Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Synthesis and characterization of designed cellulose-*graft*-polyisoprene copolymers†

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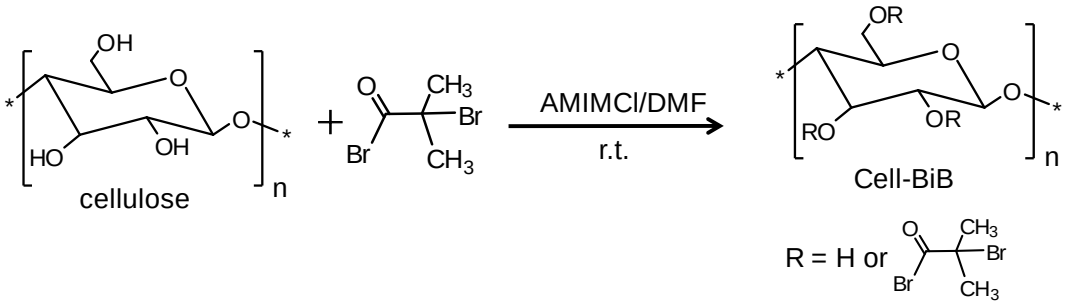

Scheme S1. Illustration of synthesis of macroinitiator Cell-BiB.

Calculation of the degree of substitution (DS) of Cell-BiB

Fig. 2a shows the ^{1}H NMR spectrum for macroinitiator Cell-BiB. The chemical shifts in the range of 1.6–2.0 ppm are attributed to the methyl protons of bromoisobutyryl group (1), and the chemical shifts in the range of 3.5–5.4 ppm are attributed to the protons of glucose (2). The degree of substitution (*DS*) of Cell-BiB can be obtained as the ratio of integrals of the NMR peaks using Formula 1 as follows:

$$DS = \frac{10S_1}{S_1 + 6S_2} \qquad (1)$$

where S_1 and S_2 are the integral intensities of the corresponding methyl protons of Cell-BiB and protons of glucose, respectively. The degree of substitution (DS) of Cell-BiB is calculated to be 0.92.

Determination of the 1,2-, 3,4- and 1,4-addition contents for isoprene units in the grafted PI chains

Fig. 3b shows the ^{1}H NMR spectrum of Cell-*g*-PI257 copolymer using $CDCl_3$ as solvent. The

sharp chemical shifts from methyl protons of cis-1,4 and trans-1,4 units are observed at 1.58 and 1.68 ppm, respectively. The olefinic proton signal of cis- and trans-1,4 units is observed at 5.13 ppm. The signal at 4.60–4.78 ppm is attributed to olefinic protons of 3,4-addition. The signals at 4.80–4.95 and 5.70–5.80 ppm indicate the olefinic protons of 1,2-addition. The contents of the 1,2- ($C_{1,2}$), 3,4- ($C_{3,4}$) vs 1,4-addition ($C_{1,4}$) for the isoprene units are obtained as ratios of the integrals of NMR peaks using formula 2-4 as follows:

$$C_{1,2}\% = \frac{S_s}{S_{b,g} + S_s + S_o/2} \times 100\% \qquad (2)$$

$$C_{3,4}\% = \frac{S_o/2}{S_{b,g} + S_s + S_o/2} \times 100\% \qquad (3)$$

$$C_{1,4}\% = \frac{S_{b,g}}{S_{b,g} + S_s + S_o/2} \times 100\% \qquad (4)$$

where S_s, S_o, and $S_{b,g}$ are the integration intensities of the corresponding olefinic proton signals of 1,2-addition, 3,4-addition and 1,4 addition units, respectively.

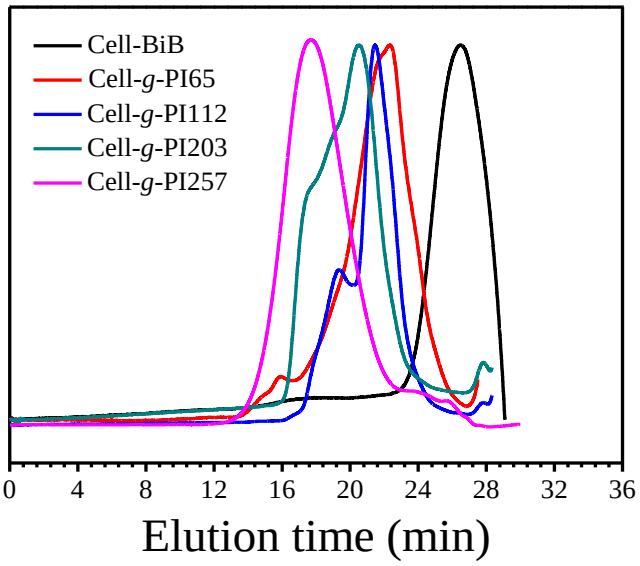

Fig. S1 GPC traces of Cell-BiB and Cell-*g*-PI copolymers.

Table S1. Molecular masses (M_n) and molecular mass distributions (M_w/M_n) for Cell-*g*-PI graft copolymers.

Sample code	M_n (g/mol)	M_w/M_n
Cell-*g*-PI65	170000	2.7
Cell-*g*-PI112	264000	3.9
Cell-*g*-PI203	371000	4.2
Cell-*g*-PI257	423000	3.2
Cell-BiB	18700	2.0

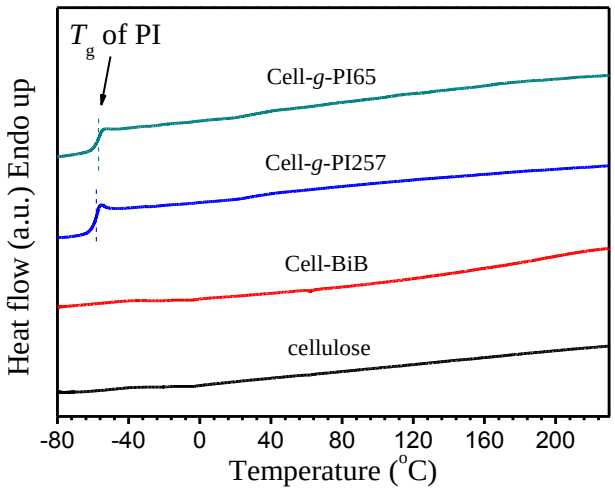

Fig. S2 DSC heat flow curves during the second heating scan for cellulose, Cell-BiB, Cell-*g*-PI257 and Cell-*g*-PI65. The heating rate was 10 °C/min.

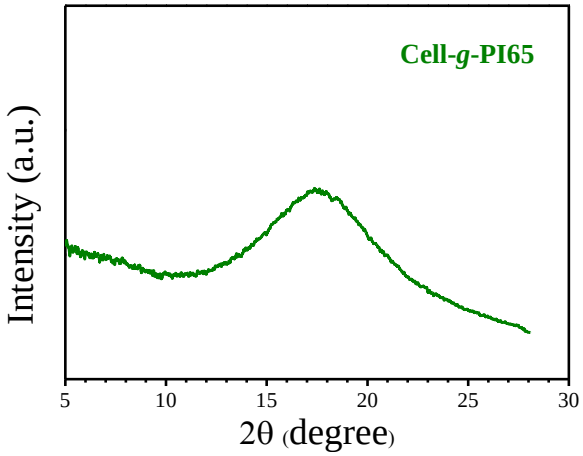

Fig. S3 1D WAXD intensity profile for Cell-*g*-PI65.

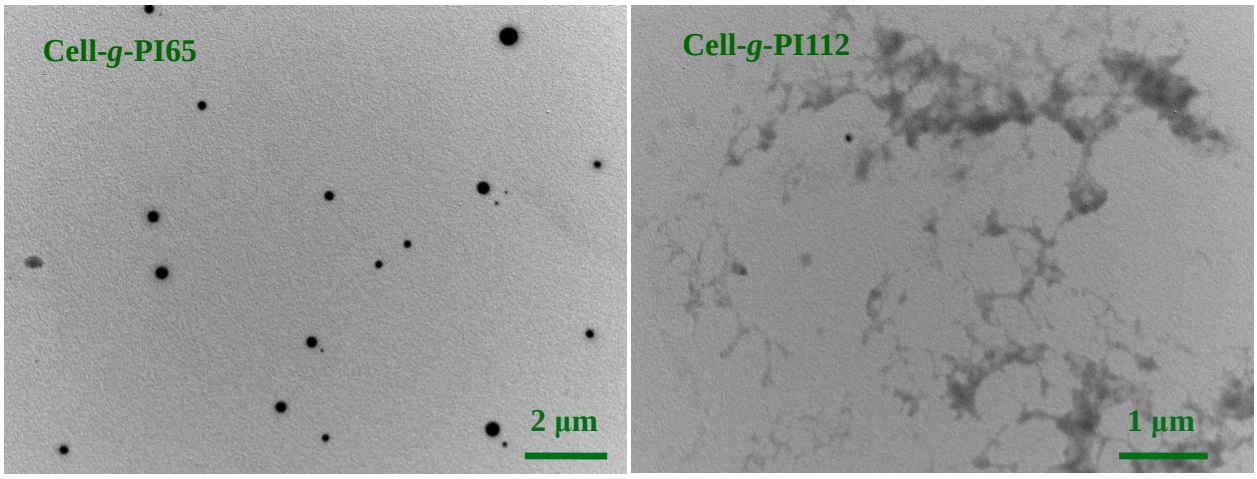

Fig. S4 TEM images of Cell-*g*-PI65 and Cell-*g*-PI112 prepared *via* the SORP method.