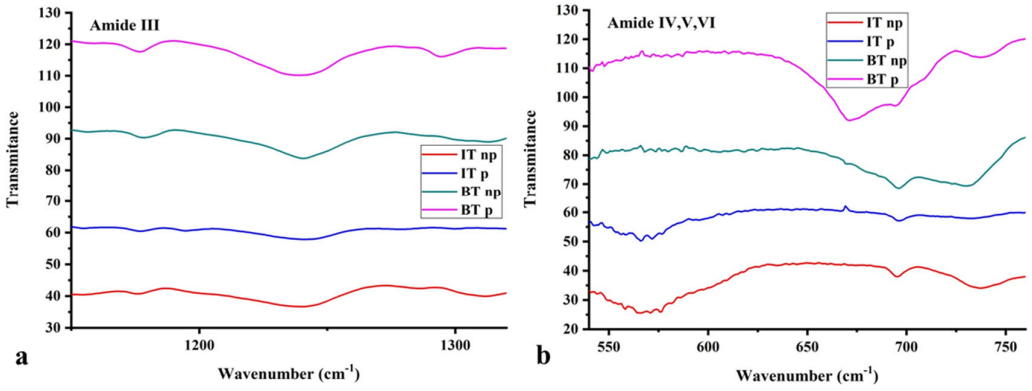

Figure S2: Magnified spectra corresponding to amide: a. III and b. IV, V, VI.

Table S1: Characteristic FT-IR peak wavenumbers corresponding to all components of the synthesized hybrid materials.

Chemical group	Range (cm^{-1})	ITnp	ITp	BTnp	BTp
Amide VI/V/IV	537-606	S	S	W	W
	640-800	M	M	S	S
	625-767	M	M	S	S
Amide III	1229-1301	M	M	S	S
Amide II	1545-1540 (α-helices)	-	-	-	-
	1530-1520 (β-sheets)	W	W	W	W
Amide I	1654-1667 (α-helices)	M	-	W	-
	1623-1643 (β-sheets)	M	S	W	S
C=O	1690-1760	٧	٧	٧	٧
C-N	1180-1360	٧	٧	٧	٧
C=C (Ar)	1500, 1600	٧	٧	٧	٧
Ar-O-CH_2	1000-1050, 1600-1650	٧	٧	٧	٧
-NH_2	1050-1250, >3000	٧	٧	٧	٧
-NH-	1050-1250, >3000	٧	٧	٧	٧

*S: strong, M: medium, W: weak, -: no existence and ٧: existence.

Table S2: Characteristic ^{1}H-NMR chemical shifts corresponding to all components of the synthesized hybrid materials.

Chemical group	Chemical shift (ppm)
sec-BuLi/PB/PI Diaminohexane	1.00-3.00
$PI_{1,4}$	1.80,2.85 & 5.44
$PI_{3,4/1,2}$	1.20-1.80, 4.90-5.70
$PB_{1,4}$	2.00, 2.85 & 5.70
$PB_{1,2}$	1.50, 3.00, 5.20 & 5.90
-NH- (main chain linkage)	>8.00
-C^aH- /-NH_2 (end group)	3.80 & 5.10
P(o-Bn-L-tyr) (R group)	3.30 & 5.20
P(o-Bn-L-tyr) (R group: aromatic)	6.90-7.50

Table S3: Characteristic ^{13}C-NMR chemical shifts corresponding to all components of the synthesized hybrid materials.

Chemical group	Chemical shift (ppm)
$PI_{1,4}$	16,32,47,124,140
$PI_{3,4/1,2}$	30,42,114,147
$PB_{1,4}$	34,38,127,131
$PB_{1,2}$	40-42,115,142
R: -$\underline{C}H_2$-ph-O-CH_2-ph	~40
-C^a-	~55
R: -CH_2-ph-O-$\underline{C}H_2$-ph	~70
Aromatic	114-130
Aromatic (quaternary)	130-160
>$\underline{C}$=O ITnp & BTnp	*167,172
>$\underline{C}$=O ITp & BTp	*174,172

*The first chemical shift is referred to the linkage between polydiene segment and the diaminohexane. The second chemical shift is referred to the polypeptide chain and was found to be the similar for all samples.

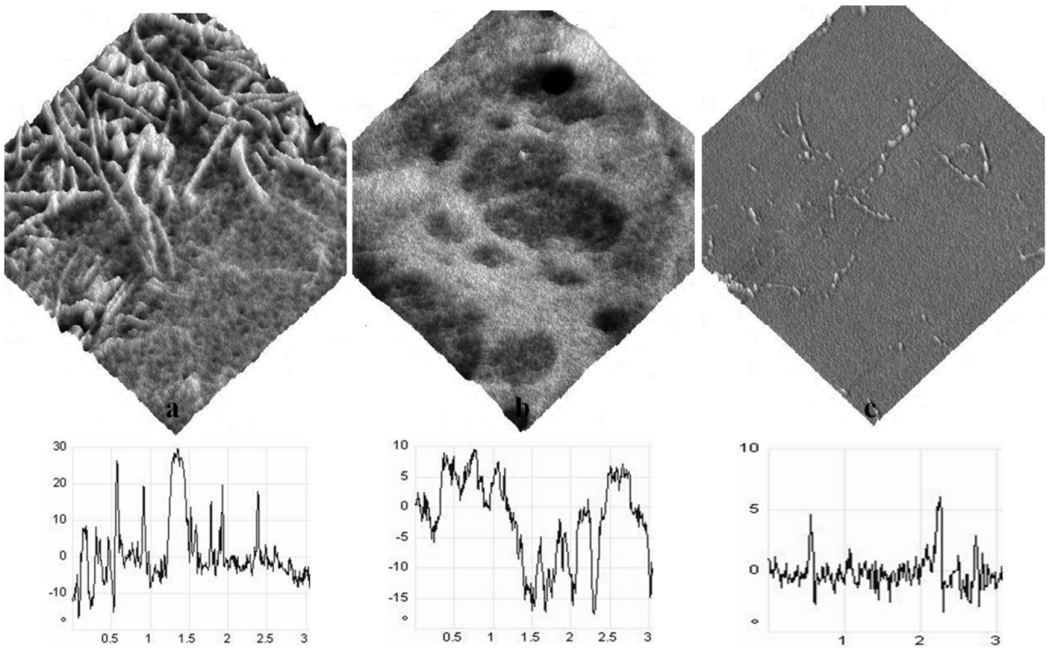

Figure S3: 3D AFM images (3 µm x 3 µm) at room temperature and the corresponding characteristic surface roughness profiles of a. $PB_{1,4}$-*b*-P(o-Bn-L-Tyr), b. $PB_{1,2}$-*b*-P(o-Bn-L-Tyr) and c. $PI_{1,4}$-*b*-P(o-Bn-L-Tyr).