Electronic Supplementary Material (ESI) for Polymer Chemistry.

A solvent-less green synthetic route toward a sustainable bio-based elastomer: design, synthesis, and characterization of poly(dibutyl itaconate-*co*-butadiene)

Xinxin Zhou[a], Haijun Ji[a], Guo-Hua Hu[b], Runguo Wang[a,*], Liqun Zhang[a,*]

[a] Beijing Advanced Innovation Center for Soft Matter Science and Engineering & State Key Laboratory of Organic-Inorganic Composites & Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

[b] Laboratoire Réactions et Génie des Procédés (CNRS UMR 7274), CNRS-Université de Lorraine, ENSIC, 1 rue Grandville, BP 20451, 54001 Nancy, France.

[*] Corresponding authors:

Runguo Wang

E-mail: wangrg@mail.buct.edu.cn

Phone: 0086-13810675108

Liqun Zhang

E-mail: zhanglq@mail.buct.edu.cn

Phone: 0086-13910215964

S1 Recipe for polymerization of PDIB elastomers

Table S1 shows a recipe used for redox-initiated polymerization of dibutyl itaconate with butadiene to obtain PDIB elastomers.

Table S1. Recipe for redox-initiated emulsion polymerization of dibutyl itaconate with butadiene to obtain PDIB elastomers.

Ingredient	Dosage (g)	Remarks
Dibutyl itaconate	Variable [a]	96 wt.%
Butadiene	Variable [a]	94 wt.%
Deionized water	90.00	Homemade
Emulsifier solution	20.00	Prepared as below
Electrolyte solution	5.00	Prepared as below
Activator solution	3.75	Prepared as below
Deoxidant solution	2.00	Prepared as below
Initiator solution	3.00	Prepared as below
Hydroxylamine	3.00	Terminator, 50 wt.% solution in water

[a] The total dosage of the monomers was fixed at 60.00 g, as shown in Table S1.

Preparation of the emulsifier solution Disproportionated potassium rosinate (15 wt.% aqueous solution) and sodium soap (13 wt.% aqueous solution) were used to prepare a compound emulsifier in the polymerization of PDIB elastomers, aiming to obtain a good emulsifying effect. The compound emulsifier was prepared by transferring 300.0 g of disproportionated potassium rosinate and 360.0 g of sodium soap into a 1000 mL volumetric flask. Deionized water was added in to complete the volume.

Preparation of the electrolyte solution Phosphoric acid (85 wt.% in aqueous solution), potassium hydroxide, and EDTA (white solid powder) were used to prepare the electrolyte solution, aiming to reduce the critical micelle concentration of the emulsifier and latex viscosity, and stabilize the latex. The electrolyte solution was prepared by transferring 9.24 g of phosphoric acid, 11.88 g of potassium hydroxide, and 0.9 g of EDTA into a 250 mL volumetric flask. Deionized water was added in to complete the volume.

Preparation of the activator solution EDTA ferric sodium salt and SFS were used to prepare the activator solution. The redox-initiated system composed of an activator and an

initiator. The activator solution was prepared by dissolving 0.6 g of EDTA ferric sodium salt and 1.0 g of SFS in deionized water in a 250 mL volumetric flask.

Preparation of the deoxidant solution Sodium thiosulfate was used to prepare the deoxidant solution. Deoxidant was used to clear up residual oxygen in the polymerization system. The deoxidant solution was prepared by dissolving 2.64 g of sodium thiosulfate into 200 mL deionized water in a 250 mL sealed glass bottle in which the air was replaced by nitrogen.

Preparation of the initiator solution *p*-Menthane hydroperoxide was used to initiate the polymerization of PDIB elastomers. The initiator solution was prepared by dissolving 1.0 g of *p*-menthane hydroperoxide in dibutyl itaconate in a 100 mL volumetric flask.

Figure S1. A shaker-bottle polymerization device for PDIB elastomers. (a) Frontal view and (b) internal view.

S2 Synthesis of PDIB elastomers

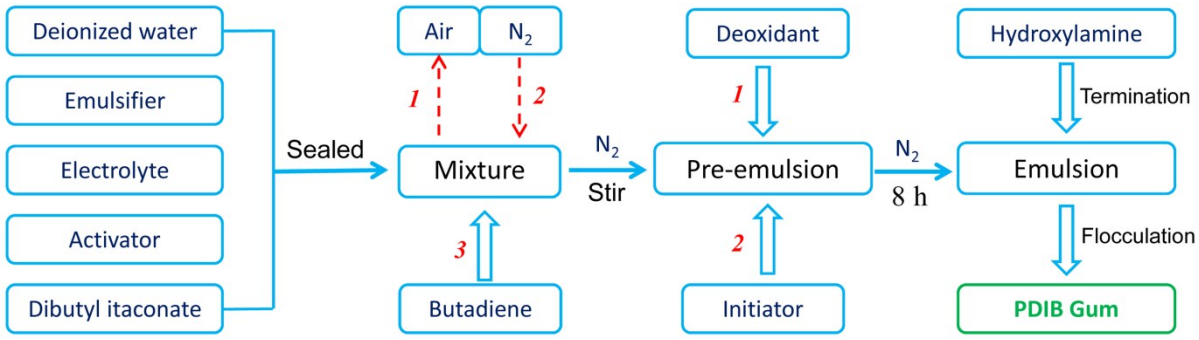


Figure S2. Flow chart of the polymerization process for PDIB elastomers.

Table S2. Feed compositions of the initiator and monomers for the polymerization of PDIB elastomers.

PDIB sample	Initiator (g)	Dibutyl itaconate (g)	Butadiene (g)
PDIB0 [a]	0.03	60	0
PDIB10	0.03	54	6
PDIB20	0.03	48	12
PDIB30	0.03	42	18
PDIB40	0.03	36	24
PDIB50	0.03	30	30
PDIB60	0.03	24	36
PDIB70	0.03	18	42
PDIB80	0.03	12	48
PDIB90	0.03	6	54
PDIB100	0.03	0	60

[a] The number represents the feed percentage content of butadiene in a polymerization.

Figure S3. Digital images of the flocculated PDIB with various butadiene contents.

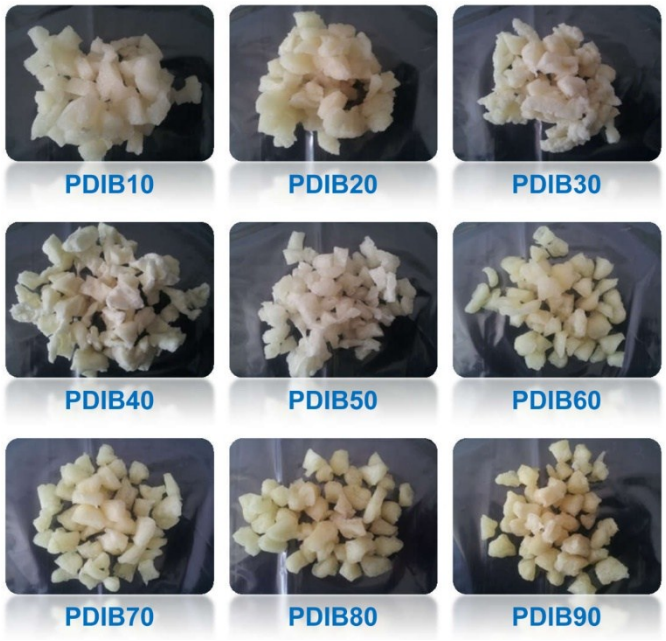


Figure S4. Digital images of PDIB copolymers with various butadiene contents.

S3 Results and discussion

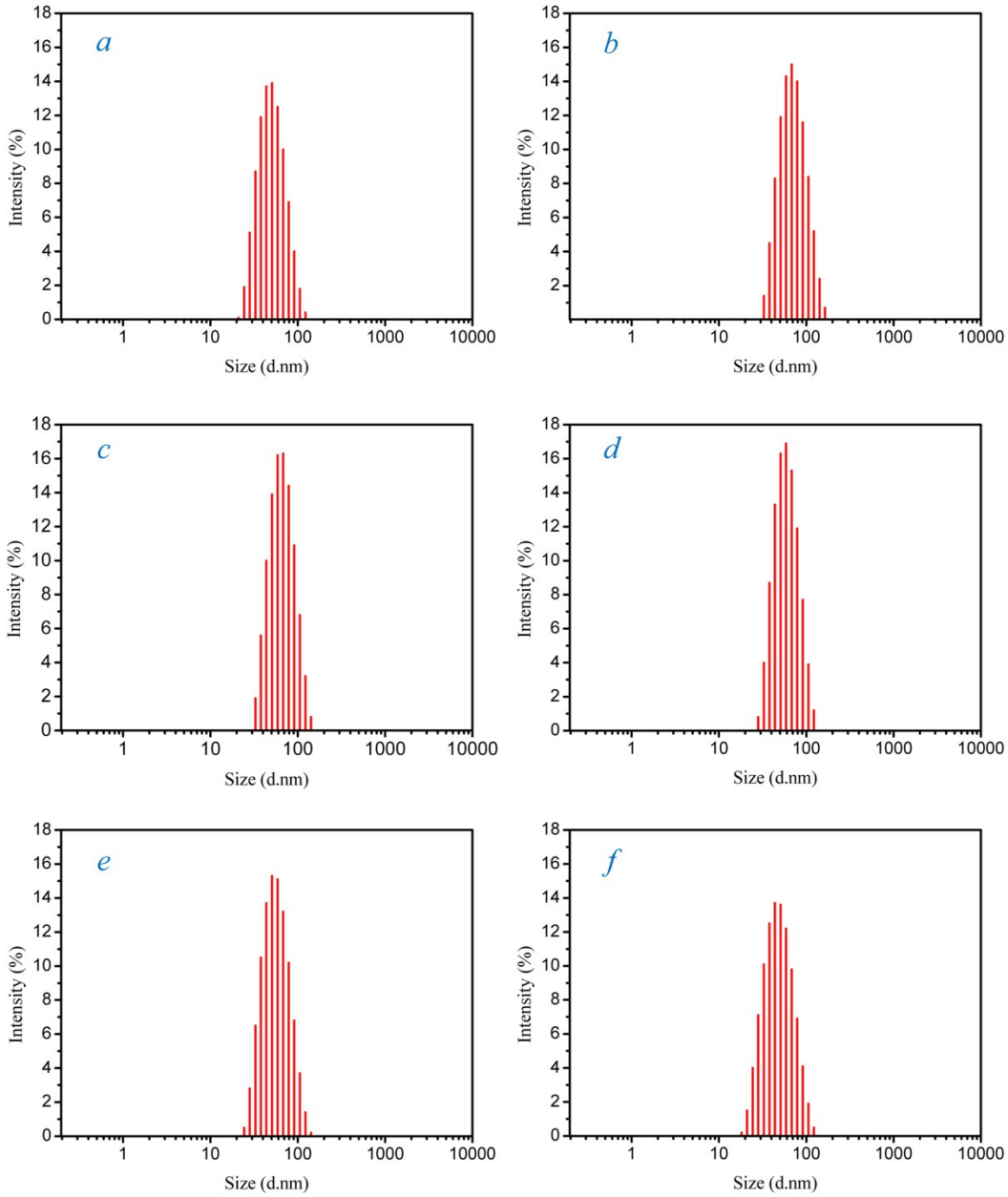


Figure S5. Size distributions of PDIB latex particles with small polydispersity indices (PdI): (*a*) PDIB0 latex (PdI: 0.198), (*b*) PDIB20 latex (PdI: 0.108), (*c*) PDIB40 latex (PdI: 0.115), (*d*) PDIB60 latex (PdI: 0.089), (*e*) PDIB80 latex (PdI: 0.185), and (*f*) PDIB100 latex (PdI: 0.303).

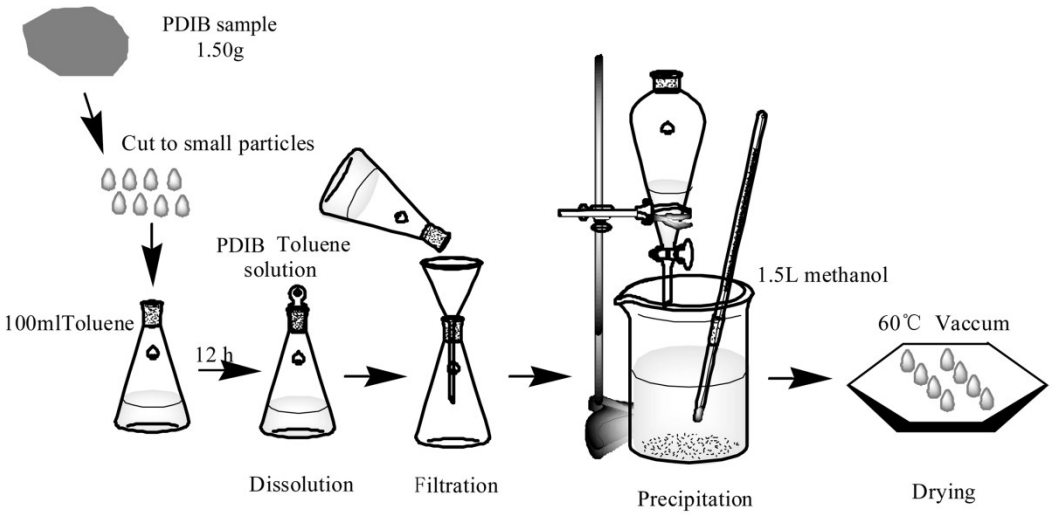


Figure S6. Purification process of PDIB by dissolution and precipitation.

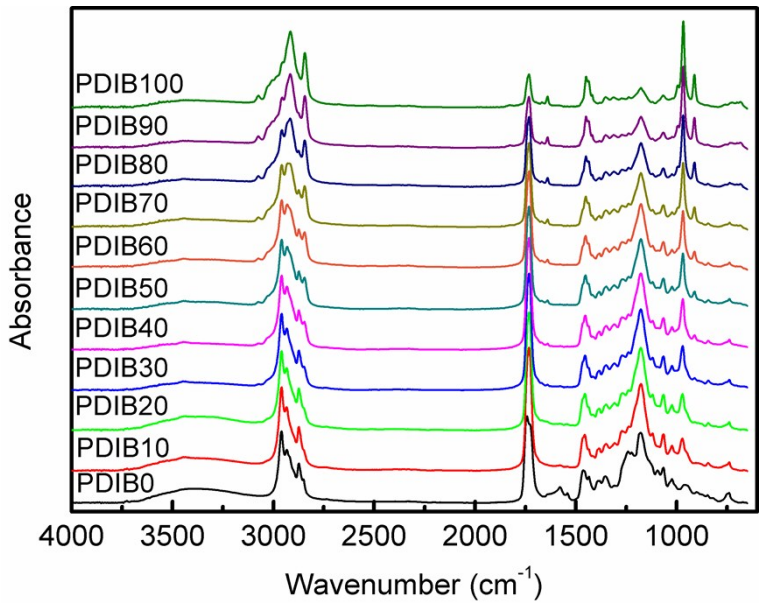


Figure S7. FTIR spectra of PDIB with various feed butadiene contents.

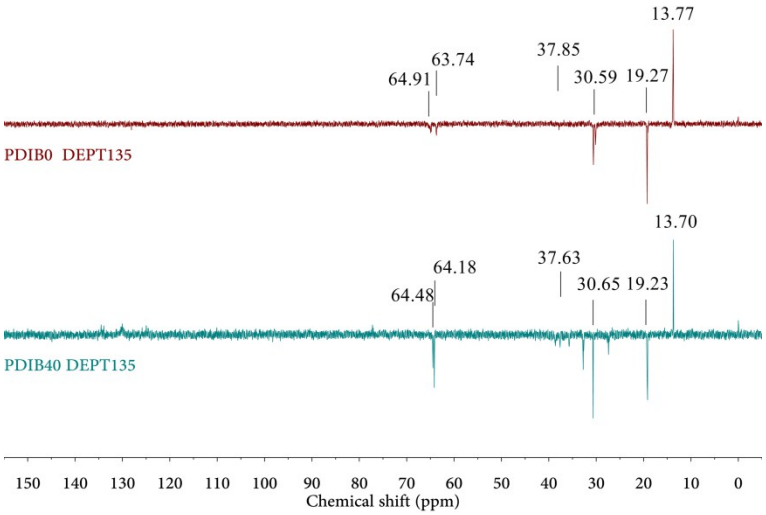


Figure S8. ^{13}C NMR spectra with DEPT135 of PDIB0 and PDIB40.

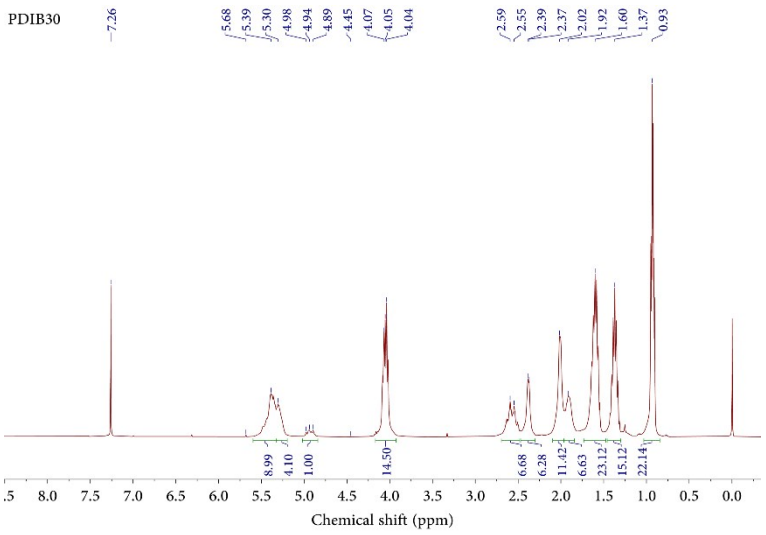


Figure S9. The integral ^{1}H NMR spectrum of PDIB30 (in $CDCl_3$).

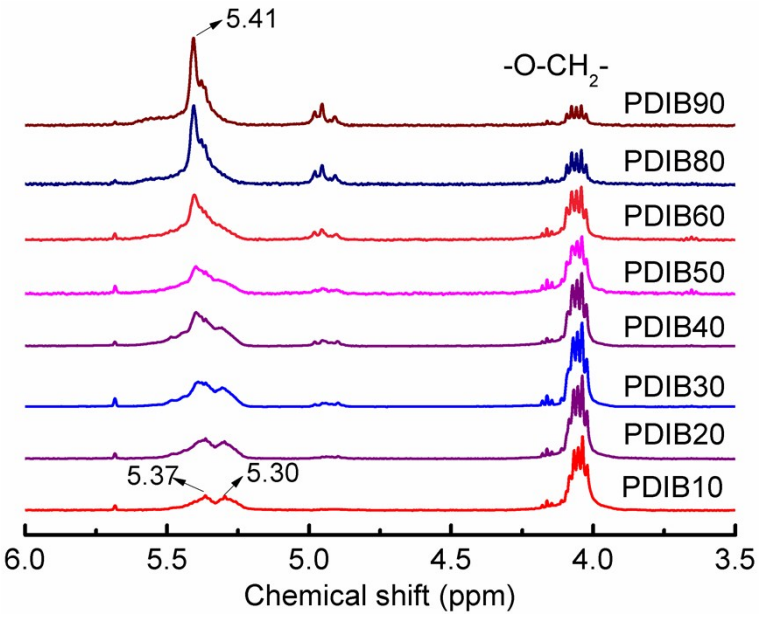
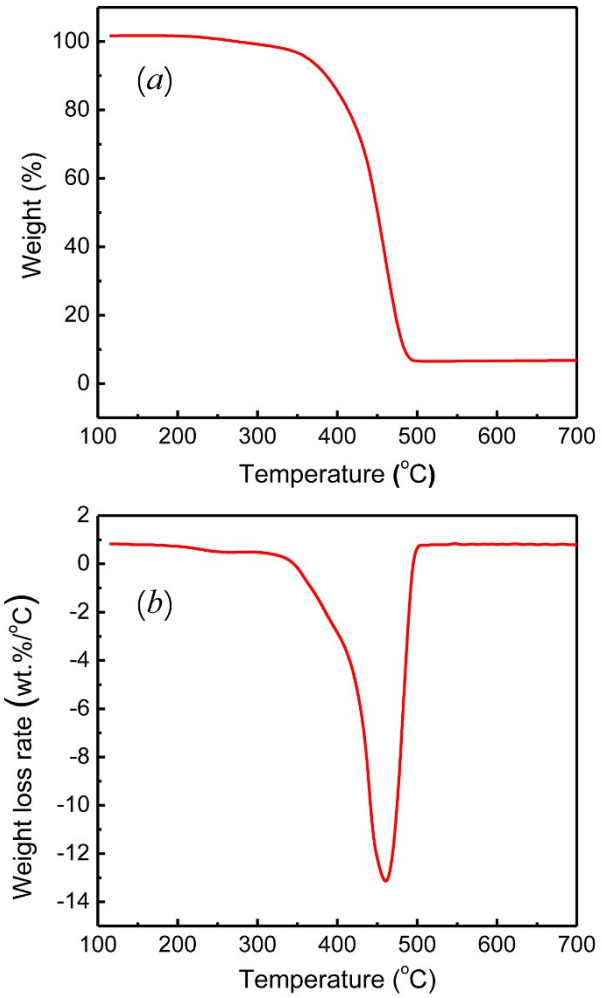


Figure S10. Expanded ^{1}H NMR spectra of PDIB (in $CDCl_3$).

Table S3. Percentages of itaconate and butadiene moieties in PDIB [a].

Sample	Molar percentages of itaconate moieties in PDIB (%)	Percentages of the different configurations of butadiene (total = 100%)			Mass ratio of itaconate moieties to butadiene ones in sample
		trans-configuration (%)	*cis*-configuration (%)	*vinyl*-configuration (%)	
PDIB10	51.92	55.77	43.25	1.98	4.84
PDIB20	42.43	60.68	34.99	4.33	3.30
PDIB30	33.97	63.80	29.09	7.10	2.31
PDIB40	29.11	68.08	23.29	8.63	1.84
PDIB50	32.64	69.33	22.49	8.19	2.17
PDIB60	22.56	74.11	15.51	10.40	1.31
PDIB70	29.49	77.33	11.16	11.50	1.87
PDIB80	11.30	80.01	6.92	13.07	0.57
PDIB90	7.12	84.35	Negligible	15.65	0.34

[a] Calculated from integral ^{1}H NMR spectra.



FigureS11. Non-isothermal TG curves (*a*) and DTG curves (*b*) for ESBR1502.

Table S4. Curing parameters for the neat PDIB elastomers.

Sample	Scorch time (min:s)	Curing time (min:s)	Torque increase (dNm)
PDIB20	2:54	7:18	11.51
PDIB30	4:28	8:51	9.44
PDIB40	2:09	3:59	17.13
PDIB50	1:58	3:38	17.56
PDIB60	1:45	3:38	18.48
PDIB70	1:41	4:05	17.80
PDIB80	2:00	10.13	11.09

Table S5. Mechanical properties of the cross-linked PDIB elastomers.

sample	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Hardness (Shore A)
PDIB20	0.58±0.05	414±34	4±2	21
PDIB30	0.80±0.10	427±25	4±1	25
PDIB40	1.60±0.08	487±41	5±1	35
PDIB50	2.17±0.23	484±16	3±1	36
PDIB60	1.78±0.11	747±32	2±2	37
PDIB70	2.03±0.15	640±38	3±1	42
PDIB80	1.77±0.21	795±57	4±2	46