–Supporting Information–

Remarkable Untangled Dynamics behavior of Multicyclic Branched Polystyrenes

Xiaoqiang Xue,[a] Yangjing Chen,[a]   Yongfang Li, [a] Kang Liang,[a] Wenyan Huang,[a] Hongjun Yang,[a] Li Jiang,[a] Qimin Jiang,[a] Fangli Chen,[a] Tao Jiang,[a] Binzhe Lin[a], Bibiao Jiang,*[a,c,d]   Hongting Pu,*[b]

[a] Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of

Materials Science and Engineering, Jiangsu Collaborative Innovation Center of

Photovolatic Science and Engineering, Changzhou University, Changzhou, Jiangsu,

213164, People's Republic of China.

[b] School of Materials Science and Engineering, Tongji University, Shanghai 201804,
China

[c] Changzhou University Huaide College, Jingjiang, Jiangsu, 214500, People's
Republic of China

[d] National Experimental Demonstration Center for Materials Science and Engineering

(Changzhou University), Changzhou, Jiangsu, 213164, People's Republic of China

Corresponding author. Tel.: 8651986330328 (B. B. Jiang); 8602169580143 (H.T. Pu)

E-mail: jiangbibiao@cczu.edu.cn (B. B. Jiang); puhongting@tongji.edu.cn (H.T. Pu)

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Materials

Styrene (analytical reagent, Shanghai Chemical Reagent Co. Ltd., Shanghai, China), tetrahydrofuran (Jiangsu Functional Chemistry Co. Ltd., China), dichloromethane (Jiangsu Functional Chemistry Co. Ltd., China) and toluene (Jiangsu Functional Chemistry Co. Ltd., China) were dried over CaH_2 and distilled prior to use; CuBr (96%, Shanghai Reagent Factory, China) was purified by stirring with glacial acetic acid followed by filtering and washing the resulting solid with ethanol; 2, 2'-Bipyridine (bpy, 99%, Shanghai Reagent Factory, China), *tert*-Butyl 2-bromoisobutyrate (*t*-BBiB, 99%, Shanghai Reagent Factory, China), nanosized Cu powder (99.9%, 10-30 nm, Aladdin Chemistry, China), 2-hydroxyethyl methacrylate and α-bromoisobutyryl bromide (analytically pure, Chinese Academy of Medical Sciences) were used as received. Other reagents were commercialized chemicals and used directly unless otherwise noted. Tris-[2(dimethylamino)ethyl]amine (Me$_6$TREN) was synthesized according to the report.[1]

Experimental Section

Synthesis of 2-(2-bromoisobutyryloxy)ethyl Methacrylate (BiBEM).

As showed in Scheme S1, a 250 mL round bottom flask was added 2-hydroxyethyl methacrylate (0.5 mol, 6.5 g), pyridine (3.5 g, 0.04 mol) and CH_2Cl_2 (30 mL), then the solution was stirred in ice bath. 2-Bromoisobutyryl bromide (4.95 mL, 0.04 mol) diluted in dry CH_2Cl_2 (30 mL) was then added to the cool stirred mixture dropwise and the resultant mixture was vigorously stirred for additional 5 h at 0-5°C after addition. The mixture was filtered, then filtrate was dissolved in hydrochloric acid solution, washed with 5% Na_2CO_3 aqueous solution, and deionized water three times. The organic phase was dried with anhydrous $MgSO_4$. After the removal of solvent under reduced pressure, the colorless product was obtained (yield: 5.1 g, 78.5%). The purity is above 96% (HPLC, Waters 515). ^{1}H-NMR (400 MHz, CDCl$_3$, Figure S1), δ (TMS, ppm): 6.10-6.20 (a, 1H, -CH=C), 6.10-6.20 (b, 1H, -C=CH), 4.40-4.43 (c, 4H, -CH$_2$-), 1.93 (d, 9H, -CH$_3$).

Synthesis of Branched Polystyrene (BPS)

A typically atom transfer radical polymerization (ATRP) procedure was given below for the polymerization of the styrene using BiBEM as inimer. Styrene (10.00 g, 100.1 mmol), BiBEM (0.37 g, 2.0 mmol), bpy (0.60 g, 2.0 mmol) and toluene (10 mL) were added into a 100 mL Schlenk flask. After two cycles of freeze-pump-thaw, CuBr (0.286 g, 2.0 mmol) were added. After the third freeze-pump-thaw cycle, the reaction mixture was warmed to room temperature, placed in an oil bath thermostated at 80 °C and allowed to stir for 48 hours. The mixture was dissolved in 20 mL THF, passed through a neutral alumina column to remove the catalyst. After removing the solvent by rotary evaporation, the residues were precipitated into an excess amount of ethanol. The final product was collected by filtration, dried at 40 °C under vacuum overnight, and the final product was named as BPS-1 (9.85 g, Yield: 98.5%).

Intramolecular Atom transfer Radical Coupling (ATRC) of BPS

General fractional precipitation method was utilized to obtain low dispersity highly branched polymers, with no unincorporated primary chains.[2] A solution of the BPS-1 (5.0 g) dissolved in THF (250 mL) was prepared in a 1 L round-bottom flask. With turbulent stirring, the ethanol was added slowly until the solution turned cloudy. The resulting solution was centrifuged to collect the solid fraction (BPS-4, 0.865 g, Yield: 17.3%) at the bottom. The transparent supernatant was set aside for a second fractional precipitation. BPS-3 (1.27 g, Yield: 25.4%) and BPS-2 (1.58 g, Yield: 31.5%) with different molecular weight were acquired through repeating the above operation, and then performed intramolecular ATRC reactions, respectively.

A 500 mL Schlenk flask was charged with 200 mL THF and Me$_6$TREN (2.00 g, 8.7 mmol), and purged with nitrogen for 3 h. Then CuBr (1.50 g, 10.4 mmol) and Cu (1.37 g, 21.6 mmol) were added to the solution under nitrogen flow and sealed from the Schlenk line. The reaction mixture was placed in an oil bath and stirred at 75 °C for 30 min. In another Schlenk flask, BPS-1 (10 mg) was dissolved in THF (20 mL), and the mixture was degassed by three freeze-pump-thaw cycles. After that, the degassed polymer solution was dropped through a medical injection pump into the THF solution of the catalyst over approximately 24 h. Finally, the reaction mixture was stirred for an

additional 4 h. Then the reaction was terminated by exposing to air. The most THF was removed by rotary evaporation. the residual copper salt was removed by passing a short natural aluminum column. Lastly, the content of the flask was concentrated under reduced pressure, and the coupled product was precipitated in methanol, and the obtained product was named as c-BPS-1 (7.82 mg, Yield: 78.2%). The c-BPS-2 (7.57 mg, Yield: 75.7%), c-BPS-3 (7.44 mg, Yield: 74.4%) and c-BPS-4 (7.98 mg, Yield: 79.8%) were prepared using the same procedure.

Cleavage of the BPS and c-BPS

The efficient Br-Br intramolecular coupling could also be further proved by the cleavage strategy.[3] The initiator BiBEM contained ester group, which subsequently located in each side chain of the BPS after polymerization, and therefore breaking ester linkages could study the ring segment detailly. For example, the BPS-3 (20 mg) and c-BPS-3 (20 mg) were respectively dissolved in 10 ml of THF/CH$_3$OH (v/v, 2/1), and the excess of KOH was charged into the solution. The mixture was stirred over 24 h under reflux in 60℃. After removing the solvent by rotary evaporation, the residues were precipitated into an excess amount of ethanol. The final product was collected by filtration, dried at 40 °C under vacuum overnight and the final hydrolysate named as BPS-3h (16.22 mg, Yield: 81.1%) and c-BPS-3h (15.7 mg, Yield: 78.5%).

Analytical Methods

The molecular weights and polydispersities were measured at 35 °C by SEC in THF using a Waters 1515 instrument equipped with a Waters 2414 differential refractive index (dRI) detector, a Wyatt DAWN HELEOS-II multiangle laser-light scattering (MALLS) detector, and a Wyatt Visco Star viscometer detector (VD). HPLC-grade THF at a flow rate of 1.0 mL/min was used as the eluent. A series of narrowly dispersed polystyrene (PS) standards were used for calibrating the number-average molecular weight ($M_{n\ SEC}$) and the molecular weight distribution ($Đ$). Polymer structures were determined using a Bruker ARX-500 type NMR spectrometer at 25 °C with deuterated chloroform (CDCl$_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. The hydrodynamic radius (R_h) were acquired by dynamic light scattering (DLS) using an ALV/CGS-3 compact goniometer system at 25℃, and a He-

Ne laser operating at a wavelength of $\lambda_0 = 632.8$ nm was used as a light source. Sample aqueous solutions for analysis (2 mg/mL) were poured into the sample bottle, which were placed in sample cell filled with toluene used as the immersion liquid. Temperature control of the sample was provided by an external thermostated circulating bath. Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) using a TA instruments DSC 2010 with a heating/cooling rate of $10°C$ min^{-1} under a continuous nitrogen flow. Thermogravimetric analysis (TGA) was performed at a heating rate of 20 °C/min from room temperature to 600 °C under a continuous nitrogen flow of 50 mL/min with a TA Instruments SDT-2960TG/DTA. The microrheological behaviors of polymers were determined by Diffusing Wave Spectroscopy (DWS, Swiss LS instrument company), and titanium dioxide (TiO_2) nanoparticles with a particle size of 360 nm were used as tracer particles. The samples dissolved in THF for DWS measurement were well mixed with 0.5 wt% particles, and an ultrasonicator was also used to ensure the homogeneity of the samples by ultrasonic mixing. After 12 h of equilibration, scattering from the sample was measured in a 1 mm glass cell on a LS Instruments RheoLab system. The transport means free path *l** was determined from the control sample with the same size particles in THF.
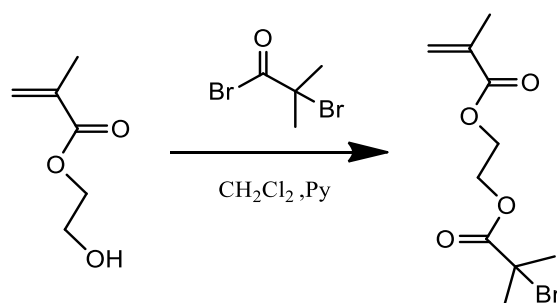
Scheme S1. The synthetic route of 2-(2-bromoisobutyryloxy)ethyl methacrylate (BiBEM)
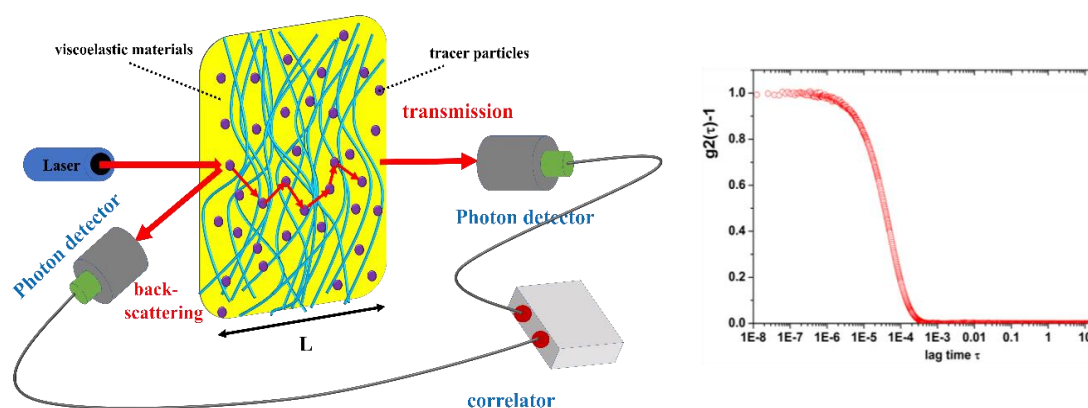
Scheme S2. Transmission and backscattering modes in a basic DWS experiment and example of a normalized ICF $g_2(\tau)^{-1}$

$$g_2(t) - 1 = \left[\frac{(L/l^*+4/3)\langle\sqrt{k_0{}^2 \triangle r^2(\tau)}\rangle}{\sinh\left[(L/l^*+4/3)\langle\sqrt{k_0{}^2 \triangle r^2(\tau)}\rangle\right]} \right]^2 \tag{1}$$

The velocity autocorrelation function for a Brownian particle, where l^* is the transport mean free path, $\triangle r^2(\tau)$ means the particle mean square displacement.

Table S1. Characteristics of the Branched and Multicyclic Branched Polystyrenes.

Sample	Yield (%)	$M_{\text{n SEC}}$ [a] (g/mol)	$Đ$ [a]	$M_{\text{w MALLS}}$ [b] (g/mol)	a [c]	R_{h} [d] (nm)
BPS-1	98.5	9600	3.08	30200	0.56	4.4
c-BPS-1	78.2	7800	2.61	28800	0.62	3.8
BPS-2	31.5	30500	1.17	39100	0.60	5.5
c-BPS-2	75.7	25700	1.19	39200	0.65	4.9
BPS-3	25.4	54800	1.26	85200	0.55	6.3
c-BPS-3	74.4	46400	1.25	83800	0.44	5.7
BPS-4	17.3	141000	1.25	311500	0.63	8.5
c-BPS-4	79.8	96200	1.29	303200	0.57	7.3

[a] Determined by SEC; [b] Measured by SEC equipped with multi-angle laser light scattering (MALLS) detector; [c] The Mark-Houwink exponent, $[\eta] = KM^{\alpha}$; [d] obtained from DLS.

Table S2. The TD-SEC Analysis Results of Branched and Cyclic Polymers before and after Hydrolysis Reaction

Sample	$M_{n\ SEC}$ [e] (g/mol)	$M_{w\ MALLS}$ [g] (g/mol)	$Đ$ [e]	Number of cyclic unit [f]
BPS-1[a]	9600	30200	3.08	-
BPS-1h[d]	4750	-	1.57	-
c-BPS-1[c]	7800	28800	2.61	4
c-BPS-1h[d]	7200	-	1.51	-
BPS-2[b]	30500	39100	1.17	-
BPS-2h[d]	4600	-	1.37	-
c-BPS-2[c]	25700	39200	1.19	5
c-BPS-2h[d]	8320	-	1.41	-
BPS-3[b]	54800	85200	1.26	-
BPS-3h[d]	4500	-	1.43	-
c-BPS-3[c]	46400	83800	1.25	10
c-BPS-3h[d]	8100	-	1.57	-
BPS-4[b]	141000	311500	1.25	-
BPS-4h[d]	4560	-	1.45	-
c-BPS-4[c]	96200	303200	1.29	34
c-BPS-4h[d]	8750	-	1.52	-

[a] BPS-1 was synthesized via atom transfer radical polymerization (ATRP) under the condition of: [St]:[BiBEM]:[bpy]:[CuBr]=50:1:2:1, 85℃, 48 h; [b] BPS-2, BPS-3 and BPS-4 were obtained from fractional precipitation of BPS-1; [c] c-BPS-1, c-BPS-2, c-BPS-3 and c-BPS-4 were prepared by ATRC: the solution of BPS (12 μM) was injected into a refluxing tetrahydrofuran solution of [CuBr] = [Me$_6$TREN] = [Cu^0] = 40 mM at high dilution addition, 24 h; [d] prepared by hydrolysis reaction of BPS and c-BPS, which were dissolved in 10 ml of THF/CH$_3$OH (v/v, 2/1), and the excess of KOH was charged into the solution, 60 ℃, 96 h; [e] determined by SEC using tetrahydrofuran (THF) as the eluent. $M_{n\ SEC}$: the number-average molecular weight. $Đ$: molecular weight distribution; [g] The absolute weight-average molecular weight, measured by multi-angle laser light scattering (MALLS) detector. [f] Average-number of cyclic unit of the obtained c-BPS was estimated as ($M_{w\ MALLS}$ of c-BPS)/ ($M_{n\ SEC}$ of the c-BPS hydrolysate).

Table S3. Microrheological Parameters of LPS-3, BPS-3 and c-BPS-3

Sample	$6\delta^2\times10^5$ [a] (um^2)	η_0 [a] (Pa s)	η_m [a] (Pa s)	G_0 [a] (Pa)	$D_0\times10^4$ [b] (μm^2 /s)	$T_R\times10^2$ [b] (s)	ξ [b] (nm)
LPS-3	1.05	119	28.00	1433	2.57	8.3	14.2
BPS-3	3.57	13	0.86	173	14.60	7.5	28.4
c-BPS-3	17.10	3	0.10	43	157.00	7.0	45.5

[a] Data acquired from DWS; [b] Data acquired from the corresponding theoretical calculation Equation.

Table S3. The Glass Transition Temperatures of LPS-3, BPS-3 and c-BPS-3 with the same molecular weight

Sample	T_g (K)
LPS-3[a]	378
BPS-3[b]	365
c-BPS-3[c]	375

[a] LPS-3 was synthesized via atom transfer radical polymerization (ATRP) under the condition of [St] : [t-BBiB] : [CuBr] : [bpy] = 800:1:1:3, $M_{w.MALLS}$ = 84200 g mol^{-1}, $Đ$ = 1.21; [b] BPS-3 was obtained from sedimentation classification of BPS-1, $M_{w.MALLS}$ = 85200 g mol^{-1}, $Đ$ = 1.26; [c] c-BPS-3 was prepared by ATRC: the solution of BPS-3 (12 μM) was injected into a refluxing tetrahydrofuran solution of [CuBr] = [Me$_6$TREN] = [Cu^0] = 40 mM at high dilution addition, 24 h, $M_{w\ MALLS}$ = 83800 g mol^{-1}, $Đ$ = 1.25)

Table S4. Micro-rheological Parameters of LPS-1, BPS-1 and c-BPS-1

Sample	$6\delta^2\times 10^5$ [b] (um^2)	η_0 [c] (Pa s)	η_m [c] (Pa s)	$D_0\times 10^4$ [d] ($\mu m^2\ s^{-1}$)	G_0 [e] (Pa)	$T_R\times 10^2$ [f] (s)	ξ [g] (nm)
LPS-1[a]	0.42	70	15	0.7	1400	5.0	14.2
BPS-1	1.71	14.56	1	11.6	313	4.6	23.5
c-BPS-1	13.45	1.58	0.1	137	38	4.2	47.3

[a] LPS-1 was synthesized via atom transfer radical polymerization (ATRP) under the condition of [St]: [t-BBiB]: [CuBr]: [bpy]= 300:1:1:3; [b] $6\delta^2$: the value of the MSD at the inflection point; [c] the zero-shear viscosity and macroscopic viscosity observed from the complex viscosity curves; [d] the local diffusion coefficient calculated via equal $\Delta r^2(t)= 6D_0\tau$; [e] elastic plateau modulus; [f] the terminal relaxation time T_R, calculated according to the formula $T_R= \eta_0/G_0$; [g] the mesh size obtained via the Equation $\xi = (k_BT/G_0)^{1/3}$.
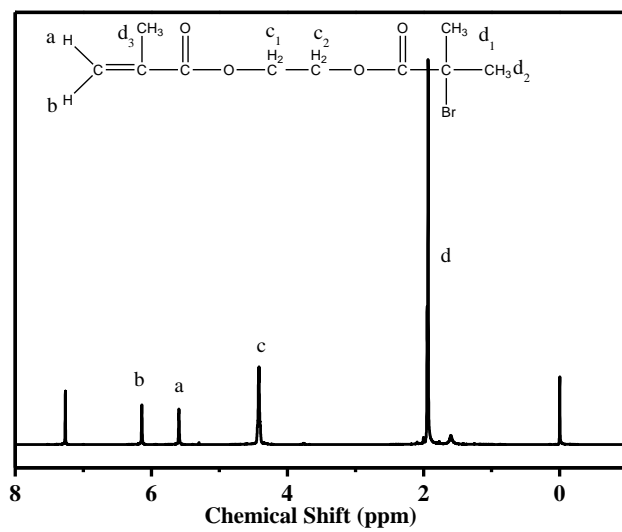
Figure S1. The ^{1}H-NMR spectrum of 2-(2-bromoisobutyryloxy)ethyl methacrylate (BiBEM)
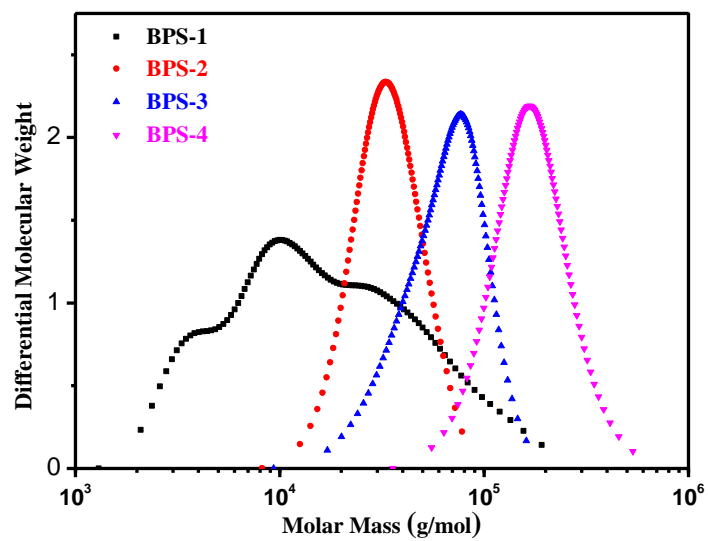
Figure S2. Curves of the differential molecular weight distributions of the branched polymers
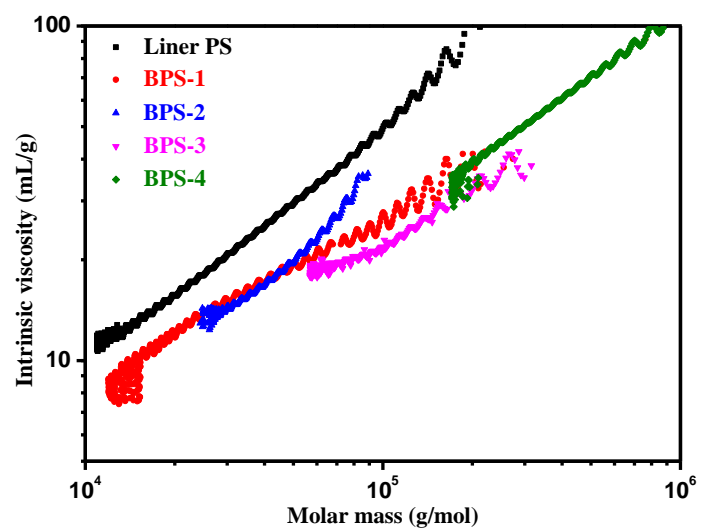
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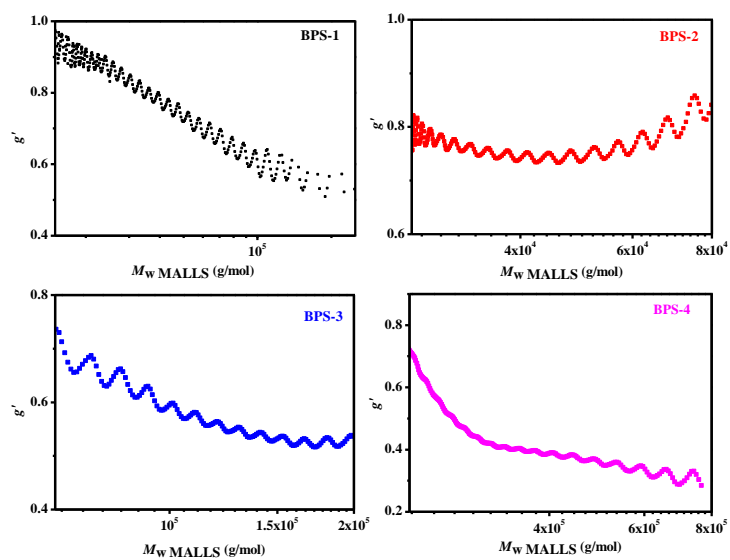
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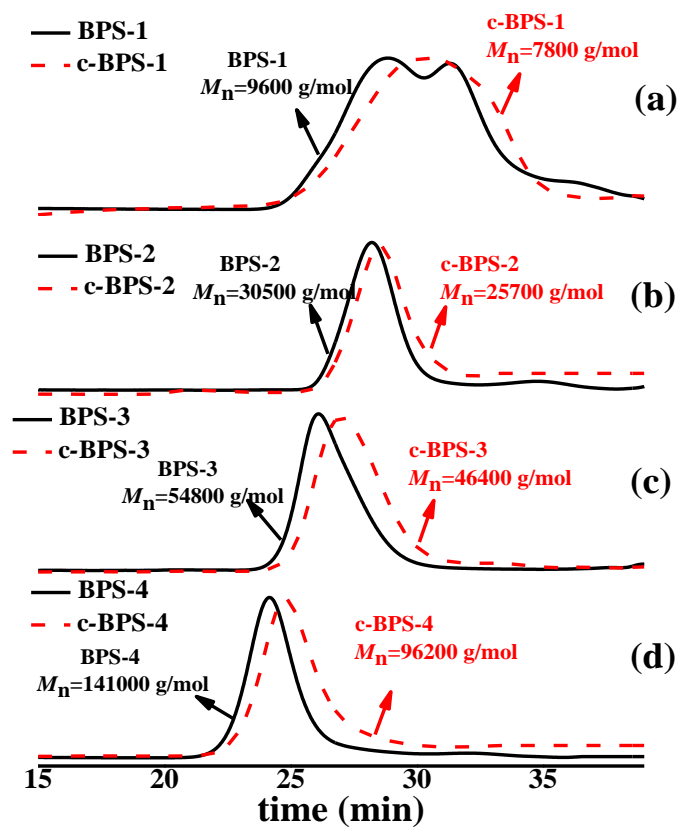
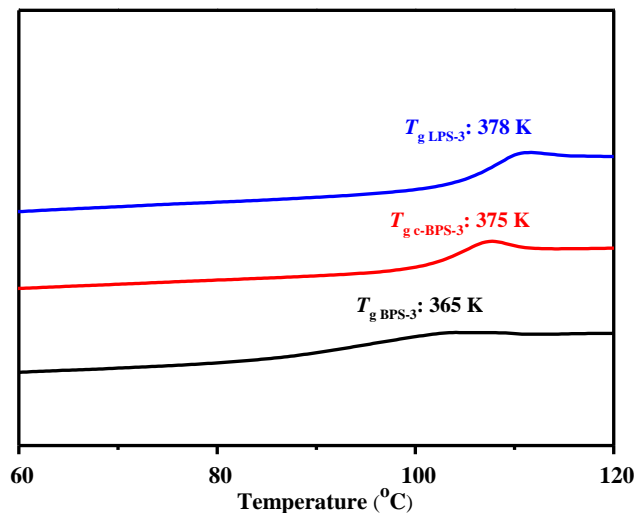**Figure S5.** SEC curves of the branched and cyclic polymers

Figure S6. The glass transition temperatures (T_g) of LPS-3, BPS-3 and c-BPS-3 with same molecular weight

Research showed that constraining the branched chains of BPS-3 into cyclic topology could significantly increase the T_g from 365 K to 375 K, which is near that of LPS-3 (378 K) due to the greatly reduced number of chain ends and the loss of conformational entropy resulting from the change in compactness and topology.
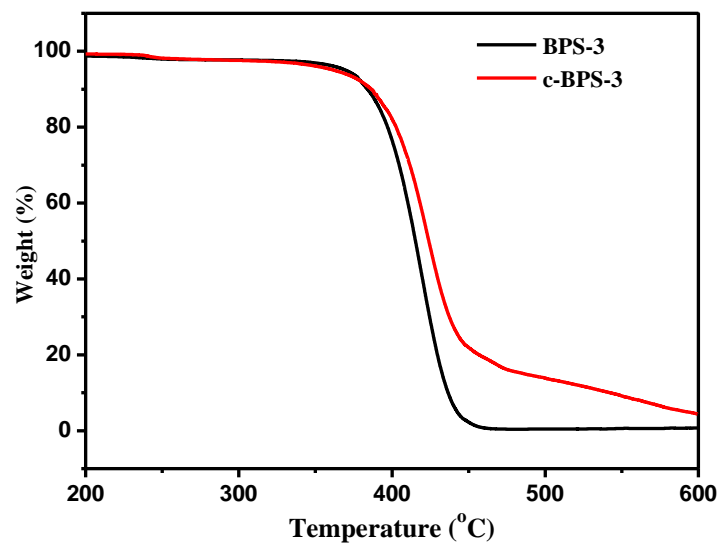
Figure S7. TG curves of BPS-3 and c-BPS-3
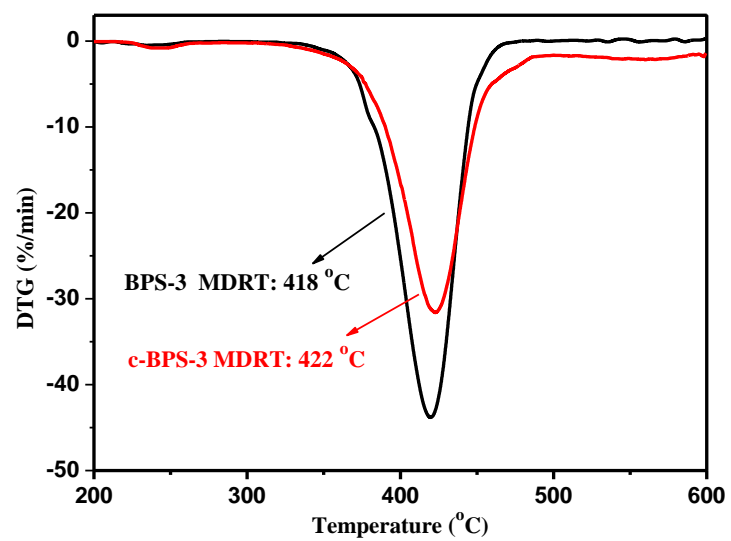
Figure S8. DTG curves of BPS-3 and c-BPS-3
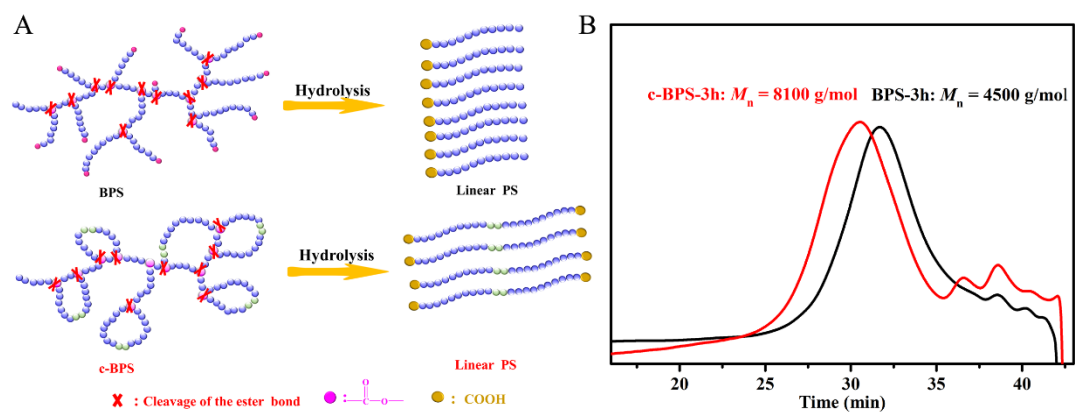
Figure S9. Hydrolysis process of BPS-3 and c-BPS-3 by cleaving ester bonds (A); SEC curves of the BPS-3 and c-BPS-3 hydrolysate (B)
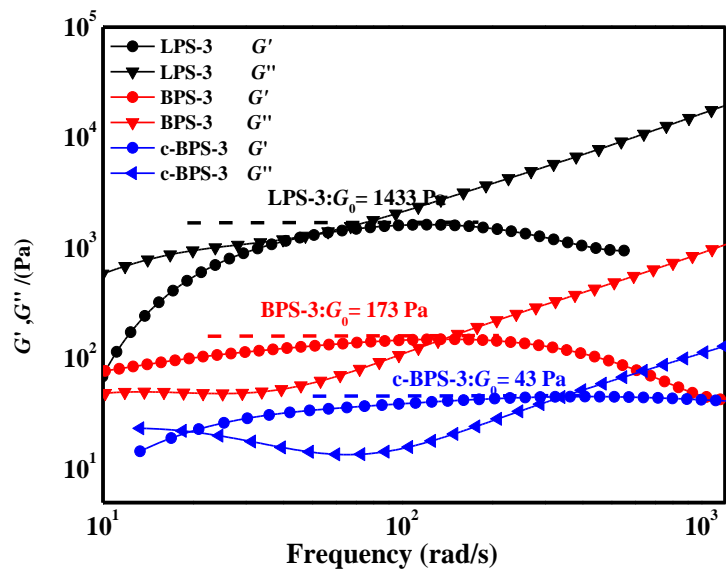
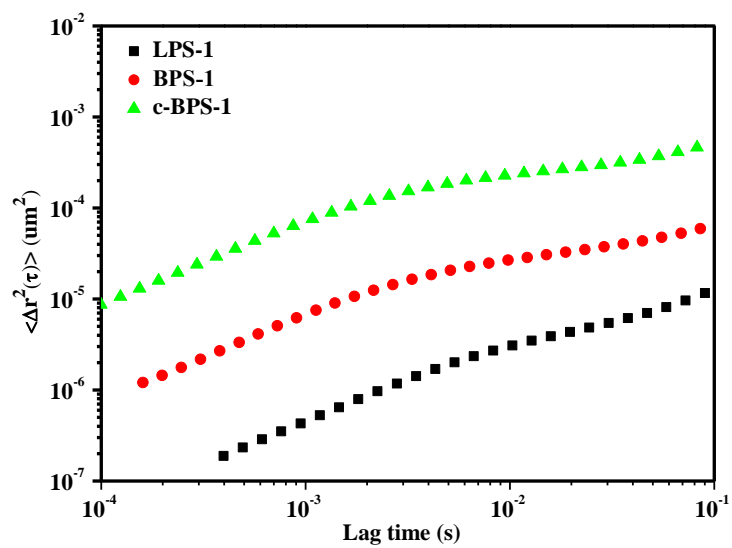**Figure S10.** The elastic G′ and loss modulus G″ curves

Figure S11. Mean square displacement, $\Delta r^2(\tau)$, using TiO$_2$ particles (R_h = 180 nm) imbedded in the 10% polymer solutions (LPS-1: $M_{w\,MALLS}$ = 31300 g/mol, Đ = 1.23; BPS-1: $M_{w\,MALLS}$ = 30200 g/mol, Đ = 3.08; c-BPS-1: $M_{w\,MALLS}$ = 28800 g/mol, Đ = 2.61)
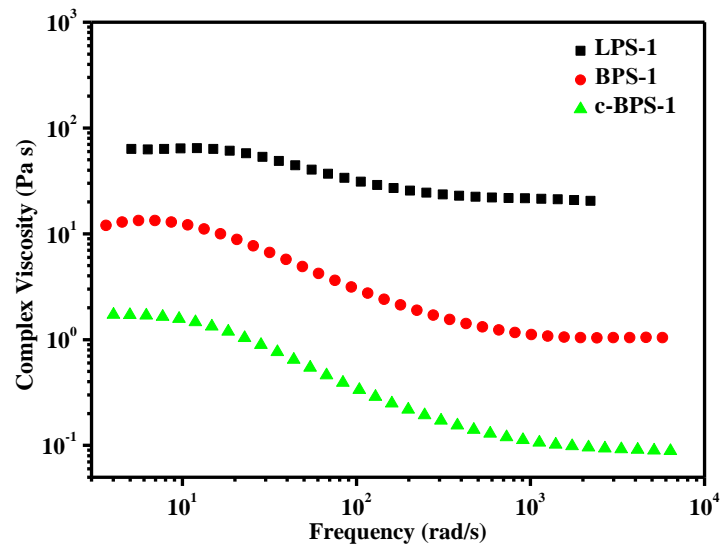
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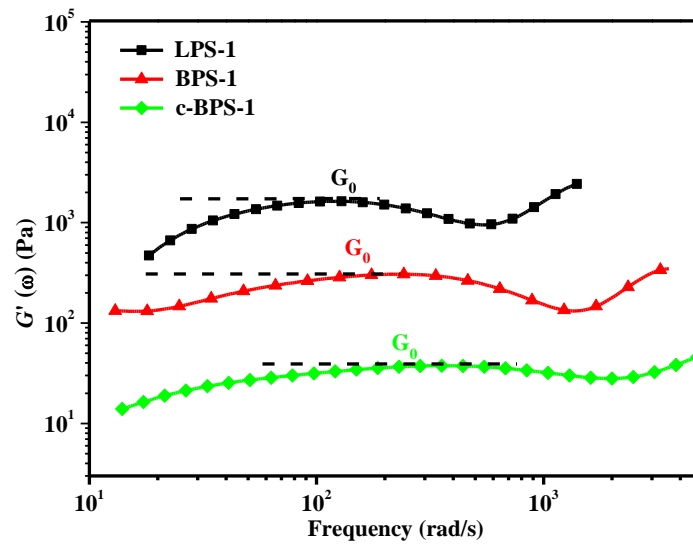
Figure S13. The elastic modulus G' curves of LPS-1, BPS-1 and c-BPS-1 (LPS-1: $M_{\text{w MALLS}}$ = 31300 g/mol, $Đ$ = 1.23; BPS-1: $M_{\text{w MALLS}}$ = 30200 g/mol, $Đ$ = 3.08; c-BPS-1: $M_{\text{w MALLS}}$ = 28800 g/mol, $Đ$ = 2.61)
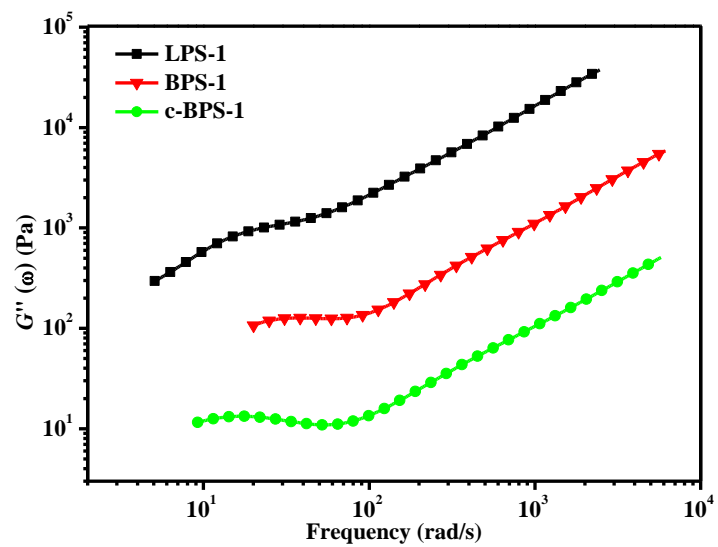
Figure S14. The loss modulus G'' curves of LPS-1, BPS-1 and c-BPS-1 (LPS-1: $M_{w \text{ MALLS}}$ = 31300 g/mol, $Đ$ = 1.23; BPS-1: $M_{w \text{ MALLS}}$= 30200 g/mol, $Đ$ = 3.08; c-BPS-1: $M_{w \text{ MALLS}}$ = 28800 g/mol, $Đ$ =2.61)

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