Electronic Supplementary Information

Facile Synthesis of 1,4-*cis*-Polyisoprene-Polypeptide Hybrids with Different Architectures

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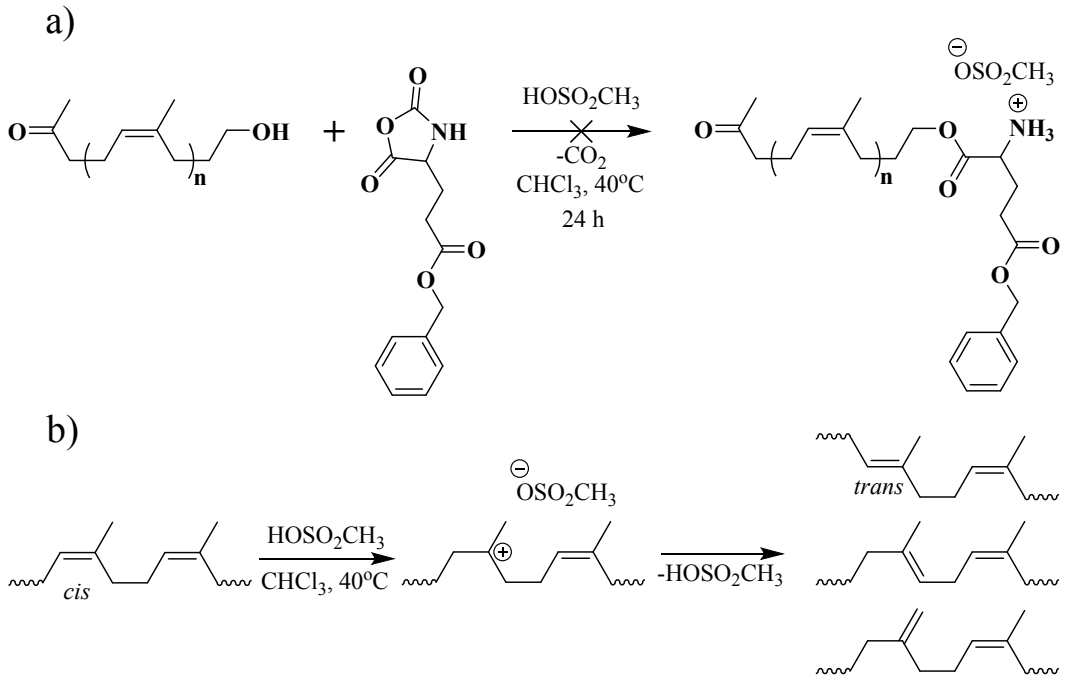
BLG-NCA polymerization with methane sulfonic acid as a catalyst.

The initiation step, that corresponds to the ring-opening of the first monomeric unit followed by the protonation of the formed terminal amino group, was carried out at 40°C for 24 h (Scheme S1a). ^{1}H NMR analysis of an aliquot revealed that initiation was not efficient as about 50% of –OH groups remained unchanged, as the signal at 3.6 ppm corresponding to the -CH_2OH end-group of the macroinitiator was still present (Figure S1). Moreover, it was reported recently that the signal corresponding to the terminal CH_2 group (8 in Figure S1) in the form of an ester should appear around 4 ppm.[1] Only very small signals are visible in this region (Figure S1 (B)) indicating that most of the reacted terminal hydroxyl groups were consumed for side-reactions. Two new signals appeared in the spectrum at 2.69 and 4.72 ppm. HMBC and HSQC NMR experiments were then performed to assign these signals. From HMBC spectrum, it was shown that the group corresponding to the signal at 2.69 ppm (in ^{1}H NMR) was in the proximity of two olefinic carbons (125.0 and 135.5 ppm) (Figure S2). Besides, it was already described in the literature[2] that a CH_2 group blocked between two double bonds had a similar chemical shift. As a consequence, it could be suggested the structure presented in Figure S1(B). HSQC (Figure S3) experiment showed that the signal at 4.72 ppm in the ^{1}H NMR spectrum corresponded to the signal at 109.1 ppm in ^{13}C NMR spectrum, which agreed well with the values reported earlier for 1,1-di-substituted double bond[2,3](Figure S1). Moreover, in HSQC spectrum, signals corresponding to 1,4-*trans*-monomer unit were detected.[4] The formation of these structures can be explained by double bond isomerization in acidic conditions (Scheme S1b). The reaction mixture was then put into an ethanol bath at 0°C and *i*-PrNEt_2 was introduced to start NCA polymerization. Expectedly, polymerization did not occur following unsuccessful initiation step and the molar mass of the final polymer determined by SEC was the same as the one of the macroinitiator (M_n= 8900 g/mol). This clearly shows that methanesulfonic acid is not suitable as a catalyst for polypeptide-polyisoprene synthesis.



Scheme S1. Expected initiation step for NCA ROP using PIOH as macroinitiator (a) and double bond isomerization (b) in the presence of methanesulfonic acid.

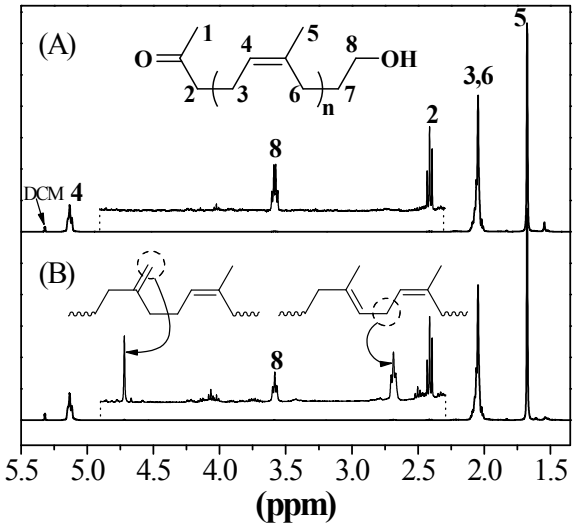


Figure S1. ^{1}H NMR spectra of PI-OH (A) and of the product of its reaction with BLG-NCA (B): [PI-OH] = $8.0 \cdot 10^{-2}$ mol/L, [CH_3SO_3H] = $2.4 \cdot 10^{-2}$ mol/L, [BLG-NCA] = 0.19 mol/L, $CHCl_3$, 40°C, 24 h.

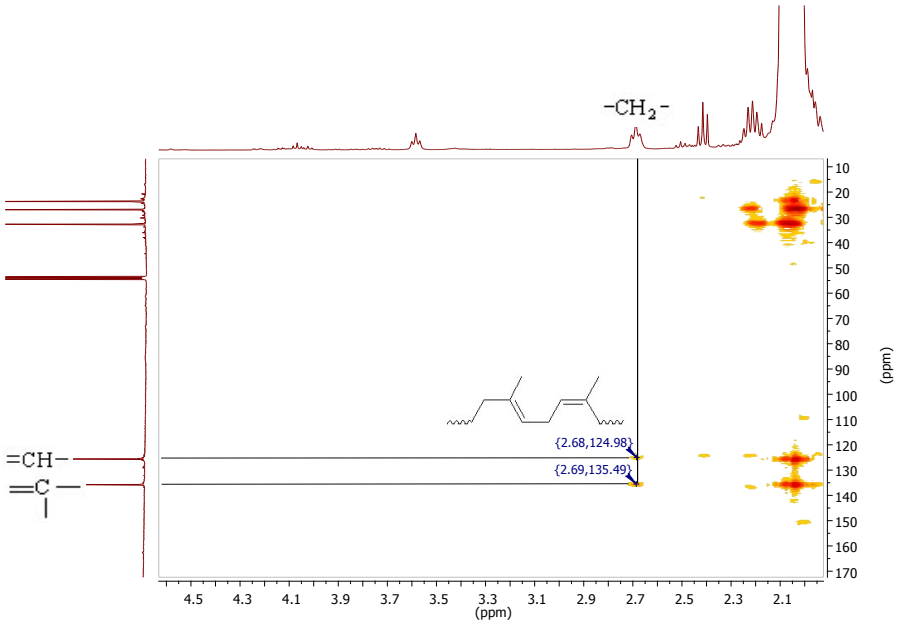


Figure S2. Fragment of HMBC NMR spectrum of the product of the reaction: [PI-OH] = $8.0 \cdot 10^{-2}$ mol/L, [CH_3SO_3H] = $2.4 \cdot 10^{-2}$ mol/L, [BLG-NCA] = 0.19 mol/L, $CHCl_3$, 40°C, 24 h.

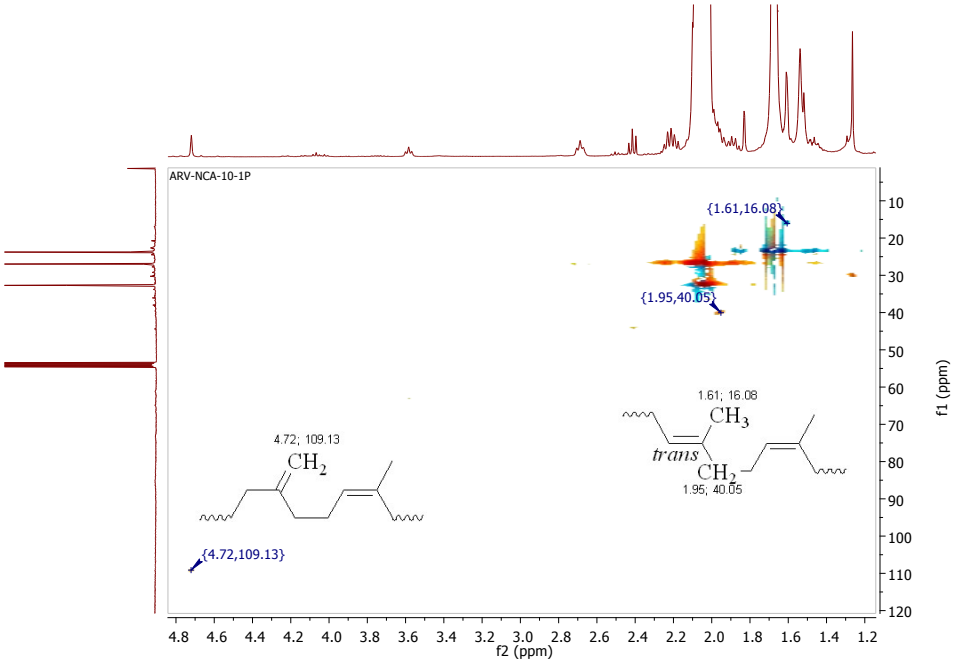
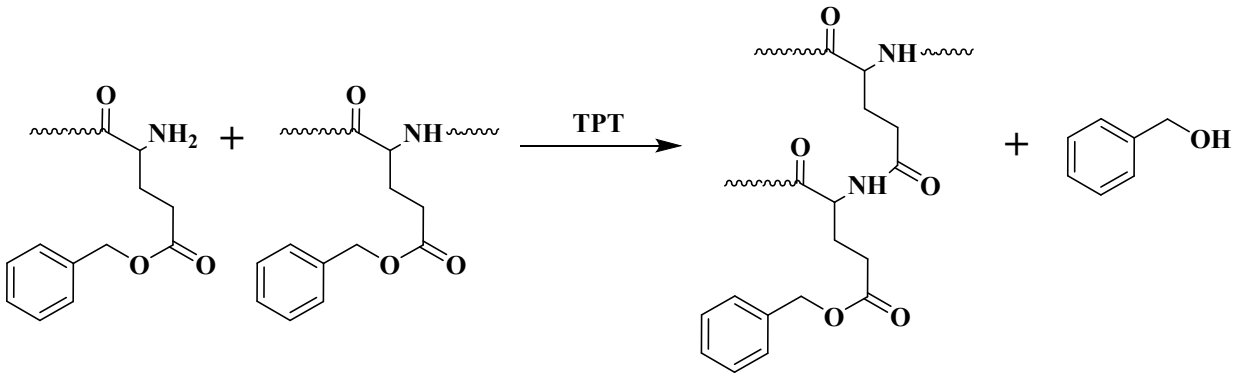


Figure S3. Fragment of phase sensitive HSQC NMR spectrum of the product of the reaction: [PI-OH] = 0.01 mol/L, [CH_3SO_3H] = 0.023 mol/L, [BLG-NCA] = 0.19 mol/L, $CHCl_3$, 40°C, 24 h.

Procedure of NCA polymerization with methane sulfonic acid as the catalyst. 0.2 g of **PI-OH** (0.02 mmol) were dissolved in dry $CHCl_3$ (0.5 mL), then 3.7 µL (0.06 mmol) of CH_3SO_3H were added, followed by 2 mL of a 0.24 M BLG-NCA solution in $CHCl_3$. The mixture was stirred at 40 °C. After 24 h, a sample of 0.7 g of reaction mixture was taken and precipitated in 7 mL of methanol containing 0.1 mL of 35% NH_3 water solution. Then, the reaction vessel was transferred into a bath

at 0 °C and 8.2 µL (0.05 mmol) of *i*-Pr_2NEt were introduced into the medium. After additional 24 h, the reaction mixture was washed several times with saturated $NaHCO_3$ solution and then dried in vacuum at 40 °C overnight.

Synthesis of polyisoprene –poly(BLG) hybrids.



Scheme S2. Possible coupling reaction between chain-end and pendant ester group.

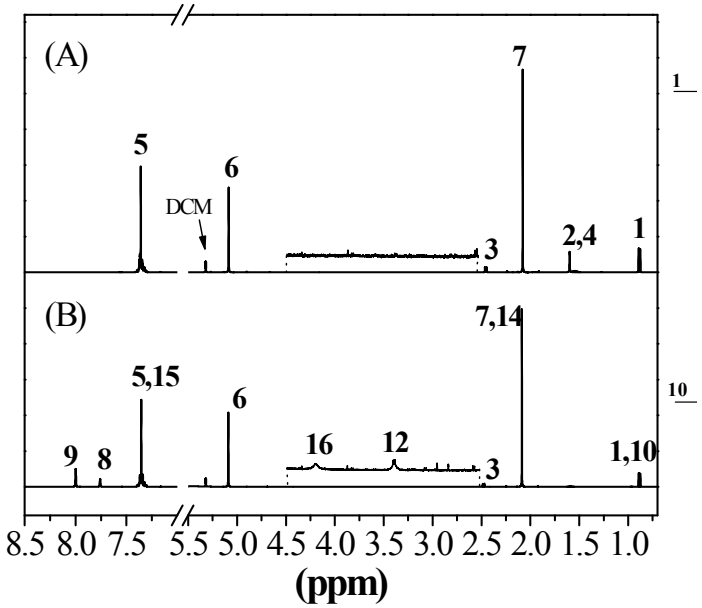


Figure S4. ^1H NMR spectra of the mixture of *i*$BuNH_2$ and benzyl acetate (A) and of the same mixture 16 h after the addition of TPT (B): [*i*$BuNH_2$] =0.027 mol/L, [benzyl acetate] = 0.13 mol/L, [TPT] = 0.054 mol/L, CD_2Cl_2, room temperature.

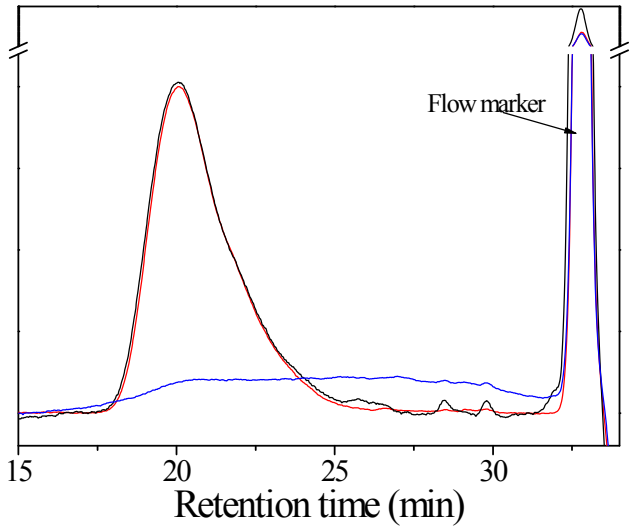


Figure S5. SEC traces of **MI2** (black line)**,** its mixture with poly(BLG) (3:2 (g/g)) (red line) and poly(isoprene-(*b*-BLG)$_2$) (Runs 4 in Table 1) (blue line) using THF without additive as eluent.

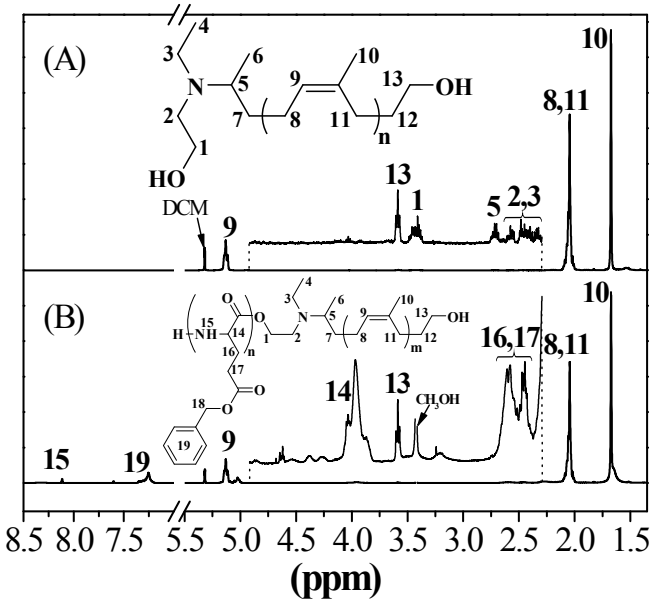


Figure S6. ^{1}H NMR spectra of **MI5** (A) and of poly(isoprene-*b*-BLG) obtained using **MI5** (B)**.**

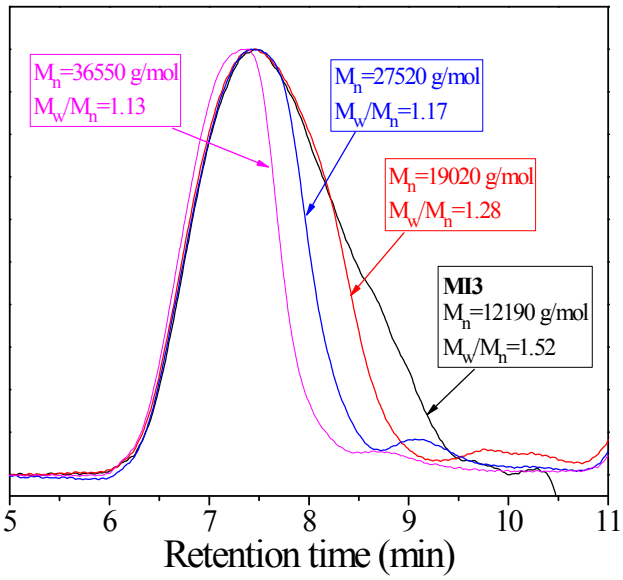


Figure S7. SEC traces of **MI3** and poly(BLG-*b*-isoprene-*b*-BLG)s (Runs 6, 7, 8 in Table 1)

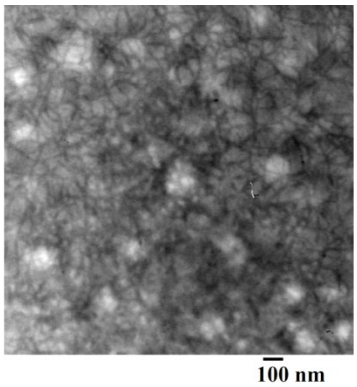


Figure S8. Transmission electron micrograph of a 20 g/L gel of poly(isoprene-b-BLG) (Runs 2 in Table 1) in toluene.

References

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3. Rozentsvet, V. A.; Khachaturov, A. S.; Ivanova V. P. Microstructure of polyisoprene produced by cationic polymerization: NMR spectroscopic study. *Polymer Science, Ser. A*, **2009**, *51*, 870–876.
4. Tanaka, Y. Structure and Biosynthesis Mechanism of Natural Cis-Polyisoprene from Goldenrod. *Rubber Chemistry and Technology* **1983**, *56*, 299–303.