

Supplementary information

High performance bio-based elastomers: energy efficient, sustainable materials for tires

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1) Materials and Methods

Chemicals. Itaconic acid (purity of 99%) was obtained from Shandong Qingdao Langyatai Group Co., Ltd. Methanol, ethanol, *n*-Propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol were purchased from Sigma-Aldrich Co.. Isoprene (purity of 95%) was purchased from Alfa Asear Co. and distilled to remove the stabilizing agent before use. Ferric ethylenediaminetetraacetic acid salt (Fe-EDTA), sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), sodium hydroxymethane sulfinate (SHS), tertbutyl hydroperoxide (TBH), potassium phosphate tribasic, potassium chloride, and hydroxylamine were purchased from Sigma-Aldrich Co. and used without further purification. Silane (VP Si 363) was purchased from Evonik Degussa Co. All other chemicals and materials were reagent-grade commercial products and were used as received without further purification.

Synthesis of di-*n*-alkyl itaconate. Into a 1-L, three-neck glass flask equipped with a condenser, a thermometer, a mechanical agitator, and a Dean-Stark decanter, 130.1 g of itaconic acid, different amounts of straight-chain mono alcohols (Table S1), and 39.0 g of cyclohexane were added. After the mixture was heated to 115-130 °C (except methanol, ethanol and *n*-propanol), 1.38 g of sulfuric acid was added as catalyst. The reaction was considered complete when the quantity of byproduct (e.g., water) reached about 36.0 ml. Because the low alcohols are soluble or partly soluble in water, which have the boiling point less than 100 °C, the reaction temperatures were lower than 100 °C, and more than 36 ml of byproduct were obtained. So these low alcohols (methanol and ethanol), the ingredients were added in an airtight kettle reactor to react at 100 °C. The mole quantity of straight-chain mono alcohols in the feed decreased as the alkyl chains increase in length, as shown in Table S1, because the boiling points increase as the alkyl chains increase in length. The products were washed by deionized water in a separating funnel and distilled in vacuum to obtain di-*n*-alkyl itaconates.

Table S1 Recipe for esterification of di-*n*-alkyl itaconates

Ingredients	Amount/g	Ingredients	Amount/g
methanol	224	<i>n</i> -hexanol	361
ethanol	276	<i>n</i> -heptanol	381

<i>n</i> -propanol	300	<i>n</i> -octanol	394
<i>n</i> -butanol	296	<i>n</i> -nonanol	399
<i>n</i> -pentanol	334	<i>n</i> -decanol	398

Synthesis of Poly(di-*n*-alkyl itaconate-co-isoprene) (PDAII). The polymerization reactor was a 500 ml, four-necked glass flask equipped with a reflux condenser, a sampling device, a nitrogen inlet, and a two-bladed anchor-type impeller. According to the recipe in Table S2, deionized water, SDS solution or SDBS solution, potassium phosphate tribasic solution, and potassium chloride solution, Fe-EDTA solution, and SHS solution were added into the flask under high-speed stirring (400 RPM). Subsequently, pre-blended di-*n*-alkyl itaconate and isoprene were added into the flask. The stable and homogeneous latex was obtained after 45 min of stirring. Later, TBH solution was injected into the flask, and the stirring speed reduced to 200 RPM. The polymerization was allowed to proceed at 20 °C for 12-24 h to form the target PDAII latex, and hydroxylamine solution was added to terminate the reaction. The PDAII latex was coagulated by using an excess of calcium chloride solution and washed with ethanol and deionized water alternately to remove the residual monomers and emulsifiers. The moist product was dried at 60 °C in vacuum until a constant weight was obtained.

Table S2 Recipe for redox-initiated emulsion polymerization of PDAII

Ingredients	Amount/g
di- <i>n</i> -alkyl itaconate	variable ^a
isoprene	27.3
deionized water	variable ^b
SDS solution (10%) ^c	5 wt. % of monomer
SDBS solution (10%) ^d	5 wt. % of monomer
K ₃ PO ₃ (10%)	2
KCl (10%)	5
SHS solution (10%)	2
Fe-EDTA solution (1%)	4
TBH solution (10%)	0.5
hydroxylamine solution (50%)	0.4

^aThe molar ratio of di-*n*-alkyl itaconate to isoprene was 2:3. ^b30 wt. % solid content of the latex compound. ^cSDS was used when the number of repeating (CH₂) unit on the side chain was 0, 1, 2, 3 and, ^dSDBS was used when the number of repeating (CH₂) unit on the side chain was 4, 5, 6, and 7. SDS: sodium dodecyl sulfonate. SDBS: sodium dodecyl benzene sulfonate. K₃PO₄: potassium phosphate. KCl: potassium chloride, SHS: sodium hydroxymethane sulfonate. Fe-EDTA: Ferric ethylenediaminetetraacetic acid. TBH: tertbutyl hydroperoxide.

Preparation of silica reinforced PDAII composites and silica reinforced PDBIB composites. PDAII elastomer (100 g) with the side chain length in the range from methyl to octyl was masticated in a 6 in. two-roll mill. The formulation and the mix procedure were listed in Table S3A and Table S3B, respectively. The resulting compound was cured in a XLB-D 350×350 hot press (Huzhou Eastmachinery Corporation, China) under 15 MPa at 150 °C for its optimum cure time as determined by a disk oscillating rheometer (P3555B2, Beijing Huanfeng Chemical Machinery Experimental Factory, China). The Silica/PDBIB compound formulation and mix procedure are the same with Silica/PDAII just replace PDAII by PDBIB.

Table S3A Silica/PDAII and silica/PDBIB compound formulation

Ingredients	Loading/phr
PDAII	100
silica	50
silane coupler (VP Si 363)	3.0

zinc oxide	5.0
stearic acid	0.5
antioxidant RD ^a	1.0
antioxidant 4020 ^b	1.0
accelerator CZ ^c	1.0
accelerator NS ^d	1.2
sulfur	1.0

^apoly(1,2-dihydro-2,2,4-trimethyl-quinoline)

^bN-1,3-dimethylbutyl-N'-phenyl-P-phenylenediamine

^cN-cyclohexyl-2-benzothiazole sulfenamide

^dN-tert-butylbenzothiazole-2-sulphenamide

Table S3B Mixing procedure of silica/PDAII and silica/PDBIB compound

<i>Stage I</i>	Two-roll mill
1	PDAII
2	antioxidant 4020 and antioxidant RD
3	1/2 silica, zinc oxide, stearic acid
4	1/2 silica, silane coupler
<i>Stage II</i>	Two-roll mill at 150
0	<i>batch stage I</i>
1	heat treatment at 150 °C, 5 min, stockpile 2 hours
<i>Stage III</i>	Two-roll mill
0	<i>batch stage II</i>
1	accelerators, sulfur
2	homogenization on two-roll mill

Preparation silica reinforced PDBII and silica reinforced PDBIB composites for green tire. Poly(*di-n*-butyl itaconate-*co*-isoprene) (PDBII) was mixed with polybutadiene (BR), colored with phthalocyanine to form silica/PDBII composites according to the formulation shown in Table S4A. The mixing procedure is shown in Table S4B. The silica/PDBIB40 compound formulation and mixing procedure are the same with silica/PDBII just replace PDBII by PDBIB40.

Table S4A Silica/PDBII and silica/PDBIB40 compound formulation

Ingredients	Loading/phr
PDBII	70.0
polybutadiene (BR 9000)	30.0
silica (833 MP)	50.0
silane coupler (VP Si 363)	7.0
zinc oxide	5.0
stearic acid	2.0
antioxidant 4020	1.0
antioxidant RD	1.0
wax	1.0
titanium oxide	3.0
phthalocyanine	3.0
accelerator CZ	1.0

accelerator NS	1.2
sulfur	1.5

Table S4B Mixing procedure of silica/PDBII and silica/PDBIB40 compound

<i>Stage I</i>	Two-roll mill
1	PDBII, BR
2	antioxidant 4020 and antioxidant RD
3	1/2 silica, zinc oxide, stearic acid
4	1/2 silica, silane coupler, wax
<i>Stage II</i>	Two-roll mill with heat equipment
0	<i>batch stage I</i>
1	heat treatment at 150 °C, 5 min, stockpile 2 hours
<i>Stage III</i>	Two-roll mill
0	<i>batch stage II</i>
1	titanium oxide, phthalocyanine
2	accelerators, sulfur
3	homogenization on two-roll mill

Table S5A Compound formulation of silica/SSBR green tire for comparison about energy dissipation

Ingredients	Loading/phr
SSBR ^a	55.0
SSBR (T2003)	30.0
polybutadiene (BR 9000)	30.0
Silica (833 MP)	50.0
carbon black (N375)	20.0
silane coupler (VP Si 363)	5.0
zinc oxide	3.0
stearic acid	2.0
antioxidant 4020	2.0
wax	1.5
accelerator NS	1.8
accelerator TMTD ^b	0.3
sulfur	2.3

^a37.5 phr oil extended

^bbis(dimethylthiocarbamoyl)disulfide

Table S5B Mixing procedure of silica/SSBR green tire

<i>Stage I</i>	Two-roll mill
1	SSBR, BR
2	antioxidant 4020
3	1/2 silica, zinc oxide, stearic acid
4	1/2 silica, silane coupler, wax
<i>Stage II</i>	Two-roll mill with heat equipment
0	<i>batch stage I</i>

1	heat treatment at 150 °C, 5 min, stockpile 2 hours
<i>Stage III</i>	Two-roll mill
0	<i>batch stage II</i>
1	carbon black
2	accelerators, sulfur
3	homogenization on two-roll mill

Table S6A Compound formulation of carbon black/ESBR tire for comparison about energy dissipation

Ingredients	Loading/phr
ESBR1502	100.0
zinc oxide	5.0
stearic acid	2.0
carbon black (N234)	50.0
antioxidant 4020	2.0
wax	1.5
aromatic naphtha	15.0
accelerator CZ	1.2
sulfur	2.0

Table S6B Mixing procedure of Carbon black/ESBR tire

<i>Stage I</i>	Two-roll mill
1	ESBR 1502
2	antioxidant 4020
3	1/2 carbon black, zinc oxide, stearic acid
4	1/2 carbon black, aromatic naphtha, wax
<i>Stage II</i>	Two-roll mill
0	<i>batch stage I</i>
2	accelerator CZ, sulfur
3	homogenization on two-roll mill

Chemical and thermal properties measurements. The molecular weights of PDAII and PDBIB were determined by gel permeation chromatography on a Waters Breeze instrument equipped with three water columns (Styragel HT3_HT5_HT6E) with tetrahydrofuran as the eluent (1 ml/min) and a Waters 2410 refractive index detector. A polystyrene standard was used for calibration. ¹H NMR spectroscopy measurements of PDAII and PDBIB were carried out on a Bruker AV400 spectrometer. The solvent was CDCl₃ containing traces of tetramethylsilane used as an internal reference. Differential scanning calorimetry measurements of PDAII and PDBIB were performed on a Mettler-Toledo differential scanning calorimeter. The samples were heated to 150 °C, maintained there for 3 min, and then cooled to -100 °C. Both the heating rate and cooling rate were 10 °C/min. All the gel content test samples were extracted in a 2 L glass reactor for 7 h with tetrahydrofuran under reflux. After the extraction, these samples were dried, and the gel content was calculated as the ratio of the weight of the dried polymer to its initial weight.

Positron annihilation lifetime spectroscopy (PALS) results were recorded at room temperature by using a fast-fast coincidence system with a time resolution of about 270 ps. A ²⁰Na/²²Na position source was sandwiched between two pieces of the same samples. Each spectrum contained approximately 1 million and 4 million counts for PATFIT³¹ and MELT³²⁻³⁵, respectively. All the measured spectra were resolved into three components by using PATFIT for discrete analysis. The third lifetime component τ_3 ($\tau_3 = 1.4 - 2.6$ ns) results from the pick-off annihilation

of o-Ps in the free volume holes. The o-Ps lifetime is related to the radius of the free volume hole by the following equation:³⁶

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1} \quad (1)$$

where R is the radius of the free volume hole and $\Delta R = 1.656A$ is obtained by fitting the observed o-Ps lifetimes for molecular solids with known hole sizes. The average free volume size was calculated by using

$$V = \frac{4\pi R^3}{3} \quad (2)$$

The relative fractional free volume f is calculated by using

$$f = (4/3)\pi R^3 I_3 \quad (3)$$

Where I_3 is the relative intensity of the longest lived component (τ_3).

Physical and mechanical properties characterization

Tensile tests of the cured silica/PDAII and silica/PDBIB nanocomposites were conducted according to ASTM D412 (dumbbell-shaped) on a LRX Plus tensile tester made by Lloyd Instruments, Ltd., UK. The internal friction loss ($\tan \delta$) as a function of temperature was measured by a DMTA dynamic mechanical thermal analyzer (Rheometrics Scientific Inc., United States) in the rectangular tension mode. The measurements were carried out at a constant frequency of 10 Hz, a heating rate of 3 °C/min, and an oscillating strain amplitude of 0.1% in the temperature range of -80 to 100 °C. Each sample was 30 mm in length, 10 mm in width, and 2 mm in thickness. The glass transition temperature value was taken to be the maximum of the $\tan \delta$ versus temperature curve. The NMR transverse magnetization relaxation (T_2) experiments for the vulcanizates were performed on a XLDS-15 solid-state low-field NMR spectrometer (IIC Innovative Imaging Corp. KG, Germany). The measurement temperature was 80±0.1 °C. The signal decay data of transverse relaxation were fitted by a nonlinear Marquardt-Levenberg algorithm in the IIC Analysis software package.³⁷

Strain sweep experiments (storage modulus (G') and loss factor ($\tan \delta$) as a function of scanning strain) were performed on vulcanizates by a RPA2000 rubber process analyzer (Alpha Technologies Corporation, Akron, Ohio, United States) at 60 °C. The strain amplitude (ϵ %) was varied from 0.28 to 42% and the frequency was 1 Hz. Shore A hardness, was measured according to ASTM D2240 by an XY-1 rubber hardness apparatus (4th Chemical Industry Machine Factory, Shanghai, China). Power loss was performed on vulcanizates by a RSS-II Rolling Test Apparatus (Beijing Rubberinfo Co. Ltd., Beijing, China) at a measure load of 30 kg and 1200 RPM. Sample external diameter is 120 mm, sample inner diameter is 63.5 mm, and sample width is 19 mm. In the Akron abrader (GT-7012-A, Gotech Testing Machines Co. Ltd., Taiwan), the contour of the circular test specimen, mounted on a motor-driven spindle, was brought into contact with the periphery of an abrasive wheel (150 × 38 mm, abrasive media: 36# grit wheel), which was mounted on another spindle. Rotation of the specimen causes the abrasive wheel to rotate and the two were held together under a force of 2.72 kgf. The axis of the specimen and the axis of the abrasive wheel were at an angle of 15°, which causes a rubbing action. The weight loss was recorded after a specified number of revolutions (1.61 km, 3418 revolutions) of the abrasive wheel. The specimen was first abraded by 800 revolutions before the Akron abrasion measurement. The abrasion resistance of the specimen was calculated from its volume loss according to the weight loss and tread density. The testing temperature was 23 ± 2 °C.

2) The structures of di-*n*-alkyl itaconates

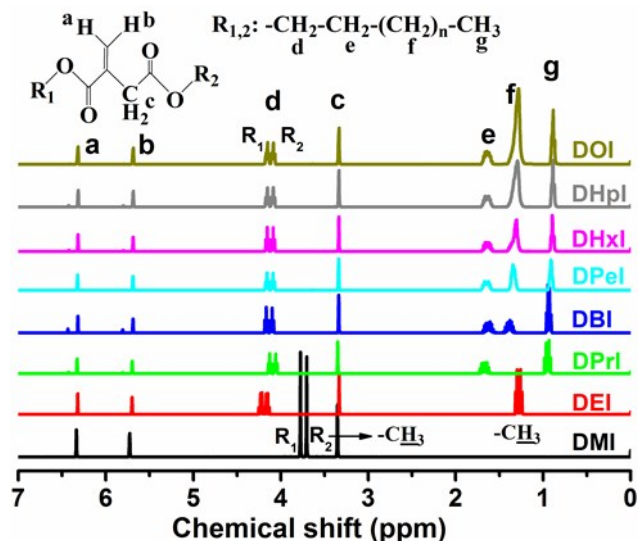


Figure S1 ^1H NMR spectra of di-*n*-alkyl itaconates (DAIs) are displayed vertically for clarity. DAI samples full name and abbreviations: dimethyl itaconate (DMI), diethyl itaconate (DEI), di-*n*-propyl itaconate (DPrI), di-*n*-butyl itaconate (DBI), di-*n*-pentyl itaconate (DPel), di-*n*-hexyl itaconate (DHxI), di-*n*-heptyl itaconate (DHpl), di-*n*-octyl itaconate (DOI).

Fig. S1 shows the ^1H NMR spectra and general formula of di-*n*-alkyl itaconates obtained by the esterification reaction. Peaks a, b and c clearly appear at the same chemical shift position in all curves because every hydrogen atom has almost the same chemical environment before and after esterification. As the deshielding effect from carboxyl groups decreasing for the methylene number increasing, the chemical shifts of $-\text{CH}_3$ at the end of alkyl chain move towards to high field. And the intensity of peak f increases obviously from di-*n*-butyl itaconate to di-*n*-octyl itaconate for the methylene number increasing. The carboxyl group signal was not detected.

3) Poly(di-*n*-alkyl itaconates-*co*-isoprene) (PDAlI) product and its properties

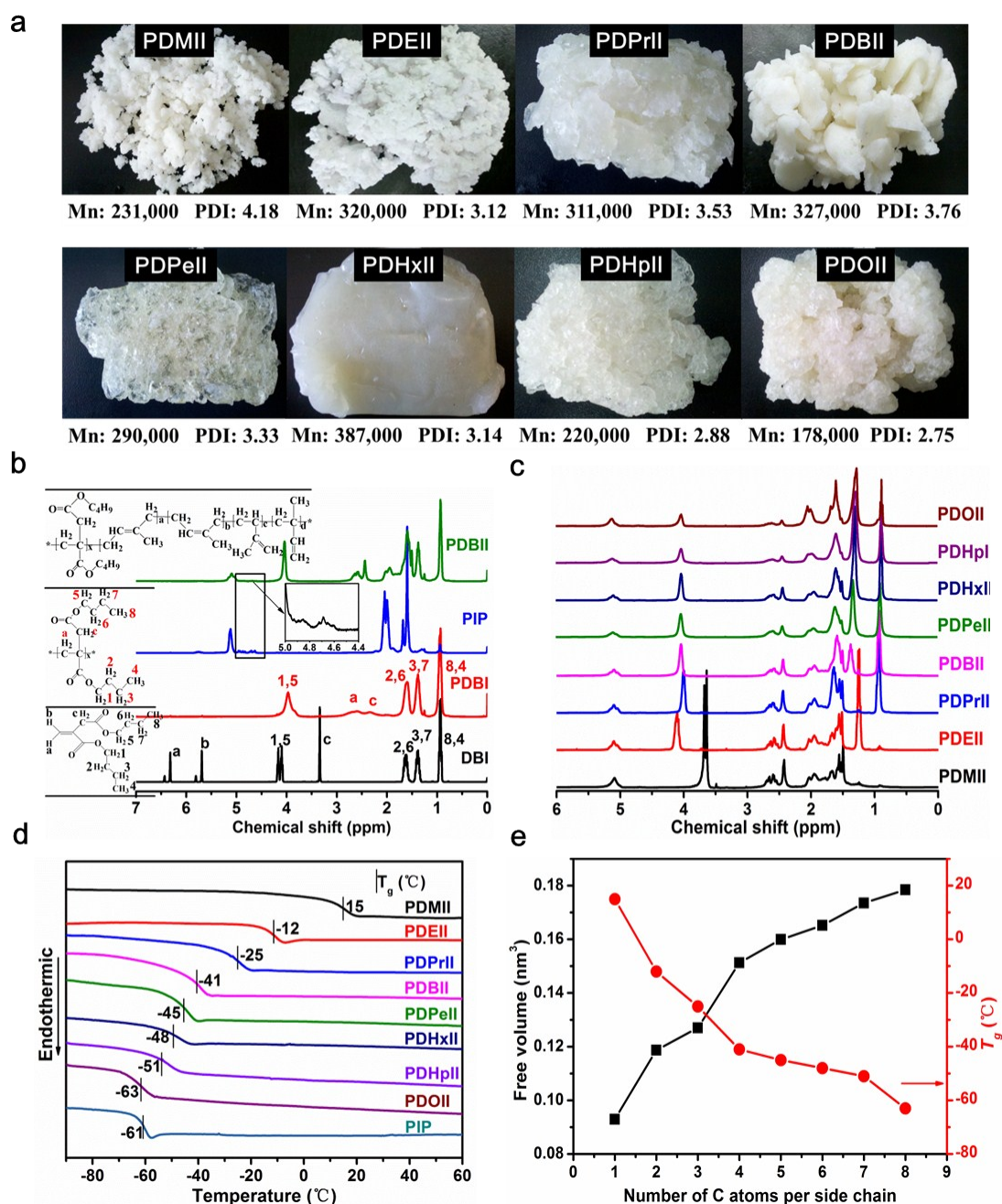


Figure S2 PDAII sample images, structures and characterization. (a) Images of various PDAII samples. The corresponding number-average molecular weight (M_n) and polydispersity index (PDI) are listed below each image. ^1H NMR spectra of (b) DBI, PDBI, PIP, PDBII and (c) PDAII. (d) Differential scanning calorimetry thermograms for PDAII and (e) variations of glass transition temperature and free volume with different number of carbon atoms on ester side chains of PDAII. The full name and abbreviations of PDAII samples: poly(dimethyl itaconate-*co*-isoprene) (PDMII), poly(diethyl itaconate-*co*-isoprene) (PDEII), poly(di-*n*-propyl itaconate-*co*-isoprene) (PDPrII), poly(di-*n*-butyl itaconate-*co*-isoprene) (PDBII), poly(di-*n*-pentyl itaconate-*co*-isoprene) (PDPeII), poly(di-*n*-hexyl itaconate-*co*-isoprene) (PDHxII), poly(di-*n*-heptyl itaconate-*co*-isoprene) (PDHpII), poly(di-*n*-octyl itaconate-*co*-isoprene) (PDOII), di-*n*-butyl itaconate (DBI), poly(di-*n*-butyl itaconate) (PDBI), and polyisoprene (PIP).

The digital images of various PDAII elastomers are shown in Fig. S2a, and the PDAII elastomers are designated by the corresponding abbreviations. Gel permeation chromatography results indicate that the molecular weights of all the PDAII samples are above 150 000—as high as conventional elastomers³⁸ and sufficiently large to ensure mechanical and elastic properties. ^1H NMR was used to characterize the polymeric structures with targeted chemical formula of

poly(di-*n*-butyl itaconate-*co*-isoprene) (PDBII), polyisoprene (PIP), poly(di-*n*-butyl itaconate) (PDBI) and di-*n*-butyl itaconate (Fig. S2b). The PDBI and PIP were also synthesized via redox emulsion polymerization to determine the structure of PDBII. The chemical shift peaks of di-*n*-butyl itaconate in PDBI are broadened because every hydrogen atom has a complex chemical environment especially on the main chain after polymerization. In the redox emulsion polymerization, isoprene can be polymerized into four types of isomeric units: *cis*-1,4-, *trans*-1,4-, 3,4-, and 1,2-units³⁹. As Fig. S2b illustrates, the chemical shift of PDBII can be easily assigned according the ¹H NMR spectra curves of PDBI and PIP. The 1,2- and 3,4-units can be detected in the enlarged region between 4.4 and 5.0 ppm. Weak peaks from 4.60 to 4.75 ppm and from 4.80 to 4.95 ppm are attributed to the =CH₂ groups of 3,4 addition and 1,2 addition, respectively. ¹H NMR spectra of PDAII with side chains from methyl to octyl are shown in Fig. S2c. The compositions listed in Table S7 were obtained by integration of the area under the peak of the methyl groups on itaconate side chain and olefinic protons in isoprene unit (Fig. S2c). The ratio of peak areas under each spectrum agrees well with the monomer proportion in the feed. Table S7 also shows that the gel contents increase slightly as the number of side chain carbon atoms increase mainly because of the micro-cross-linking between the macromolecular chains.

Thermal properties such as crystallization and glass transition temperatures are vital for determining whether a material is an elastomer at the end-use temperature. The thermograms of the PDAII samples show that these samples are completely amorphous (Fig. S2d). The *T_g*s of PDAII samples decreases with increasing side chain lengths because the side chains act as a uniformly distributed plasticizer and the polar effect of the dual ester groups on the end carbons decrease as the side chain length increases. The effect of side groups on the free volume of PDAII elastomers was measured by positron annihilation lifetime spectroscopy. The fractional free volumes and radius of free volume holes for the eight PDAII samples increased as side chain length increase because the flexible side chains reduce the packing density of the main chains. (Table S8). It is clear that the free volumes of PDAIIs increase with side chain length increasing can be divided into two stages (Fig. S2e). The increase in free volume is rapid from *n* = 0 to 3, but slows down as *n* exceeds 4. Because the polarity of the ester groups strongly restricts the mobility of the main chains relative to the short side chains. But the polarity was weakened by the long side chains, and the rate of free volume increase reduced with side chain length increasing. The polarity exerts great influence upon viscoelastic properties and further impacts on roll-resistance of tires.

Table S7 Compositions and gel contents of PDAII

PDAII	Isoprene content/%		Itaconate Content/%	Gel content/%
	1,4-units	3,4- and 1,2-units		
PDMII	55.9	0.5	43.6	0
PDEII	56.6	0.6	42.8	0
PDPrII	56.8	0.5	42.6	0.4
PDBII	56.5	0.4	43.1	0.9
PDPeII	56.4	0.1	43.5	1.3
PDHxII	56.7	0.2	43.1	1.3
PDHpII	60.0	0.2	39.8	2.1
PDOII	72.6	1.4	26.1	4.5

Table S8 Lifetime and intensity of positron annihilation of PDAIIs. The radius, the free volume and the relative fractional free volume are also listed.

PDAII	τ_3 /ns	I_3 /%	Radius/nm	Volume/nm ³	$I_3 \cdot \text{Volume}/\text{nm}^3$
PDMII	1.96±0.015	14.2±0.18	0.281	0.0929	0.00132
PDEII	2.23±0.015	14.1±0.14	0.305	0.118	0.00167
PDPrII	2.31±0.015	14.1±0.14	0.312	0.127	0.00179
PDBII	2.55±0.016	14.4±0.13	0.331	0.151	0.00218
PDPeII	2.63±0.017	14.0±0.12	0.337	0.160	0.00225

PDHxII	2.68±0.017	13.8±0.12	0.340	0.165	0.00229
PDHpII	2.76±0.017	13.9±0.12	0.346	0.174	0.00241
PDOII	2.80±0.018	13.9±0.12	0.349	0.178	0.00248

I_3 : the relative intensities of the longest lived component

4) The properties of poly(di-*n*-butyl itaconate-*co*-butadiene) (PDBIB)

Table S9 Molecular weight, T_g , gel content of PDBIB

samples	DBI/g	Bd/g	$M_n/10^4$	M_w/M_n	$T_g/^\circ\text{C}$	Gel/%
PDBIB20	80	20	31.4	3.23	-44	2
PDBIB30	70	30	36.8	3.76	-48	3
PDBIB40	60	40	39.2	3.81	-52	5
PDBIB50	50	50	35.3	4.12	-55	6
PDBIB60	40	60	33.7	3.96	-58	8
PDBIB70	30	70	34.5	4.32	-63	11
PDBIB80	20	80	32.6	4.29	-68	15

Di-*n*-butyl itaconate (DBI), butadiene (Bd), number-average molecular weight (M_n), weight-average molecular weight (M_w), glass transition temperature (T_g), gel content (Gel).

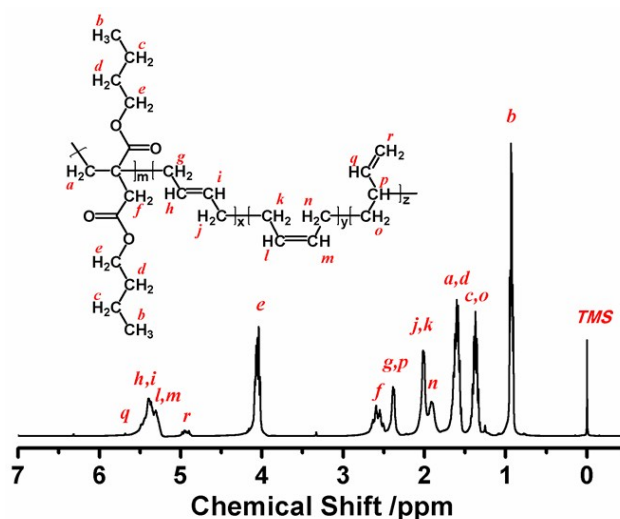


Figure S3 ^1H NMR spectrum of PDBIB40

The chemical structures and compositions of the poly(di-*n*-butyl itaconate-*co*-butadiene) (PDBIB) were evaluated by using ^1H NMR spectroscopy. An example illustrating this evaluation is shown in Fig. S3, which shows the spectrum of the PDBIB40 with the assignment for all proton signals. The sharp signal at δ 0.93 ppm corresponds to the protons of methyl groups (*b*) in the di-*n*-butyl itaconate units. The signals from olefinic protons of *cis*-1,4 unit (*l* and *m*) and *trans*-1,4 (*h* and *i*) were observed at δ 5.31 and δ 5.39 ppm, respectively. The peaks at 4.88-4.98 and 5.68 ppm originate from the olefinic protons of 1, 2-addition units (*r* and *q*), demonstrating the introduction of pendent olefinic groups to the PDBIB macromolecular chains. The peaks at δ 1.37, δ 2.39, δ 2.5-2.7 and δ 4.04 ppm are assigned to the protons of the methylene groups in the PDBIB macromolecular chains. Additionally, the percentage compositions of PDBIB were calculated from the relative peak areas of the protons of each unit in the ^1H NMR spectra. We find that the molar ratio of *trans*-1,4 units to *cis*-1,4 units increases with the increase of butadiene content.

Molecular weight is an important property for the mechanical properties of elastomer. In practical applications, polymer chain length is the key determinant of mechanical properties. The

gel permeation chromatography results of PDBIB with butadiene feed from 20 wt% to 80 wt% were summarized in Table S9. With increase of butadiene content, the number-average molecular weight of the PDBIB copolymer vary between 314, 000 g/mol and 392, 000 g/mol and reaches a maximum at 40 wt%. The polydispersity index increase with the butadiene content because the increase of chain transfer effect increases the number of branch structures. Furthermore, the glass transition temperature (T_g) keeps on decreasing with the increase of butadiene units because the butadiene structure confers the high flexibility to the polymer chains. The gel content of PDBIB increases with butadiene content as a result of the micro-cross-linking between the macromolecular chains due to the existence of double bonds.

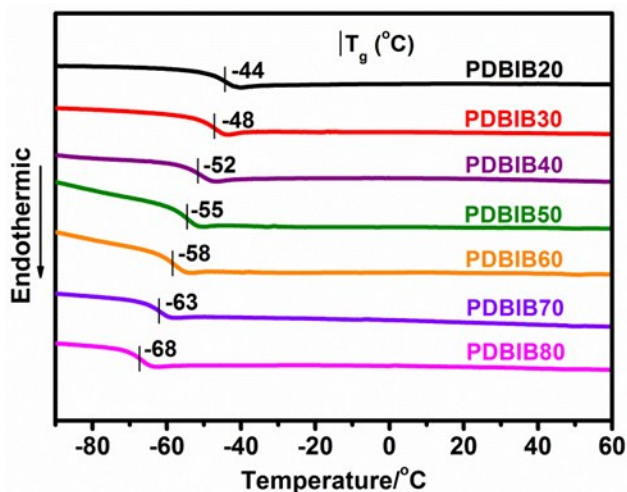


Figure S4 Differential scanning calorimetry thermograms of PDBIB with butadiene content from 20% to 80%.

Thermal properties such as crystallization and T_g are critical for elastomers because a crystalline polymer is not elastic. Fig. S4 indicate a completely amorphous structure of PDBIB. The T_g of PDBIB copolymers was lower than that of many industrial synthetic rubbers, indicating that PDBIB chains possessed excellent internal rotation capacity and high elasticity at ambient temperatures. The tensile strength and elongation at break of the silica/PDBIB are all above 17 MPa and 500%, respectively, except those of silica/PDBIB20. The moduli at 100% and 300% and the permanent set are shown in Table S10b. The mechanical properties of silica/PDBIB can meet the most requirements of engineering applications.

5) Mechanical properties of silica filled PDAII and silica filled PDBIB

Table S10 Mechanical properties of silica filled PDAII and silica filled PDBIB

Items	Modulus at 100% strain/MPa	Modulus at 300% strain /MPa	Tensile strength /MPa	Elongation at break /%	Permanent set /%	Shore A hardness
a) Mechanical properties of silica/PDAII						
Si-PDMII	2.4	-	2.8	226	40	96
Si-PDEII	1.9	4.8	9.3	558	24	71
Si-PDPrII	4.3	8.8	8.9	312	12	83
Si-PDBII	1.9	7.4	12.3	437	8	76
Si-PDPeII	2.7	9.0	11.6	404	24	70
Si-PDHxII	3.3	9.8	9.9	311	14	75
Si-PDHpII	2.9	-	7.6	241	10	72
Si-PDOII	2.5	-	5.6	203	8	61
b) Mechanical properties of silica/PDBIB						
Si-PDBIB20	1.66	7.5	12.7	492	40	68

Si-PDBIB30	1.70	8.8	17.4	509	32	68
Si-PDBIB40	1.15	6.1	18.6	590	16	59
Si-PDBIB50	1.38	6.4	21.2	640	16	65
Si-PDBIB60	1.46	6.5	23.6	643	16	65
Si-PDBIB70	1.25	4.3	25.0	774	16	71
Si-PDBIB80	2.36	9.3	24.8	545	10	71

Si-PDAII represent for 50 phr silica filled PDAII, Si-PDBIB represent for 50 phr silica filled PDBIB and the number after Si-PDBIB represent for butadiene content in the feed.

6) Silica/PDBIB green tire manufacture and roll-resistance test.

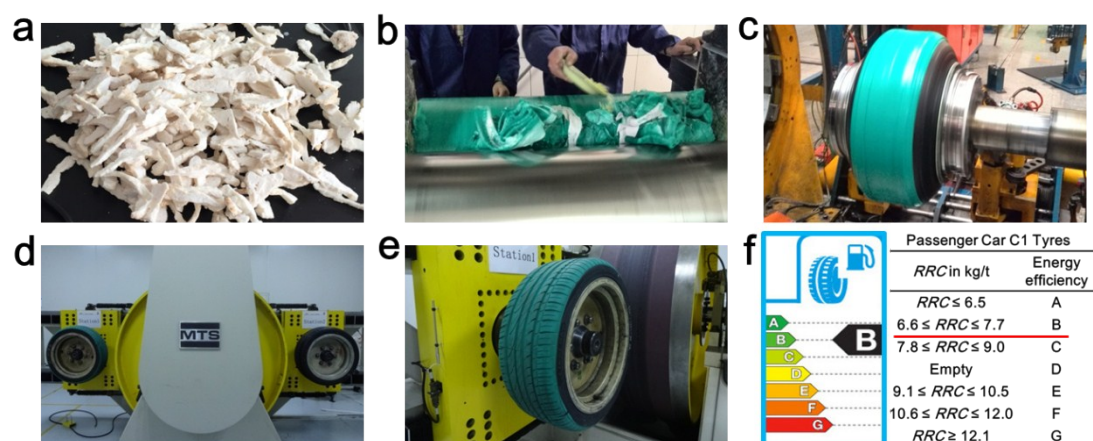


Figure S5 Photographs of fabrication and roll-resistance test of silica/PDBIB green tire. (a), Unfilled elastomer. (b), Mixing silica and other ingredients under industry scale two roll mill. c, Tire assembling. d and e, Tire roll-resistance test. (f), EU Tyre Labeling Regulation 1222/2009, roll-resistance grading of bio-based green tire.

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