Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

Determination of Refractive Index Increasement of Synthetic Polybutadienes and Microstructural Control of Grafting Density and Liquid Crystalline Properties

Shuai Huang, Li Han*, Hongwei Ma, Lan Lei, Ruixue Zhang, Heyu Shen, Lincan Yang, Chao Li, Songbo Zhang, Yang Li*

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, Liaoning key Laboratory of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning 116024, China.

Corresponding authors:

*E-mail: hanli@dlut.edu.cn (Li Han)

*E-mail: liyang@dlut.edu.cn (Yang Li)

Experimental materials and methods

Materials. Butadiene (Bd, Dalian Date Special Gas, polymerization grade) purified with a small amount of *n*-butyllithium (*n*-BuLi). *n*-BuLi (Energy Chemical, 1.6 M in *n*-hexane) used as received. Tetrahydrofuran (THF, Sinopharm, analytical reagent), N, N, N', N'-tetramethylethylenediamine (TMEDA, Acros Organics, 98%) and 1,2-dipiperidinoethane (DPE, Acros Orcannics, 98%) served as vinyl polar additives in living anionic polymerization of Bd, were stirred over CaH_2 and distilled under high vacuum conditions before using and then diluted with dry benzene. Cyclohexane, hexane and isopropanol (Sinopharm, analytical reagent) degassed via three freezing-evacuation-thawing cycles before using. Toluene (Sinopharm, analytical reagent) was taken from a solvent purification system (Innovative Technologies, Inc.). Phenol (Sinopharm Chemical Reagent Co., Ltd., China, 99%), Ethyl 4-aminobenzoate (Alfa Aesar, 98%), 1,1,3,3-Tetramethyldisiloxane (Alfa Aesar, 97%), 10-Undecylenoyl chloride (Acros Organics, 98%), p-Hydroxybenzoic acid (Alfa Aesar, 99%) and Pt(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex solution in xylene (Karstedt-type catalyst, Pt~2%, Sigma-Aldrich) used as received.

Methods. Gel permeation chromatography (GPC) was performed on both Viscotek TDA-305 and Waters 1515. Viscotek TDA-305 GPC (Viscotek Corp., Houston, TX) equipped with tetra detectors [Differential refractive index (RI), UV, Viscosity (VISC), and Laser light scattering (7° and 90°, wavelength of λ = 670 nm), volume of sample cell: 18 uL] and two separation columns (Malvern, T6000 M×2), calibrated with Polystyrene (PS) standards (Mw = 104.071 kg/mol, Mn = 100.967 kg/mol, Viscotek Corp.). Mobile phase: THF (1.0 mL/ min at 35 °C). The data was analyzed using OmniSEC software version 4.7.0 (Viscotek Corp.). Waters 1515 GPC (USA) equipped with one 2414 RI detector and two separation columns (Waters, HT4 and HT5 columns), calibrated with PS standards. Mobile phase: THF (1.0 mL/ min at 35 °C). X-ray: WAXD and SAXS (sample detector distance of D=1074mm, the resolution ration of the detector was 100 μm×100 μm) were performed using a Bruker D8 Advance X-ray diffractometer with a CuKa radiation source (λ=1.54 Å). Differential Scanning Calorimeter (DSC) was performed using both TA Q2000 and TA Q20 instruments at a heating and cooling rate of 10 °C/min under nitrogen atmosphere. FT-IR (Nicolet 6700 Flex spectrometer, using KBr sampling). ^{1}H NMR (Advance Bruker Co., Ltd., Germany, 400MHz NMR spectrometer, using $CDCl_3$ as solvent). Polarized optical microscopy (POM, Leica

DMLP equipped with a hot stage).

Synthesis.

The synthesized route of *Azo*-M_1 and *Azo*-M_2 are shown in **Scheme 1**.

Synthesis of 4-(4-hydroxy-phenylazo) benzoic acid ethyl ester **(1)**. A solution of sodium nitrite (5.12 g, 74 mmol in 50 mL water) was added dropwise to a suspension of 10 g (60.5 mmol) of ethyl p-aminobenzoate in a mixture of 22 mL HCl (2 M) and 100 mL of water, keeping the temperature at 0 ºC. After stirring for 1h at 0 ºC, the diazonium salt was obtained. Then, this solution was added slowly to a mixture of phenol (6.79 g, 72.18 mmol) and sodium hydroxide (8.7 g, 216.54 mmol) in 50 mL water. This reaction was stirred for 2 h at 0 ºC and then HCl (2 M) was added to PH = 3. A brown solid was obtained using vacuum filtration and washed by water 3 times to neutral. This product **(1)** was recrystallized from hot ethanol and get the final orange powder. Yield **(1)**: 75%. ^{1}H NMR ($CDCl_3$): δ(ppm) = 8.18 (2H, d, Ar-**H**), 7.92 (4H, m, Ar-**H**), 6.97 (2H, d, Ar-**H**), 5.48 (1H, s, O**H**), 4.42 (2H, q, -O-C$\mathbf{H_2}$-CH_3), 1.43 (3H, t, -O-CH_2-C$\mathbf{H_3}$). FT-IR: 3500-3300 cm^{-1} (OH), 1689 cm^{-1} (C=O).

Synthesis of Azo-M$_1$ **(3)**. 10-Undecenoyl Chloride (3 g, 14.8 mmol) was added dropwise to a mixture of 5g (18.5 mmol) of 4-(4-hydroxy-phenylazo) benzoic acid ethyl ester **(1)** in 50 mL tetrahydrofuran with 6 mL pyridine. This reaction was stirred for 30 min at 25 ºC and then reflux for 6 h at 60 ºC. After the removal of solvent, the residue was poured into aqueous solution of HCl (pH = 3-4) overnight in order to remove the pyridine and filtered by washing to neutral. This product **(2)** was recrystallized from hot alcohol in 90% yield. And then, 1,1,3,3-Tetramethyldisiloxane (30.8 g, 229 mmol) and toluene (70 mL) were mixed at room temperature. A solution of **(2)** (5 g, 11 mmol in 50 mL toluene) with 0.5 mL Karstedt catalyst was added dropwise to the aforementioned solution. This reaction was stirred and refluxed for 24 h at 60 ºC under argon. After the removal of solvent, the residue was poured into hot alcohol to recrystallize. Yield **(3)**: 70%. As shown in **Fig. S5**, ^{1}H NMR ($CDCl_3$): δ(ppm) = 8.19 (2H, d, Ar-**H**), 7.99 (2H, d, Ar-**H**), 7.94 (2H, d, Ar-**H**), 7.26 (2H, d, Ar-**H**), 4.68 (1H, s, Si**H**), 4.42 (2H, q, -O-C$\mathbf{H_2}$-CH_3), 2.59 (2H, t, -CH_2-C$\mathbf{H_2}$-COO), 1.78 (2H, q, -CH_2-C$\mathbf{H_2}$-CH_2-COO), 1.23-1.33 (17H, q, undecene moiety and -O-CH_2-C$\mathbf{H_3}$), 0.53 (2H, t, -Si-C$\mathbf{H_2}$-CH_2), 0.21 (6H, s, -Si-C$\mathbf{H_3}$), 0.14 (6H, s, -Si-C$\mathbf{H_3}$). FT-IR: 2119 cm^{-1} (Si-**H**), 1753 cm^{-1} (CH2-**CO**O), 1689 cm^{-1} (Ar-**CO**O).

Synthesis of Azo-M$_2$ **(6)**. 2.6 g (18.5 mmol) of 4-hydroxybenzoic acid and 6 mL of pyridine were dissolved in THF (50 mL), then 3g (14.8 mmol) of 10-Undecenoyl Chloride were added dropwise. The reaction was heated to reflux at 60 ºC, and stirred for 24 h. After the removal of solvent, the mixture was subsequently acidified with 2 M HCl overnight until pH = 3-4 in order to remove the pyridine and then filtered by washing to neutral. 4-(undec-10-enoyloxy) benzoic acid **(4)** was recrystallized from hot alcohol in 90% yield. 4-(4-hydroxy-phenylazo) benzoic acid ethyl ester (4.44 g, 16.4 mmol), **(4)** (5 g, 16.4 mmol), dicyclohexyl-carbodiimide (3.2 g, 16.4 mmol), 4-dimethylaminopyridine (2 g, 16.4 mmol) and 300 mL THF were mixed at room temperature, which was stirred for 24 h. The powder product **(5)** was filtered, which was poured into water and kept in water overnight with pH = 3-4. The mixture was washed to PH=7, where a brown solid was obtained by recrystallization with hot ethanol. Yield: 60%. **A**nd then, 1,1,3,3-Tetrame-thyldisiloxane (24 g, 180 mmol) were dissolved in THF (50 mL) at room temperature. A second solution with **(5)** (5 g, 9 mmol), THF (160 mL), and a Karstedt-type catalyst (0.5 mL) were mixed at room temperature. The second solution was added to the first solution under argon and then this reaction was heated to reflux at 60 ºC, and stirred for 24 h. After the removal of solvent, a red-orange power was obtained by recrystallized from hot ethanol. Yield: 90%. As shown in **Fig. S5**, ^{1}H NMR (CDCl$_3$): δ(ppm) = 8.26 (2H, d, Ar-**H**), 8.21 (2H, d, Ar-**H**), 8.04 (2H, d, Ar-**H**), 7.96 (2H, d, Ar-**H**), 7.41 (2H, d, Ar-**H**), 7.26 (2H, d, Ar-**H**), 4.68 (1H, s, Si-**H**), 4.43 (2H, q, -O-C$\mathbf{H_2}$-CH$_3$), 2.60 (2H, t, -CH$_2$-C$\mathbf{H_2}$-COO), 1.78 (2H, q, -CH$_2$-C$\mathbf{H_2}$-CH$_2$-COO), 1.25-1.5 (17H, q, undecene moiety and -O-CH$_2$-C$\mathbf{H_3}$), 0.53 (2H, t, -Si-C$\mathbf{H_2}$-CH$_2$), 0.21 (6H, s, -Si-C$\mathbf{H_3}$), 0.14 (6H, s, -Si-C$\mathbf{H_3}$). FT-IR: 2119 cm^{-1} (Si-**H**), 1760 cm^{-1} (CH2-**CO**O-Ar), 1732 cm^{-1} (Ar-**CO**O), 1719 cm^{-1} (Ar-**CO**O-Ar).

Synthesis of a series of polybutadiene (PB) with different microstructures. Butadiene (5 g, 92.6 mmol) was dissolved in 65 mL cyclohexane and a quantitative number of polar additives (THF, TMEDA, DPE) were added. n-BuLi (based on the well-designed Mn) was added quickly. And then, 2-propanol were added quickly through a syringe to terminate the polymerization after it was heated to 35 ºC for 4h, which was precipitated from 500 mL methanol and dried under vacuum for 48h. The resulting PBs were calculated according to **Eq. S1**: 1,2-olefin mole content was tuned from approximately 8% to 80% (moles). For another polymerization, butadiene (5 g, 92.6 mmol) was dissolved in hexane (65 mL), and then DPE as a polar additive was added before injecting n-BuLi, ([DPE]: [n-BuLi] = 1:1, molar ratio) at room temperature. By changing the polymerization temperature, this system was cooled to -18 ºC for 72 h, which was precipitated from 500 mL methanol and dried under vacuum for 48h. The resulting PBs were calculated according to **Eq. S1**: 94 moles % 1,2-olefins.

Synthesis of PB-based LCPs. At the beginning of the reaction, both Azo moieties (Azo-M_1 and Azo-M_2) and PBs with different 1,2-olefins were kept in the glove box. PBs (150 mg, 2.78 mmol) with different 1,2-olefins were dissolved in 20 mL toluene and *Azo*-M_1/*Azo*-M_2 (Si-H: double bonds = 1.2:1, molar ratio) was added. The mixture was stirred and then Karstedt's catalyst (0.5 mL) was added. And then, this reaction solution was taken out and stirred for 72 h at 50 ºC. All reactions were carried out under inert gas protection. After the removal of solvent, PB-M_1 was purified by multiple precipitation from THF/alcohol (v/v=1:20), and PB-M_2 was purified by precipitation from THF/ether/alcohol (v/v/v = 1:20:4). PB-M_1 and PB-M_2 were dried under vacuum.

Results and Discussion

Calculation of PB-Microstructures and Grafting Density (E_A) of PB-based LCPs using ^1H NMR.

As shown in **Fig. 1b** and **Fig. S3b**, the integral area of the typical peaks δ (ppm) = 4.7-5.15 (2H of 1,2-olefins of PBs) were defined as **A1**, where **A1**/2 represented the content of 1,2-olefins. The integral area of the peaks δ = 5.15-5.7 (2H of 1,4-olefins and 1H of 1,2-olefins of PBs) were defined as **A2**. According to our previous work, (**A2**-**A1**/2)/2 represents the content of 1,4-olefins, **A1**/2+(**A2**-**A1**/2)/2 represented the content of the total double bonds of PBs. Hence, PB microstructures (1,2-olefins and 1,4-olefins) were calculated as the following equations:

$$1{,}2\% = \frac{A1/2}{A1/2 + (A2 - \frac{A1}{2})/2} * 100\% \; (Eq.S1)$$

$$1{,}4\% = \frac{(A2 - \frac{A1}{2})/2}{A1/2 + (A2 - \frac{A1}{2})/2} * 100\% = 1 - 1{,}2\% \; (Eq.S2)$$

As shown in **Fig. S5** and **Fig. 2a**, the typical peaks δ (ppm) = 4.3-4.6 attributed to terminals (2H, -O-C$\boldsymbol{H}_2$-CH_3) of *Azo*-M_1 and *Azo*-M_2, which can be served as the standard of calculation. As shown in

Fig. 2a and **Fig. S6**, the typical peaks δ = 4.3-4.6 (2H of *Azo*-M_1/*Azo*-M_2) appeared in the ^{1}H NMR of PB-M_1/PB-M_2. Hence, the integral area of δ = 4.3-4.6 (2H) can be defined as **A3**, where **A3**/2 represented the content of grafted *Azo*-M_1/*Azo*-M_2, as well as the content of reacted double bonds in PBs. The integral area of the typical peaks δ (ppm) = 4.7-5.15 (2H of 1,2-olefins of PBs) of PB-based LCPs were defined as **A1**, where **A1**/2 represented the remnant 1,2-olefins in PBs. The integral area of the peaks δ = 5.15-5.7 (2H of 1,4-olefins and 1H of 1,2-olefins of PBs) of PB-based LCPs were defined as **A2**, where (**A2**-**A1**/2)/2 represented the remnant 1,4-olefins in PBs. Hence, the sum of (**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2 represented the content of total double bonds in original PBs. 1,2%*[(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2] represented the content of total 1,2-olefins of original PBs. 1,2%*[(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2]- **A1**/2 represented the content of reacted 1,2-olefins in PBs. 1,4%*[(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2] represented the content of total 1,4-olefins of original PBs. 1,4%*[(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2]- (**A2**-**A1**/2)/2 represented the content of reacted 1,4-olefins in PBs. In other words, (**A1**/2)/[(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2] represented the percentage of remnant1,2-olefins in total double bonds, and [(**A2**-**A1**/2)/2]/ [(**A3**/2) + (**A1**/2) + (**A2**-**A1**/2)/2] represented the percentage of remnant 1,4-olefins in total double bonds. Here, the addition efficiency, i.e., grafting density, was defined as E_A (mole%). The percentage of reactive double bonds in total double bonds was defined as E_A(Total). Similarly, the percentage of reactive 1,2-olefins in total 1,2-olefins was defined as 1,2-E_A, and the percentage of reactive 1,4-olefins in total 1,4-olefins was defined as 1,4-E_A. The detailed calculation equations as follows:

$$E_A(Total) = \frac{A3/2}{A1/2 + (A2 - \frac{A1}{2})/2 + A3/2} * 100\% \ (Eq. S3)$$

$$1{,}2 - E_A = \frac{1{,}2\% - \frac{A1}{A1 + (A2 - \frac{A1}{2}) + A3} * 100\%}{1{,}2\%} * 100\% \ (Eq. S4)$$

Equivalent formula：

$$1{,}2 - E_A = \frac{1{,}2\% * [\,(A3/2)\ +\ (A1/2)\ +\ (A2 - A1/2)/2] - A1/2}{1{,}2\% * [\,(A3/2)\ +\ (A1/2)\ +\ (A2 - A1/2)/2]} * 100\%$$

$$1{,}4 - E_A = \frac{1{,}4\% - \dfrac{A2 - \dfrac{A1}{2}}{A1 + \left(A2 - \dfrac{A1}{2}\right) + A3} * 100\%}{1{,}4\%} * 100\%\ (Eq.\,S5)$$

Equivalent formula：

$$1{,}4 - E_A = \frac{1{,}4\% * [\,(A3/2)\ +\ (A1/2)\ +\ (A2 - A1/2)/2] - \ (A2 - A1/2)/2}{1{,}4\% * [\,(A3/2)\ +\ (A1/2)\ +\ (A2 - A1/2)/2]} * 100\%$$

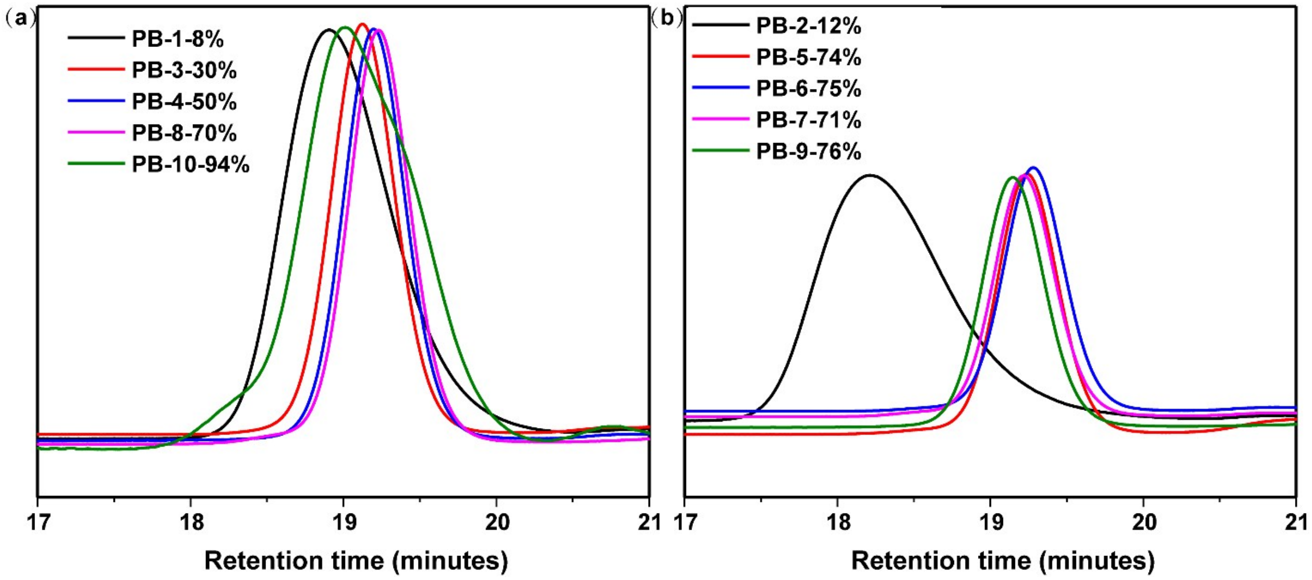

Fig. S1 GPC-RI/LALLS of PBs with various 1,2-olefin microstructures.

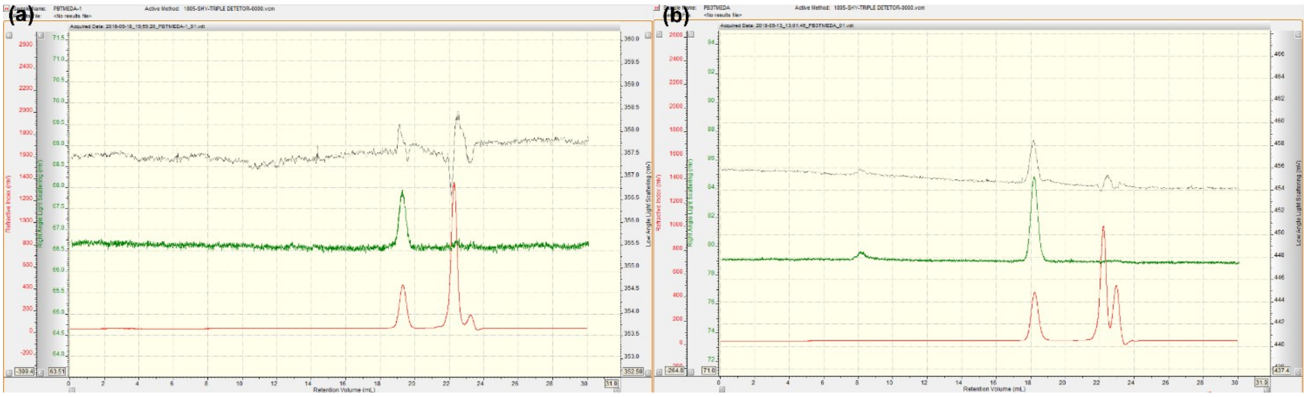

Fig. S2 Two representative GPC-RI/LALLS of the whole elution of (a) PBs with 5kg/mol and (b) 10kg/mol, where RI was marked in red color, LALLS (at 7°) was marked in black color, in addition, right angle laser light scattering (RALLS, at 90°) was also marked in green color for better presentation.

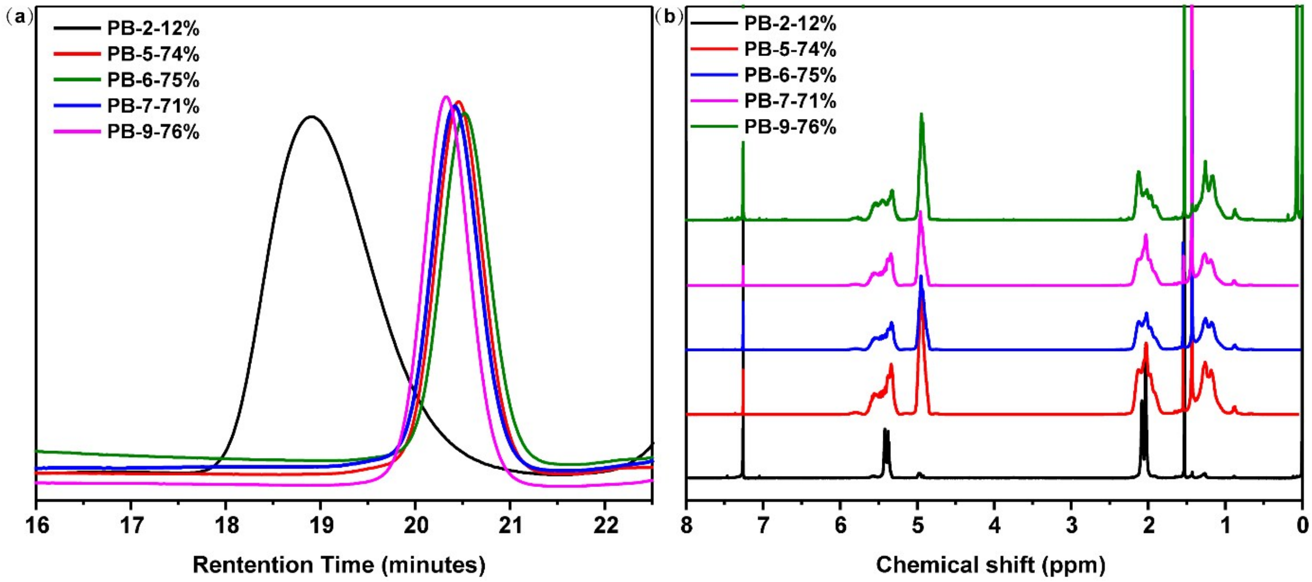

Fig. S3 (a) GPC with RI only traces and (b) ^{1}H NMR spectra of PBs with various 1,2-olefin microstructures.

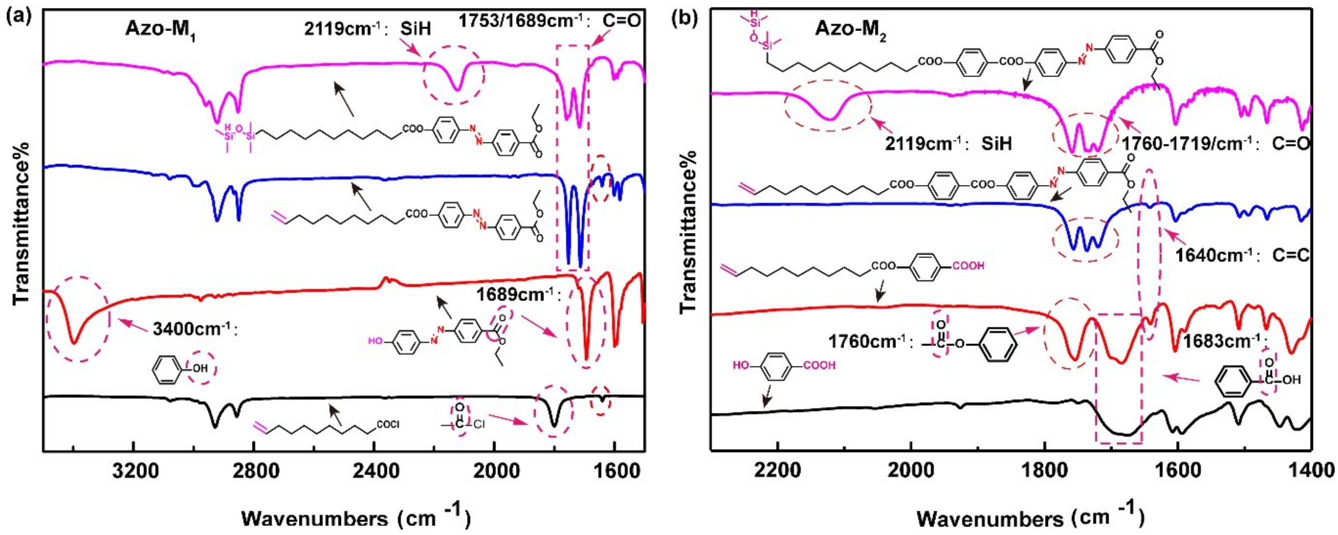

Fig. S4 FT-IR comparison of some representative intermediates, precursor molecules and *Azo*-M$_1$/*Azo*-M$_2$ in the synthetic process with regard to the part of synthesis.

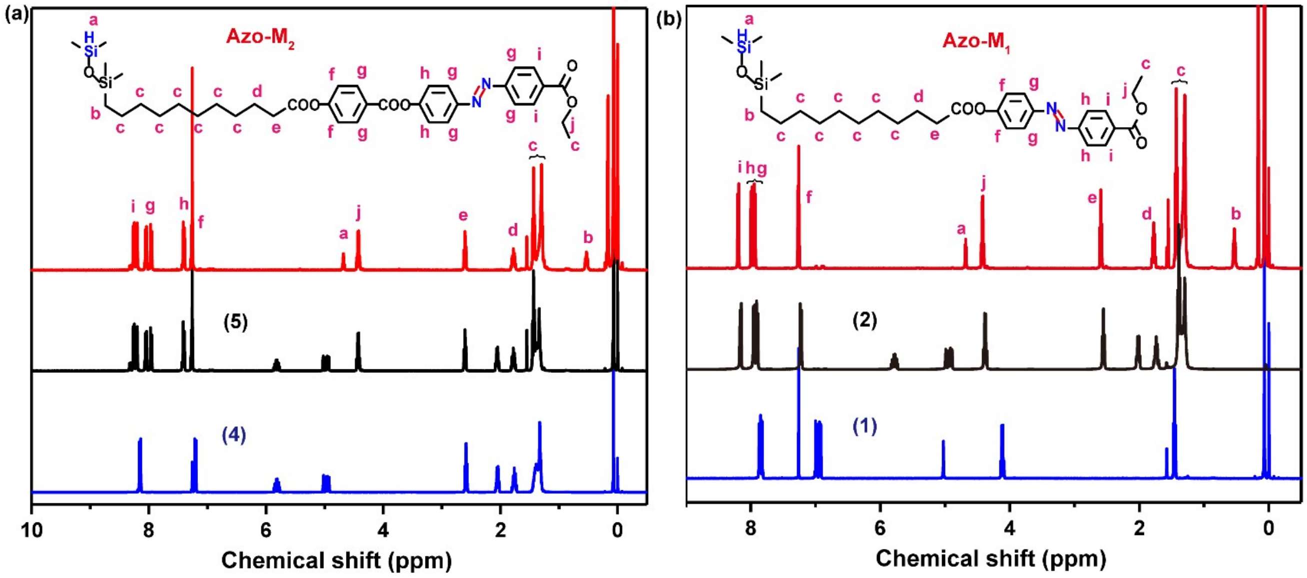

Fig. S5 ^{1}H NMR comparison of *Azo*-M$_1$/*Azo*-M$_2$ and the responding precursor molecules.

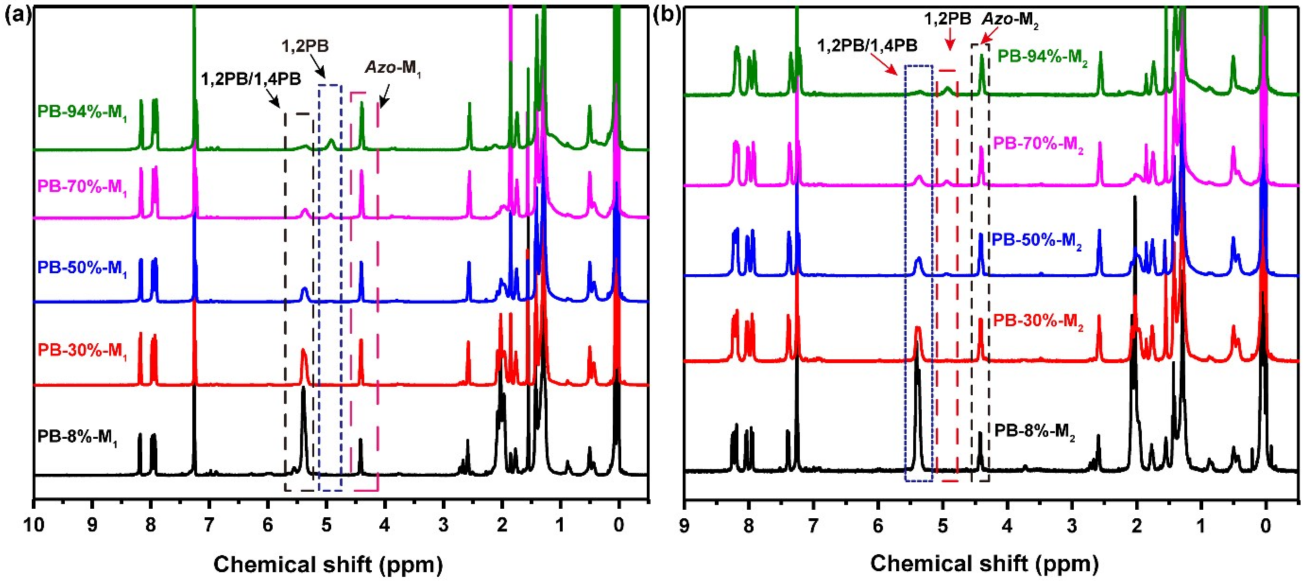

Fig. S6 ^{1}H NMR of (a) PB-based LCPs with *Azo*-M$_1$ as side attachment and (b) PB-based LCPs with *Azo*-M$_2$ as side attachment, as well as the typical assignments for calculation of grafting density (E$_A$).

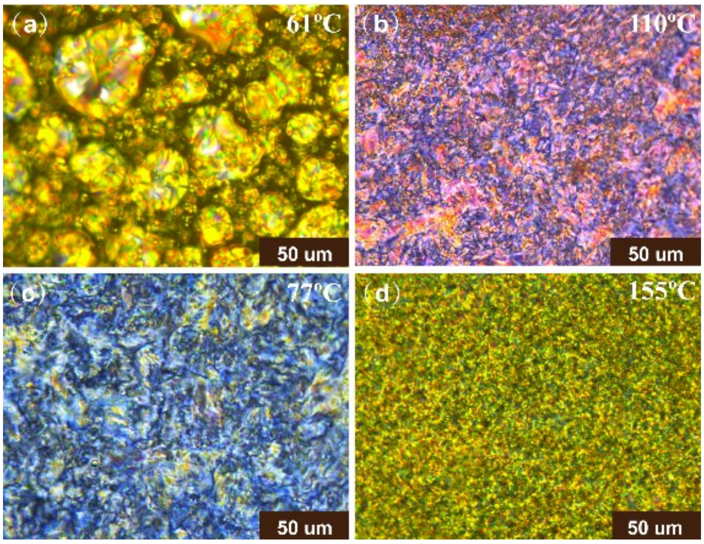

Fig. S7 POM (50 μm) images depending on temperature: (a) sphere-shaped textures of *Azo*-M$_1$, 61ºC on heating; typical colorful textures of *Azo*-M$_2$ (b, 110ºC on cooling), (c, 77ºC on heating) and (d, 155ºC on heating).

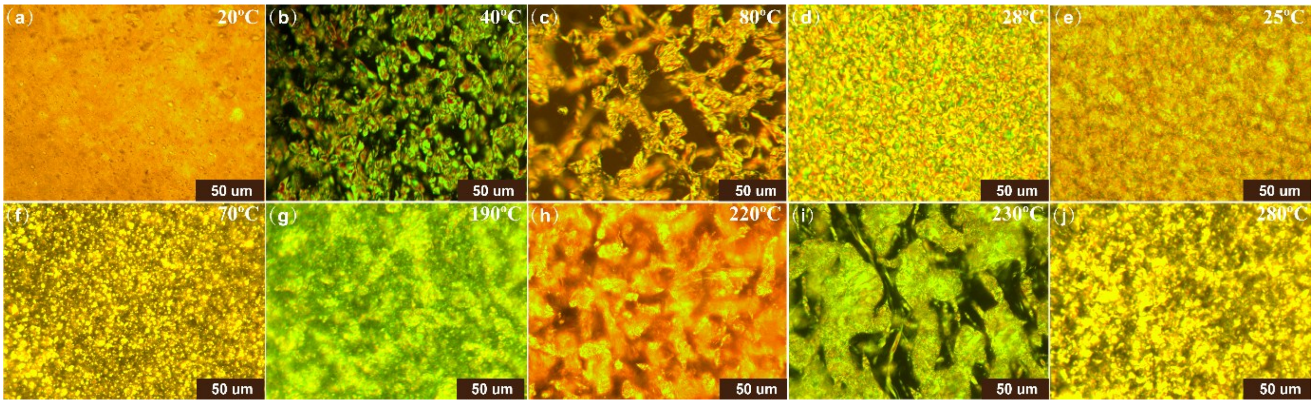

Fig. S8 POM (50 μm) images on heating or cooling cycle of (a, b, c, d, e) PB-based LCPs with *Azo*-M$_1$ as side attachment: (a) E_A(Total) =17%, (b) E_A(Total) = 30%, (c) E_A(Total)= 47% (50% 1,2-olefin PB), (d) E_A(Total)= 53% (70% 1,2-olefin PB), and (e) E_A(Total)= 53% (94% 1,2-olefin PB); (f, g, h, i, j) PB-based LCPs with *Azo*-M$_2$ as side attachment: (f) E_A(Total)=15%, (g) E_A(Total)=35%, (h) E_A(Total)= 47% (50% 1,2-olefin PB), (i) E_A(Total)=50% (70% 1,2-olefin PB) and (j) E_A(Total)=50% (94% 1,2-olefin PB).

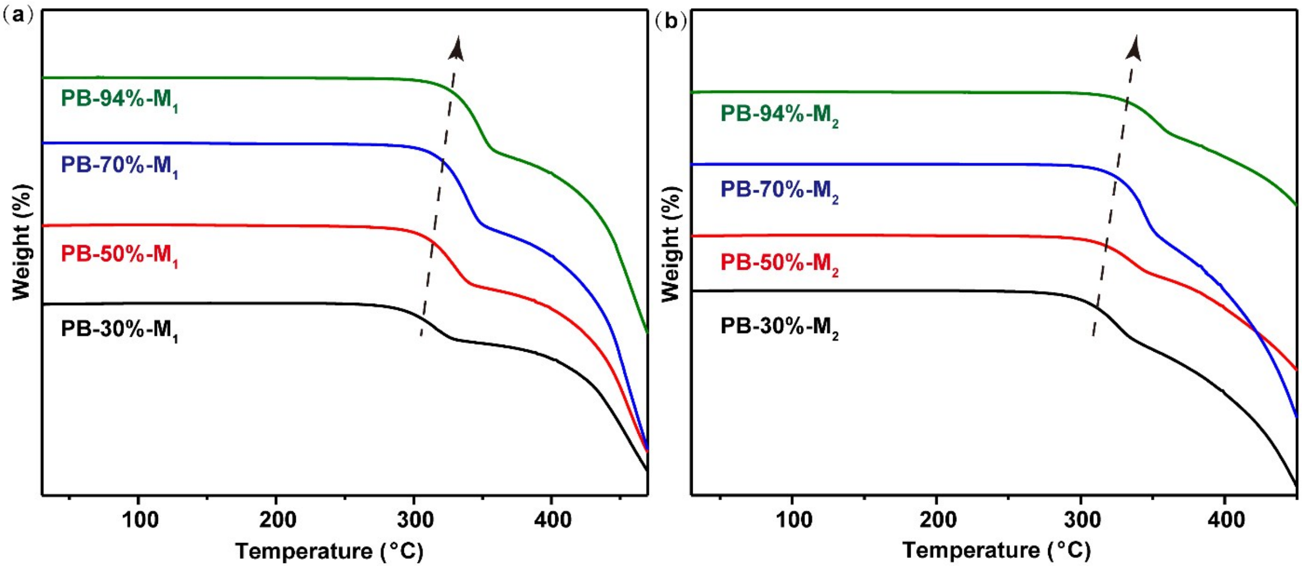

Fig. S9 Several representative TGA curves of PB-based LCPs with various 1,2-olefin microstructures (a) *Azo*-M_1 as side attachment and (b) *Azo*-M_2 as side attachment.

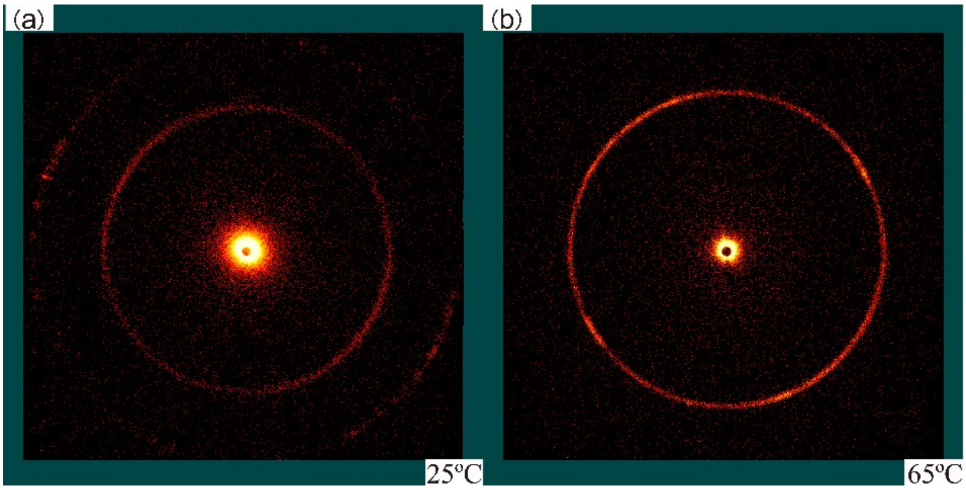

Fig. S10 Representative 2D SAXS patterns depending on temperature of *Azo*-M_1.

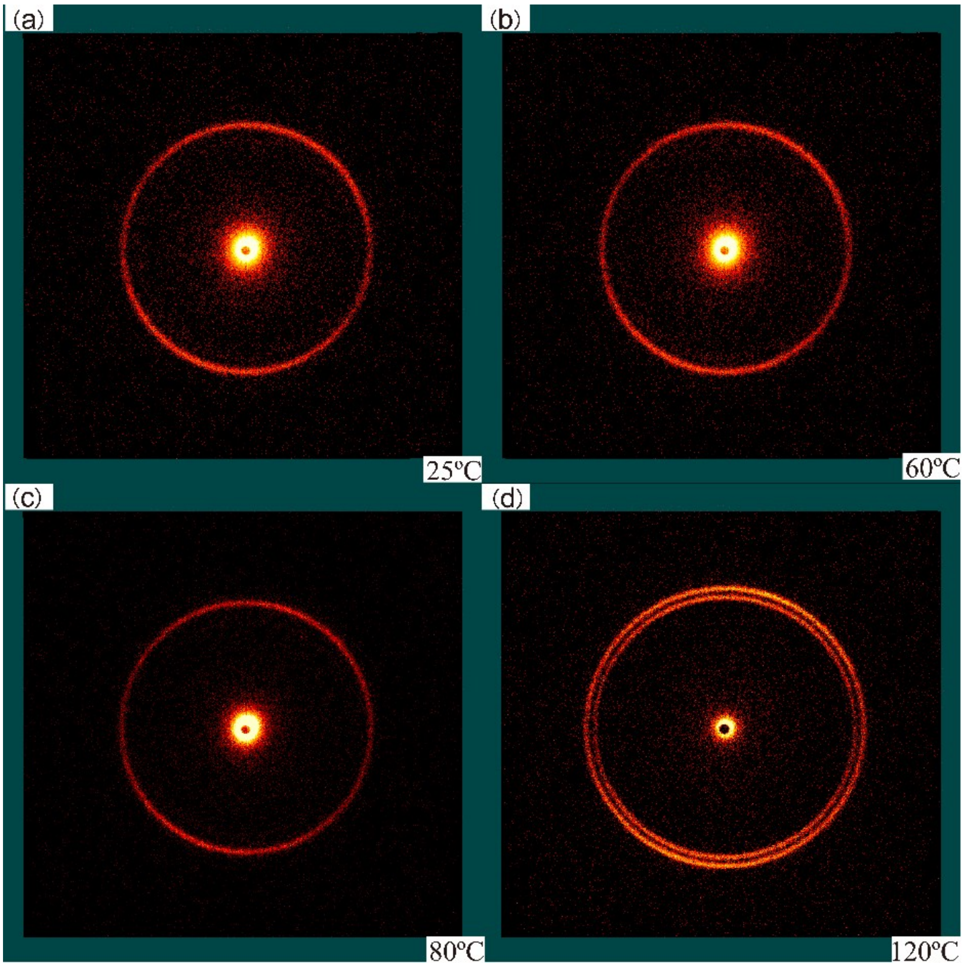

Fig. S11 Representative 2D SAXS patterns depending on temperature of *Azo*-M_2.