Synthesis of periodic polyolefins based on anionic alternating copolymerization

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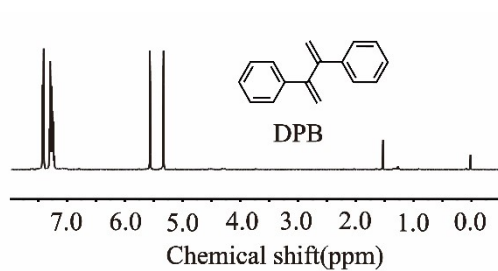
Table of the Content

1. Experimental section

Materials

1,1-Diphenyl-ethylen (DPE, Aldrich, 97%), Benzil (Energy Chemical, 98%), Cinnamaldehyde (Energy Chemical, 98%), 2,3-Dimthyl-1,3-butadiene (Energy Chemical, 98%, stabilized with BHT), Isoprene (IP, Energy Chemical, 99%), Cyclobutyl (Phenyl) methadone (Energy Chemical,97%), Potassium tert-butoxide (*t*-BuOK, Energy Chemical, 99%), Methyltriphenyl-phosphonium bromide (Energy Chemical, 99%), Tetrahydrofuran (THF, Sinopharm, 99%), Benzene (Sinopharm, 99%), Triisobutyl aluminum (0.298mol/l in toluene, Energy Chemical, Seal), Nickel naphthenate (Energy Chemical, 97%).
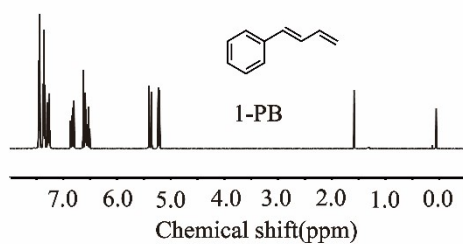
Measurements:

SEC (Size exclusion chromatography was performed on a Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 ml min^{-1} in THF at 30°C after calibration using polystyrene standards. ^{1}H nuclear magnetic resonance (NMR, 5 wt.%, CDCl$_3$) spectra were recorded on Bruker Avance II 400 MH$_Z$ NMR spectrometer at ambient temperature with (CH$_3$)$_4$Si (tetramethyl-silane, TMS) as the internal standard. MALDI-TOF-MS analysis was carried out on a Waters MALDI micro MX mass spectrometer (Water, Milford, CT, USA) with 2-[(2E)-3-(4-tertbutylphnyl)-2-methyprop-2-enylidne〕malonitrile (DCTB) and silver trifluoroacetate as dopants. DSC curves were performed on TA Q20 at a heating rate of 10°C/min under a nitrogen atmosphere. Polymers of Runs1-1#, 1-2#, 3-1#, 3-2#, 4-1#,4-2#, 5-1#, 5-2#, 6-1#, 8-1#, 8-2# were performed on TA Q20 at a heating rate of 10°C/min under a nitrogen atmosphere. Polymer of Run6-2# was performed on TA Q20 at a heating rate of 20°C/min under a nitrogen atmosphere.
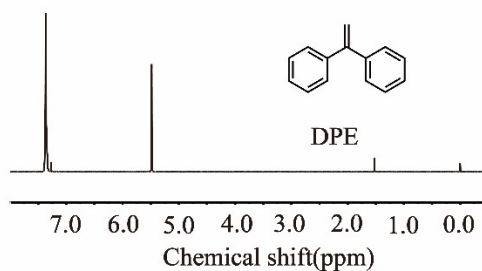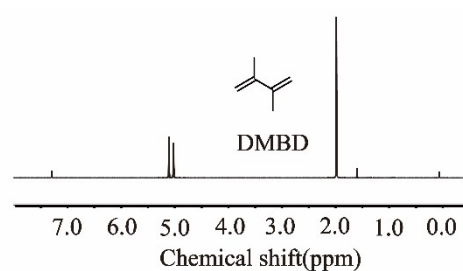
2. ^{1}H NMR of monomers

Supplementary Figure S1. ^{1}H NMR spectrum of DPB in CDCl$_3$

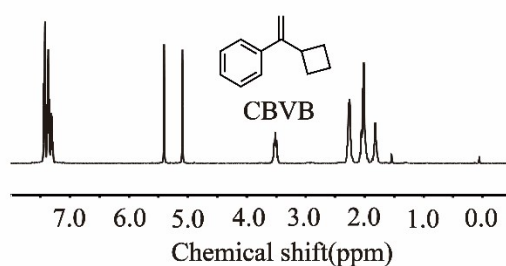**Supplementary Figure S2.** ^{1}H NMR spectrum of 1-PB in CDCl$_3$

Supplementary Figure S3. ^{1}H NMR spectrum of DPE in CDCl$_3$

Supplementary Figure S4. ^{1}H NMR spectrum of DMBD in CDCl$_3$

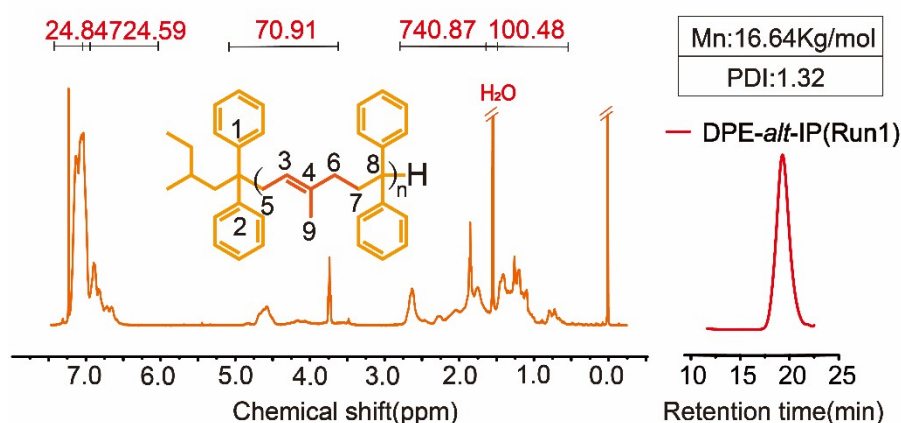**Supplementary Figure S5**. ^{1}H NMR spectrum of CBVB in CDCl$_3$

3. Synthesis of alternating copolymers（DPE-*alt*-IP, DPE-*alt*-DMBD, DPE-*alt*-1-PB, DPE-*alt*-DPB, DPE-*alt*-CBVB）

All anionic polymerization processes must be carried out under strict conditions without water or oxygen. Taking the binary copolymerization of DPE: IP=1.5:1 as an example, the steps of living anionic polymerization are as follows: add 5.4g (30mmol) of DPE into a polymerization bottle, dissolve it with 70ml of anhydrous and oxygen free THF distilled under normal pressure, and add 1.236ml (0.429mmol, 0.347mol/L) of *sec*-BuLi initiator benzene solution. Half an hour after initiation, the reaction solution showed purplish red of DPE active species (red and black in benzene), which proved that butyl lithium active species were successfully converted into DPE active species. Then 2.724g (wt.% is 50%, 20mmol) of IP was added, the reaction solution was shaken, the polymerization bottle was sealed, and it was transferred to at 0 ℃ refrigerator for reaction for 72h. At the end of the reaction, use isopropyl alcohol to terminate the reaction, pour in anhydrous methanol to precipitate the gel, and filter after standing. Then, the polymer is dissolved and settled three times to remove redundant monomers. Other aggregation steps are the same, and the specific values are shown in the following **Supplementary Table S1**.

Supplementary Table S1. Copolymerization Conditions of DPE and olefins

Run	M_1/M_2	Eq.	M_1 (g)	M_2 (g)	Solvent(ml)	sec-BuLi (ml, mol)	Temp.℃	Time	N_{D0}
1	DPE/IP	1.5	5.400	2.724	THF	1.236ml, 0.347mol/L	0	3days	70
2（a）	DPE/DMBD	1	0.360	0.160	Benzene	0.096ml, 0.347mol/L	25	5days	60
2（b）	DPE/DMBD	4	0.360	0.640	Benzene	0.416ml, 0.240mol/L	25	5days	50
2（c）	DPE/DMBD	5	1.800	0.160	Benzene	0.166ml, 0.240mol/L	25	5days	50
2（d）	DPE/DMBD	6	2.160	0.160	Benzene	0.166ml, 0.240mol/L	25	5days	50
3	DPE/DMBD	4	10.800	1.200	Benzene	0.720ml, 0.347mol/L	25	5days	60
4	DPE/1-PB	1.5	0.360	0.173	THF	0.064ml, 0.347mol/L	-25	3days	60
5	DPE/1-PB	1.5	5.400	2.600	THF	0.823ml, 0.347mol/L	-25	3days	70
6	DPE/DPB	1.5	2.160	1.648	THF	0.461ml, 0.347mol/L	-25	3days	50
7	DPE/CBVB	1	0.720	0.632	Benzene	0.333ml, 0.240mol/L	25	5days	50
8	DPE/CBVB	1	1.440	1.264	Benzene	0.639ml, 0.254mol/L	25	10days	50

3.1 ^{1}H NMR spectra of copolymers of DPE and IP

Supplementary Figure S6. ^{1}H NMR spectrum and GPC curves of Run 1 in CDCl$_3$

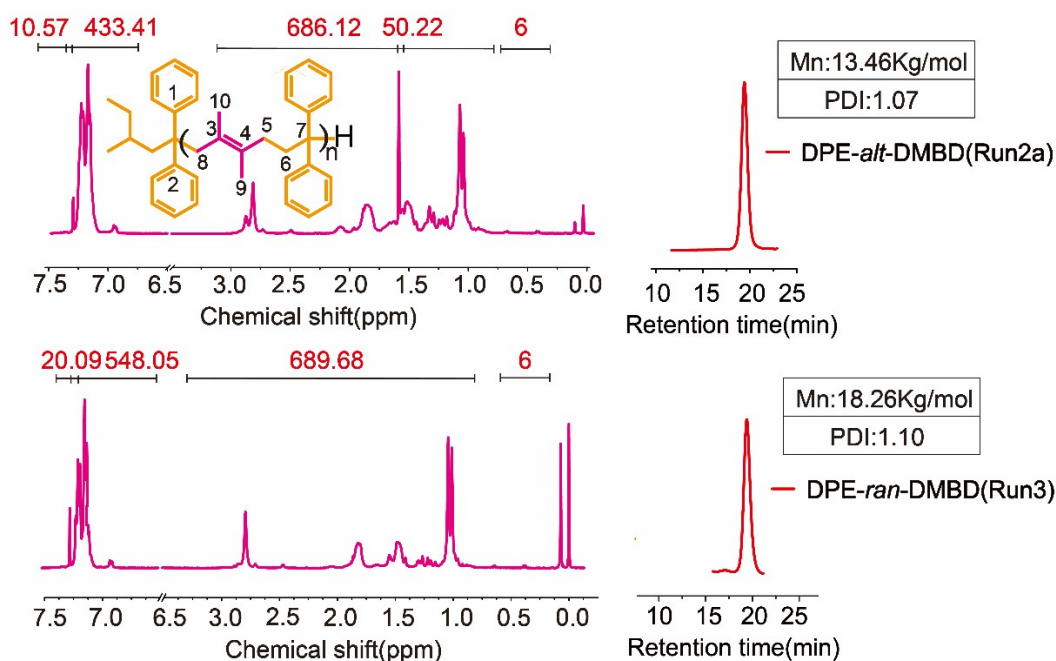$$\frac{10N_D}{2N_D + 7N_I} = \frac{Area(aromatic\ region)}{Area(Saturated\ region)}$$

Equation (Figure S6)

$$\frac{N_I}{2N_D + 7N_I} = \frac{Area(Double\ bond)}{Area(Saturated\ region)}$$

$$2x + 7y = 740.87 - 100.48$$

$$10x = 724.59 - 24.84$$

$$x = 70$$
$$y = 70.91$$

3.2 ^{1}H NMR spectra of copolymers of DPE and DMBD

10.57 433.41   686.12 50.22   6

Mn:13.46Kg/mol
PDI:1.07
— DPE-*alt*-DMBD(Run2a)

7.5 7.0 6.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift(ppm)

10 15 20 25
Retention time(min)

20.09 548.05   689.68   6

Mn:18.26Kg/mol
PDI:1.10
— DPE-*ran*-DMBD(Run3)

7.5 7.0 6.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift(ppm)

10 15 20 25
Retention time(min)

Supplementary Figure S7. ^{1}H NMR spectrum and GPC curves of Run2 and Run3 in CDCl$_3$

$$\frac{10N_D}{6N_{Sec-BuLi}} = \frac{Area(aromatic\ region)}{Area(initiator\ region)}$$

Equation (Figure S7)

$$\frac{2N_D + 10N_M}{6N_{Sec-BuLi}} = \frac{Area(Saturated\ region)}{Area(initiator\ region)}$$

$$10x = 433.41 - 10.57$$

$$2x + 10y = 686.12$$

$$x = 43 \quad y = 55$$

$$10x = 548.05 - 20.09$$

$$2x + 10y = 689.68$$

$$x = 53 \quad y = 58$$

3.3 ^{1}H NMR spectra of copolymers of DPE and 1-PB

Supplementary Figure S8. ¹H NMR spectrum and GPC curves of Run4 and Run5 in CDCl₃

$$\frac{2N_1}{6N_{Sec-BuLi}} = \frac{Area(double\ bond\ region)}{Area(initiator\ region)}$$

Equation (Figure S8)

$$\frac{5N_1 + 10N_D}{6N_{Sec-BuLi}} = \frac{Area(aromatic\ region)}{Area(initiator\ region)}$$

$$10x + 5y = 276.96 - 16.38 \qquad 10x + 5y = 1167.21 - 84.48$$
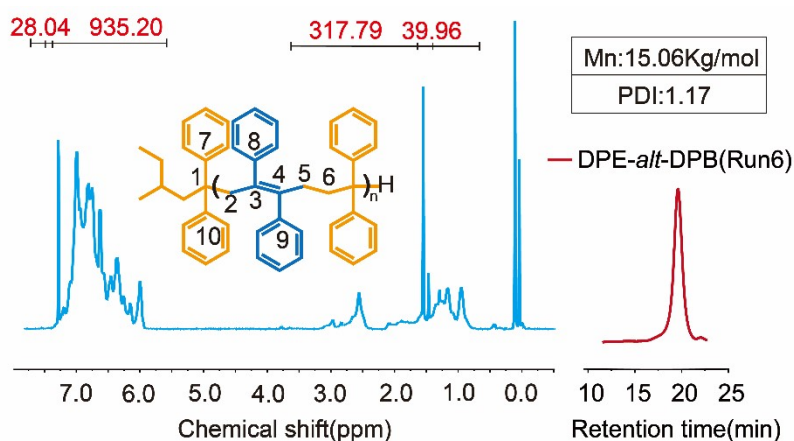
$$2y = 46.78 + 1.60 \qquad 2y = 146.71 + 4.92$$

$$x = 71 \quad y = 75$$

3.4 ¹H NMR spectra of copolymers of DPE and DPB

Supplementary Figure S9. ¹H NMR spectrum and GPC curves of Run6 in CDCl₃

$$\frac{10N_P + 10N_D}{2N_D + 4N_P} = \frac{Area(aromatic\ region)}{Area(Saturated\ region)}$$
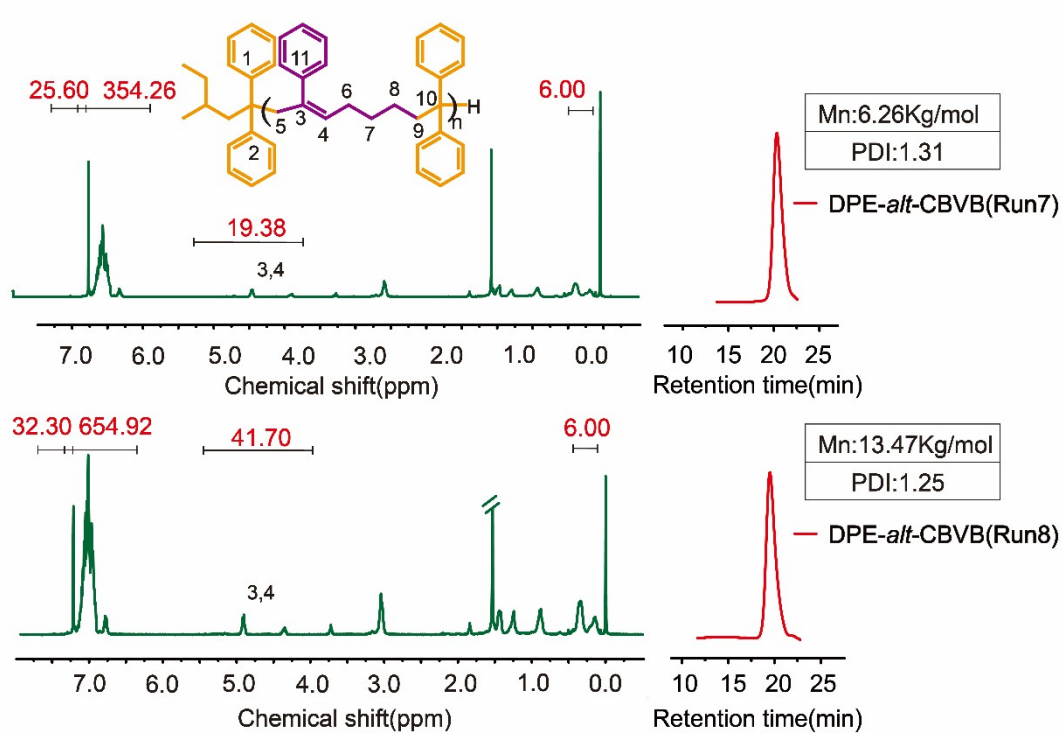

$$10x + 10y = 935.20 - 28.04$$

$$2x + 4y = 317.79 - 39.96$$

$$x = 43 \quad y = 48$$

3.5 ^{1}H NMR spectra of copolymers of DPE and CBVB

Supplementary Figure S10. ^{1}H NMR spectrum and GPC curves of Run7and Run8 in CDCl$_3$

$$\frac{N_C}{6N_{Sec-BuLi}} = \frac{Area(double\ bond\ region)}{Area(initiator\ region)}$$

$$\frac{5N_C + 10N_D}{6N_{Sec-BuLi}} = \frac{Area(aromatic\ region)}{Area(initiator\ region)}$$

Equation (Figure S10)

$$10x + 5y = 354.26 - 25.60$$

$$y = 19.38$$

$$x = 23 \quad y = 20$$

$$10x + 5y = 654.92 - 32.30$$

$$y = 41.70$$

$$x = 41 \quad y = 42$$

4. Synthesis of periodic copolymers

According to the alternating copolymer DPE-*alt*-DMBD obtained by living anionic polymerization, the next step is to functionalize it to obtain an innovative polymer structure. The main post-functionalization method is to transform the carbon chain structure of the polymer through hydrogenation. First, 3ml (0.480mol/L) of nickel naphthenate and 14ml (0.298mol/L) of are aged at 69 °C for 20 minutes, then 1g of sample is dissolved in 400ml of cyclohexane and heated to 60 °C. Finally, the nickel aluminum solution was added to the polymer solution to make the whole system react for 2 hours at 800 rpm and 3 MPa.

4.1 NMR spectra of copolymers of *pd*-DPP

Supplementary Figure S11. NMR spectrum of *pd*-DPP in CDCl₃

Hydrogenation degree =

$$1 - \frac{\dfrac{Area(\delta = 133.4 - 133.7\,(ppm))}{2}}{\dfrac{Area(\delta = 148.1 - 148.7)}{2} * 1.09}$$

Equation (Figure S11-1)

$$\text{Hydrogenation degree} = 1 - \cfrac{\cfrac{34}{2}}{\cfrac{104}{2}*1.09} = 70\%$$

$$1 - \cfrac{\cfrac{Area(\delta = 133.4 - 133.7\,(ppm))}{2}}{\cfrac{Area(\delta = 124.5 - 129\,(ppm))}{2}*1.09}$$

Equation (Figure S11-2)

$$\text{Hydrogenation degree} = 1 - \cfrac{\cfrac{34}{2}}{\cfrac{563}{10}*1.09} = 72.3\%$$

$$\text{Hydrogenation degree} = \cfrac{10N_D}{6N_{Sec-BuLi}} = \cfrac{Area(aromatic\ region)}{Area(initiator\ region)}$$

Equation (Figure S11-3)

$$\cfrac{2N_D + 10N_{M1} + 12N_{M2}}{6N_{Sec-BuLi}} = \cfrac{Area(Saturated\ region)}{Area(initiator\ region)}$$

$$10x = 543.81 - 14.58$$
$$2x + 10y_1 + 12y_2 = 869.77 - 77.41$$
$$x = 53 \quad y_1 = 5 \quad y_2 = 53$$

$$conv._{double\ bond} = \cfrac{y_2}{y} = \cfrac{53}{58} = 91\%$$

4.2 NMR spectra of copolymers of *pd*-DSS

Supplementary Figure S12. **NMR spectrum of *pd*-DSS in CDCl₃**

$$\text{Hydrogenation degree} = 1 - \cfrac{\cfrac{12.7}{2}}{\cfrac{98.7}{2}} \quad \cfrac{\cfrac{Area(\delta = 132.7 - 136.1\,(ppm))}{2}}{\cfrac{Area(\delta = 140.6 - 144.5)}{2}}$$

Equation (Figure S12-1)

$$\text{Hydrogenation degree} = 1 - \cfrac{\cfrac{Area(\delta = 132.7 - 136.1\,(ppm))}{2}}{\cfrac{Area(\delta = 124.2 - 130.2\,(ppm))}{10}} = 87.1\%$$

Equation (Figure S12-2)

$$\text{Hydrogenation degree} = 1 - \cfrac{\cfrac{Area(\delta = 132.7 - 136.1\,(ppm))}{2}}{(1 + 1/1.12)*10}$$

Hydrogenation degree = 1- $\dfrac{\dfrac{12.7}{2}}{\dfrac{910}{(1 + 1/1.12) * 10}}$ = 85.2%

4.3 NMR spectra of copolymers of *pd*-DEP

Supplementary Figure S13. NMR spectrum of *pd*-DEP in CDCl₃

$$\frac{10N_D}{2N_D + 7N_{y1} + 10N_{y2}} = \frac{Area(aromatic\ region)}{Area(Saturated\ region)}$$

$$\frac{10N_D}{N_{y2}} = \frac{Area(aromatic\ region)}{Area(Unsaturated\ region)}$$

$$10y_1 + 7y_2 = 1030.71 - 196.60 - 2 \times 70$$

Equation (FigureS13-1)

$$y_1 + y_2 = 71$$

$$conv._{double\ bond} = \frac{y_1}{y} = \frac{65}{71} = 91.5\%$$

$$y_1 = 65.7 \qquad y_2 = 6$$

Hydrogenation degree =1-

$$\frac{\dfrac{Area(\delta = 3.13 - 5.95(ppm))}{1}}{\dfrac{Area(\delta = 6.37 - 7.96(ppm))}{10} * 1.01} \quad \frac{6.28}{1}$$

Equation (Figure S13-2)

4.4 NMR spectra of copolymers of *pd*-DES

Hydrogenation degree =1- $\dfrac{\dfrac{700}{10} * 1.01}{} $ =91.1% $\dfrac{6.00}{}$

c) DPE-*alt*-1-PB

d) H-DPE-*alt*-1-PB

Ar-C₆H₆

a) DPE-*alt*-1-PB

b) H-DPE-*alt*-1-PB

Supplementary Figure S14. ¹H NMR spectrum of *pd*-DES in CDCl₃

Hydrogenation degree =1-

$$\frac{Area(\delta = 3.13 - 5.95(ppm))}{2}$$

Equation (Figure S14)

Hydrogenation degree =1-

$$\frac{Area(\delta = 6.37 - 7.96(ppm))}{1 * 5 + (1/1.06) * 10}$$

$$\frac{\dfrac{4.21}{2}}{\dfrac{1112 - 29.25}{1 * 5 + (1/1.06) * 10}} = 97.2\%$$

4.5 NMR spectra of copolymers of *pd*-DSEE

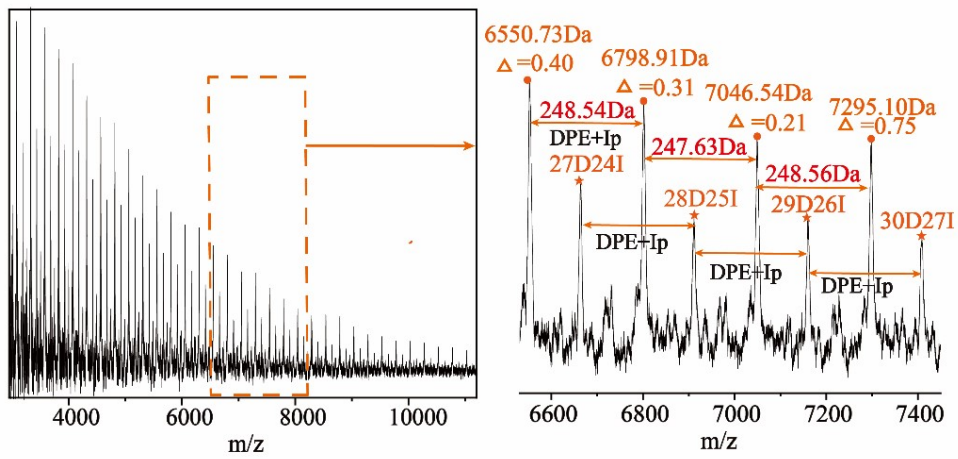**Supplementary Figure S15**. NMR spectrum of *pd*-DSEE in CDCl₃

Hydrogenation degree =1-

$$\text{Hydrogenation degree} = 1 - \frac{Area(\delta = 4.28 - 5.14(ppm))}{1}$$
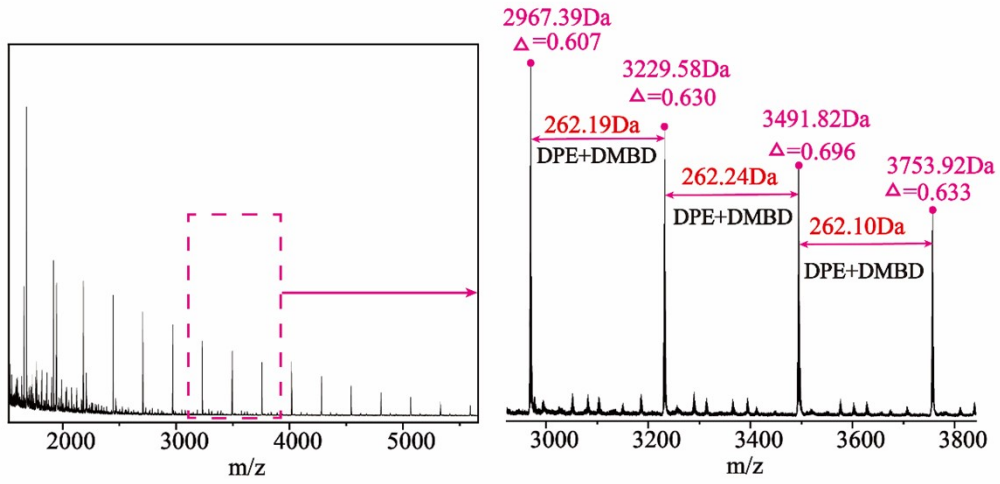
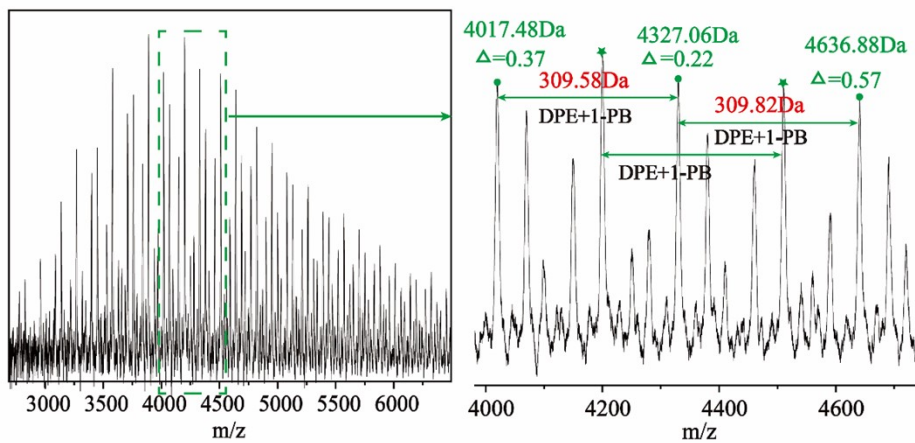$$= 1 - \frac{6.56}{1}$$

Equation (Figure S15)

5. MALDI-TOF-MS of copolymers
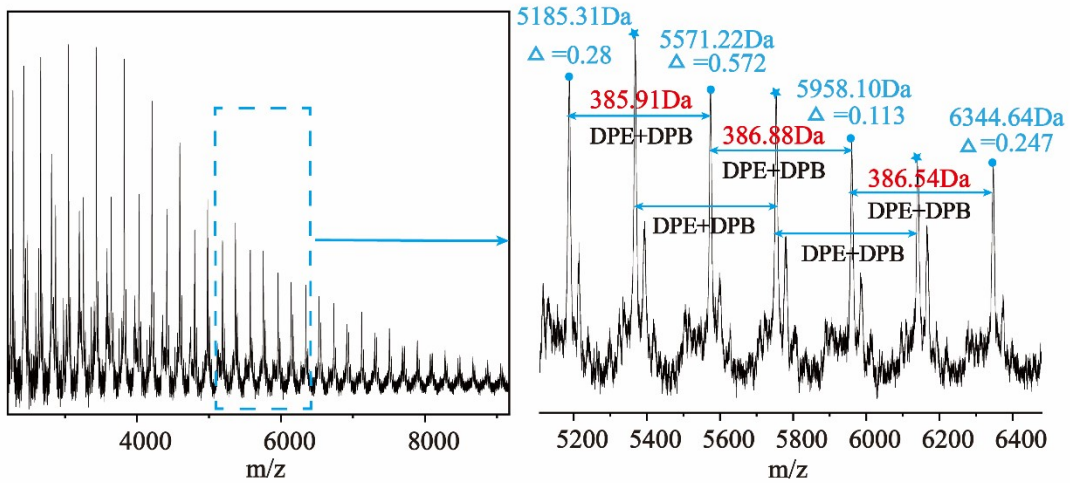
Supplementary Figure S16. MALDI-TOF-MS of Run1
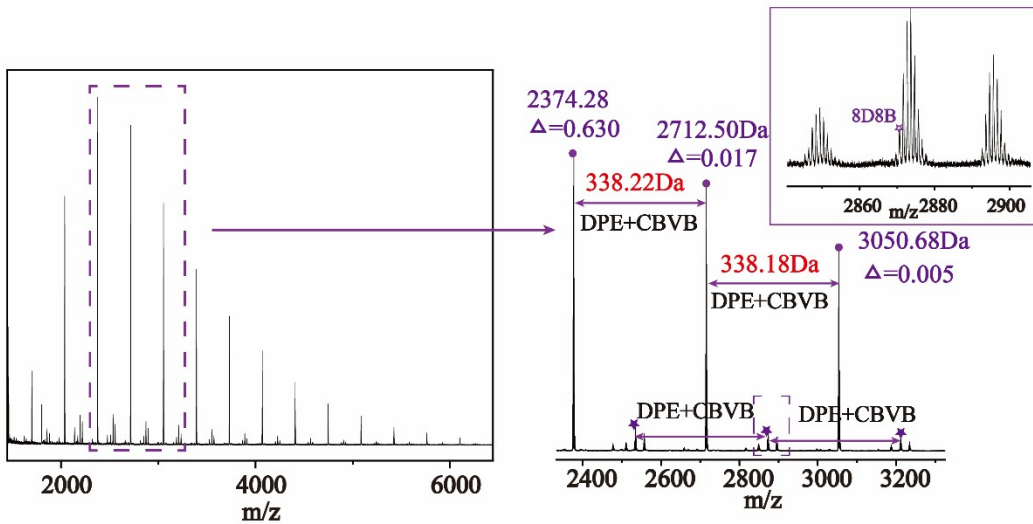

Supplementary Figure S17. MALDI-TOF-MS of Run 2
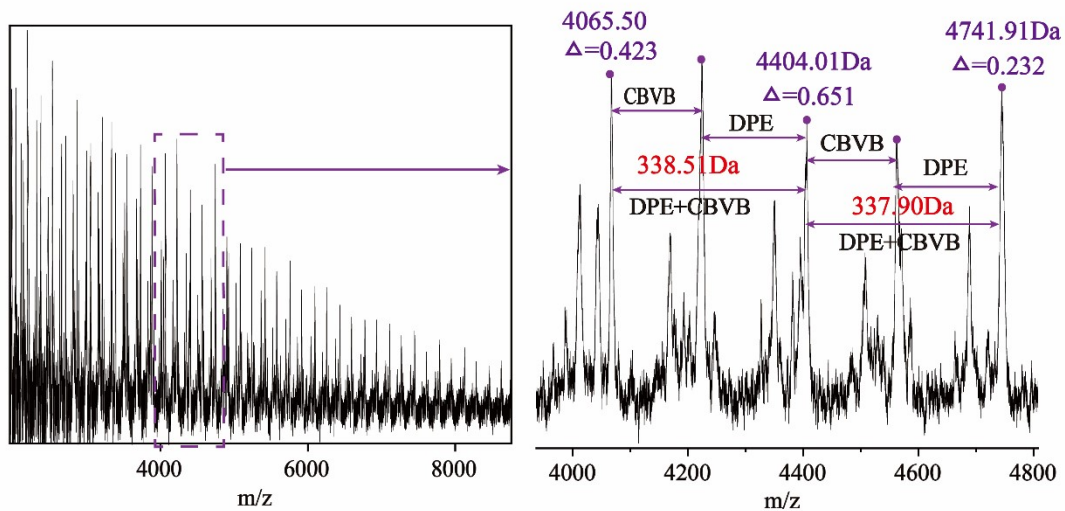

Supplementary Figure S18. MALDI-TOF-MS of Run 3

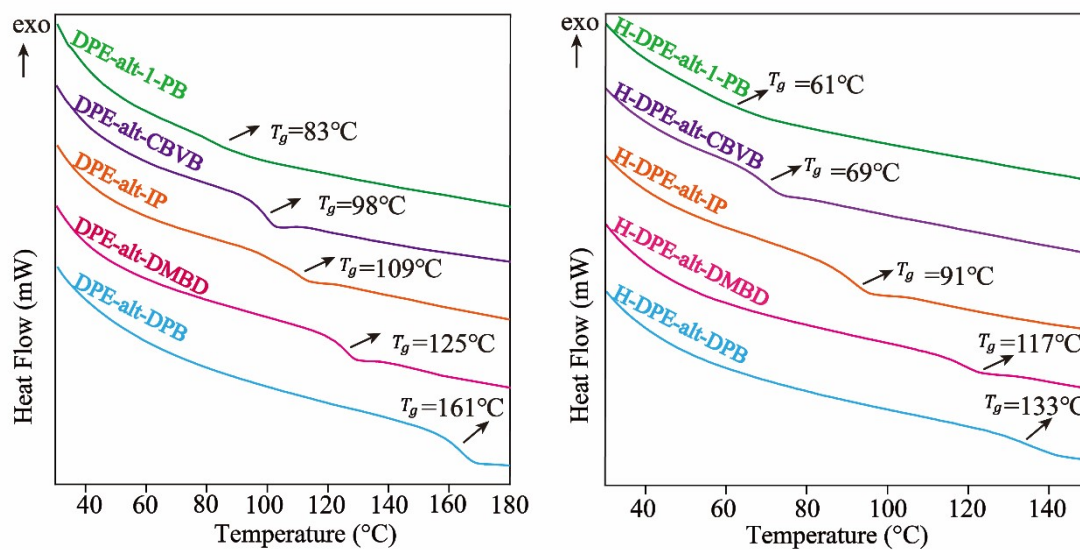**Supplementary Figure S19**. MALDI-TOF-MS of Run 4

Supplementary Figure S20. MALDI-TOF-MS of Run 5

Supplementary Figure S21. MALDI-TOF-MS of Run6

6. TGA curves of copolymers

Supplementary Figure S22. **DSC curves of base polymers, hydrogenated polymers**