

# Thermal Controlling of Multi-Block Sequence Using Anion-Migrated Ring-Opening Polymerization

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## Experimental Section

### Materials

Cyclopropyl phenyl ketone (TCI, 98%), p-tertbutyl benzaldehyde (Energy Chemical, 95%), benzene (Sinopharm, 99%), tetrahydrofuran (THF) (Sinopharm, 99%), *tert*-BuOK (Energy Chemical, 98%), methyltriphenylphosphonium bromide (Energy Chemical, 98%), n-butyllithium (n-BuLi, J&K Chemical, 1.6 M solution in hexanes) and sec-butyllithium (s-BuLi, J&K Chemical, 1.3 M solution in hexanes) were used as purchased.

The purification process for tetrahydrofuran (THF) and benzene were carried out under high vacuum conditions, as in the procedures detailed in our previous report.<sup>1</sup> sec-BuLi used in the polymerization was diluted by benzene, and then the concentrations of it were determined by titration: 1.0 mL sec-BuLi was added into 10.0 ml deionized water containing phenolphthalein, titrate with 0.02633 M dilute hydrochloric acid solution, repeat three times. According to  $C_{\text{HCl}}V_{\text{HCl}}=C_{\text{sec-BuLi}}V_{\text{sec-BuLi}}$ , the initiator concentration of each titration can be calculated and the average of three groups of initiator concentration is the accurate concentration ( $C_{\text{sec-BuLi}}=0.24$  M). Similarly, the concentrations of *sec*-BuLi as 0.35 M in C<sub>6</sub>D<sub>6</sub> were determined with the above method.

### Instruments

<sup>1</sup>H nuclear magnetic resonance (NMR, 5 wt%, CDCl<sub>3</sub>) spectra were recorded on a Bruker Avancell 400 MHz NMR spectrometer with (CH<sub>3</sub>)<sub>4</sub>Si (tetramethylsilane, TMS) as the internal standard. Size exclusion chromatography (SEC) was performed on a Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 mL min<sup>-1</sup> in THF at 30 °C after calibration using polystyrene standards. MALDI-TOF-MS analysis was performed on a Waters MALDI micro MX mass spectrometer (Waters, Milford, CT, USA) with 2-[(2E)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene] malonitrile (DCTB) and silver trifluoroacetate as dopants. Gas chromatography/triple quadrupole mass spectrometry (EI source, American Agilent Corporation, 7000B) and differential scanning calorimetry (DSC, TA, Q20), ultraviolet visible (UV-Vis, Shimadzu, UV-2600) and fluorescence detector (HITACHI, F-4600) were also carried out. Sample preparation details were mentioned in our previous report.<sup>1</sup>

## Synthesis of CPVB

The synthetic process of CPVB has been detail described in our previous report,<sup>2</sup> and the corresponding <sup>1</sup>H NMR spectrum was shown in Figure S2.

## Synthesis of *t*-St

Methyltriphenylphosphonium bromide (36.0 g, 0.10 mol) and dry THF (125 mL) were added into three-necked flask equipped with a magnetic stir bar under argon. Then the potassium tert-butoxide (12.2 g dissolved in 100 mL of THF, 0.11 mol) was added into the reaction flask through a constant pressure funnel at 0 °C under argon. After the reaction mixture was stirred for 2h, p-tertbutyl benzaldehyde (8 g, 0.05 mol) was dissolved in 125 mL THF, and drop-wise added into the flask. The mixture reacted under argon for 24 hours at room temperature, and then 10.0 mL H<sub>2</sub>O was added into the flask to quench the reaction. The mixture was poured into a separatory funnel and diluted with saturated sodium chloride solution and extracted with ether 3 times. Then the organic layer was collected and dried with anhydrous MgSO<sub>4</sub> overnight. The turbid fluid was filtrated and concentrated under reduced pressure, and then the flash column chromatography was taken twice using hexane. Finally, the monomers were purified by vacuum distillation and the obtained monomer as a transparent oil. The corresponding characterization was shown in Figure S1.

## Copolymerization of CPVB with *t*-St at 20 and 60 °C (*in situ* <sup>1</sup>H NMR monitoring)

All the polymerization processes were performed in a glovebox.

The copolymerization of CPVB with *t*-St at 20 and 60 °C are the same. CPVB (0.34 g, 2.36 mmol) and *t*-St (0.1 g, 0.625 mmol) in 3.5 mL of C<sub>6</sub>D<sub>6</sub> was initiated by adding 36.0 μL of sec-BuLi (0.350 M, 0.0126 mmol) at the ordinary temperature and the solution was immediately transferred to a sealed NMR tube. The whole process was monitored by *in situ* <sup>1</sup>H NMR spectroscopy at the ordinary temperature, and the NMR spectra were collected every other minute.

## Copolymerization of CPVB with *t*-St at 20 and 60 °C

All the polymerization processes were performed in a glovebox.

The copolymerization of CPVB with *t*-St at 20 and 60 °C are the same. CPVB (1.01 g, 7.0 mmol) and *t*-St (0.3 g, 1.88 mmol) in 12.0 mL benzene was initiated by adding 45.0 μL of sec-BuLi (0.24 M, 0.0108 mmol) at the ordinary temperature. After 3 days, the reaction was quenched by adding isopropanol (1.0 mL) and the

products were precipitated with excess methanol and dried to a constant weight in a vacuum oven. All the obtained products were white powder.

### **Copolymerization of CPVB with *t*-St (Run 3)**

CPVB (1.13 g, 7.85 mmol) and *t*-St (0.5 g, 3.13 mmol) in 18.0 mL benzene was initiated by adding 73.0  $\mu$ L of sec-BuLi (0.24 M, 0.035 mmol) at the ordinary temperature, and the mixture solution was well distributed into 2 vessels. Then, 2 vessels were immediately placed into a water bath at 20 °C. After 29.0 h, one of the vessels was terminated, and another was immediately placed in a water bath at 60 °C. After 4.5 h, the vessel was terminated. The products were precipitated with excess methanol and dried to a constant weight in a vacuum oven. All the obtained products were white powder.

### **Copolymerization of CPVB with *t*-St (Run 4)**

CPVB (3.38 g, 23.45 mmol) and *t*-St (1.0 g, 6.25 mmol) in 38.0 mL benzene was initiated by adding 146.0  $\mu$ L of sec-BuLi (0.24 M, 0.035 mmol) at the ordinary temperature, and the mixture solution was well distributed into 3 vessels. Then, 3 vessels were immediately placed into a water bath at 20 °C. After 9.0 h, one of the vessels was terminated, and the others were immediately placed in a water bath at 60 °C. After 5.5 h, one of the two vessels was terminated, and another was immediately placed in a water bath at 20 °C. After 15.0 h, the vessel was terminated. The products were precipitated with excess methanol and dried to a constant weight in a vacuum oven. All the obtained products were white powder.

### **Copolymerization of CPVB with *t*-St (Run 5)**

CPVB (3.38 g, 23.45 mmol) and *t*-St (1.0 g, 6.25 mmol) in 38.0 mL benzene was initiated by adding 146.0  $\mu$ L of sec-BuLi (0.24 M, 0.035 mmol) at the ordinary temperature, and the mixture solution was well distributed into 3 vessels. Then, 3 vessels were immediately placed into a water bath at 20 °C. After 9.5 h, one of the vessels was terminated, and the others were immediately placed in a water bath at 60 °C. After 1.0 h, one of the vessels was terminated, and the others were immediately placed in a water bath at 20 °C. This cycle was repeated two times (11.0 h-20 °C, 1.3 h-60 °C, 11.0 h-20 °C, 2.0 h-60 °C). All the products were precipitated with excess methanol and dried to a constant weight in a vacuum oven and the obtained products were white powder.

## Cyclization Procedures of the copolymers for Run 1 to Run 5

The whole process of the cyclization was performed under argon. As an example,  $\text{CF}_3\text{SO}_3\text{H}$  (0.68 mmol, 12.0 mL) was added to a three-necked flask of the copolymer (Run 1) solution containing copolymer (0.1 g) and cyclohexane (2.0 mL) under argon, and then the reaction temperature was increased to 50 °C. After stirring for 4 h, the mixture reaction was quenched with 1% aqueous solution of  $\text{Na}_2\text{CO}_3$  (1.0 mL), and the mixture solution was wash with water three times, the products were precipitated with sufficient methanol, isolating the filtrate and then dried under vacuum overnight, all the obtained cyclization products as light-yellow powder.

## Characterization of monomers

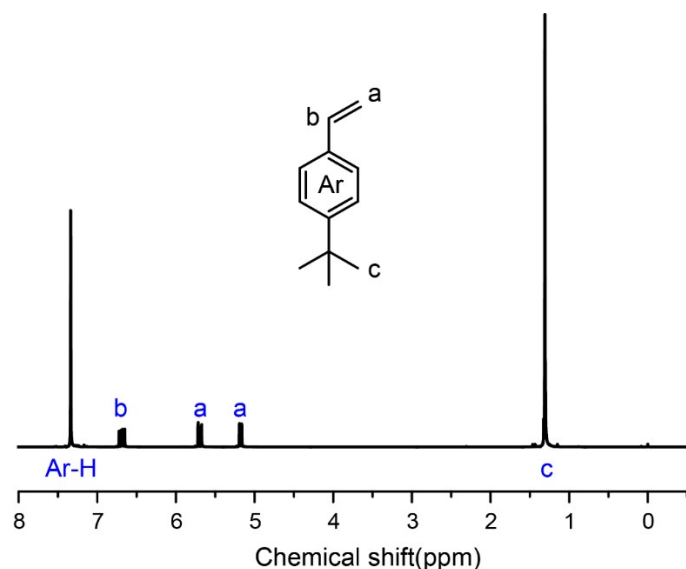


Figure S1. The  $^1\text{H}$  NMR spectrum of *t*-St.

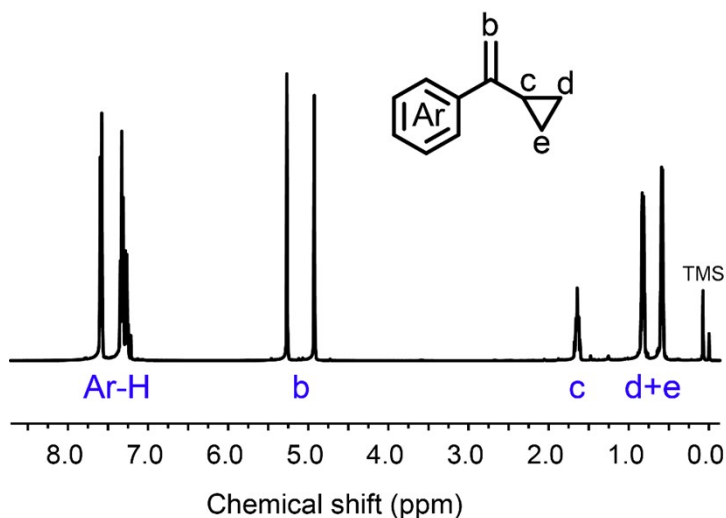


Figure S2. The  $^1\text{H}$  NMR spectrum of CPVB.

## Kinetic results of the copolymerization of CPVB with *t*-St

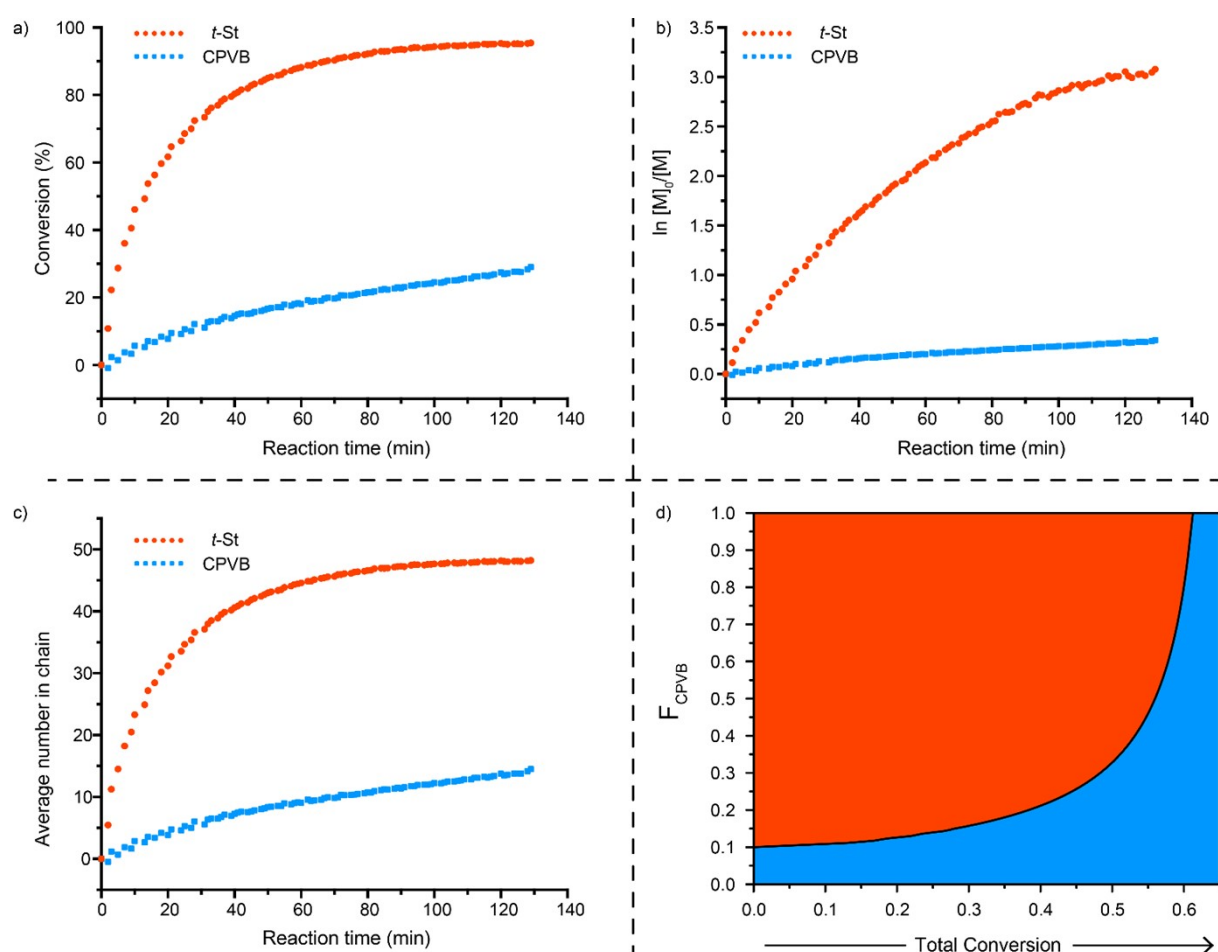


Figure S3. Kinetic results of the copolymerization of CPVB with *t*-St at 60 °C (in 1/1 feeding ratio).

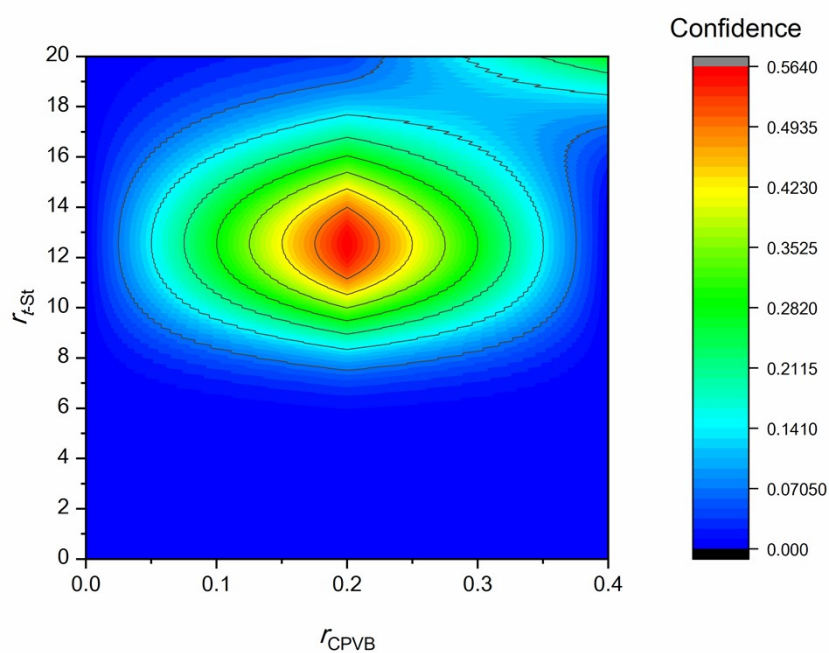


Figure S4. Confidence interval for the calculation of the reactivity ratio in 15/4 feeding ratio at 60 °C.

Owing to the area of vinyl-H overlapped with the area of Ar-H; thus, the chain ratio calculation method was listed as following (the area of CDCl<sub>3</sub> and the area of H<sub>2</sub>O had been deleted in Ar-H and in Saturated-H during the calculation):

$$4x+6y = \text{Area (Ar-H+Vinyl-H)} - \text{Area (CDCl}_3)$$

$$12x+6y = \text{Area (Saturated-H)} - \text{Area (H}_2\text{O)}$$

$$N_{\text{CPVB}} / N_{t\text{-st}} = y/x \quad \text{Equation S1}$$

x represents the number of *t*-St units in chain; y represents the number of CPVB units in chain.

$$160.13x+144.09y = M_n \quad \text{Equation S2}$$

$$y/x = N_{\text{CPVB}} / N_{t\text{-st}} \quad \text{Equation S2}$$

$$\text{Conversion (CPVB)} = N_{\text{CPVB in chain}} / N_{\text{CPVB design}} \quad \text{Equation S3}$$

$$\text{Conversion (}t\text{-St)} = N_{t\text{-St in chain}} / N_{t\text{-St design}} \quad \text{Equation S4}$$

$$N_{\text{CPVB design}} = 638 \quad N_{\text{CPVB design}} = 170 \text{ (Runs 1-2 and 4-5)}$$

$$N_{\text{CPVB design}} = 430 \quad N_{\text{CPVB design}} = 170 \text{ (Run 3)}$$

### <sup>1</sup>H NMR spectra of the obtained copolymers for Runs 1-3

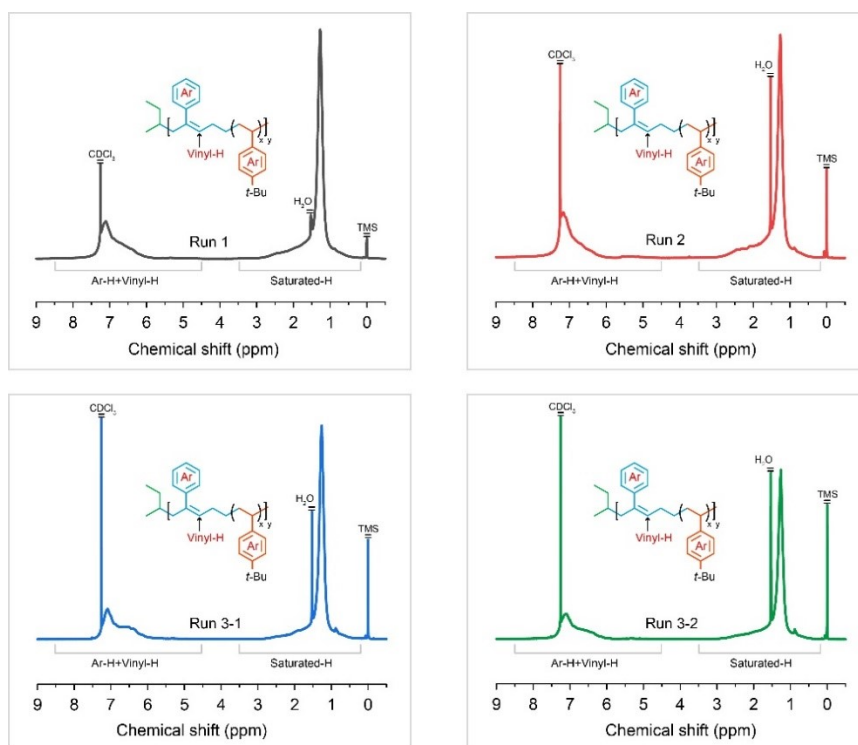


Figure S5. The <sup>1</sup>H NMR spectra of copolymers for Runs 1-3.

## <sup>1</sup>H NMR spectra of the obtained copolymers for Runs 4-5

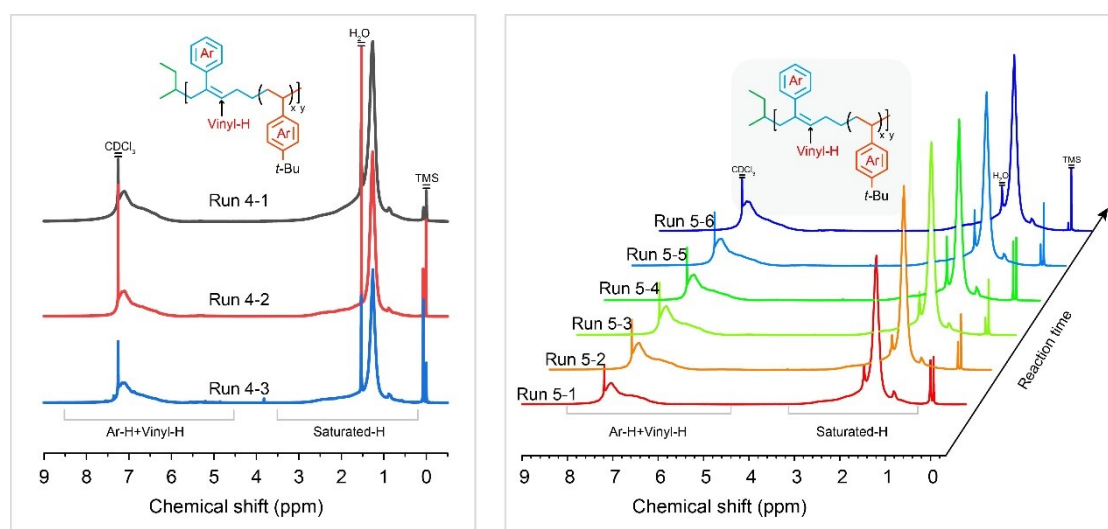


Figure S6. The <sup>1</sup>H NMR spectra of copolymers for Runs 4-5.

Table S1. The characterization results of the cyclized multi-block copolymers.

Sample	$M_n^a$ (kg/mol)	$M_n^b$ (kg/mol)	$D^b$	Block numbers	$T_g^c$ (°C)
C1	27.0	6.6	1.69	1	142.7
C2	30.0	4.8	1.62	1	126.9
C3	34.0	6.1	1.69	2	137.2
C4	22.7	6.4	1.70	3	137.6
C5	28.0	5.9	1.64	6	134.3
C6 <sup>d)</sup>	8.6	3.0	1.80	-	93.5

a) the molecular weight of the polymer from Run 1/Run 2/Run 3-2/Run 4-3/Run 5-6/PCPVB; a)  $M_n$  and  $D$  values of the cyclized polymers that were determined using SEC with PS as a standard, and the corresponding results were shown in Figure S7; c) glass transition temperature; d) the cyclized CPVB homopolymer was from our previous work in ref 3.



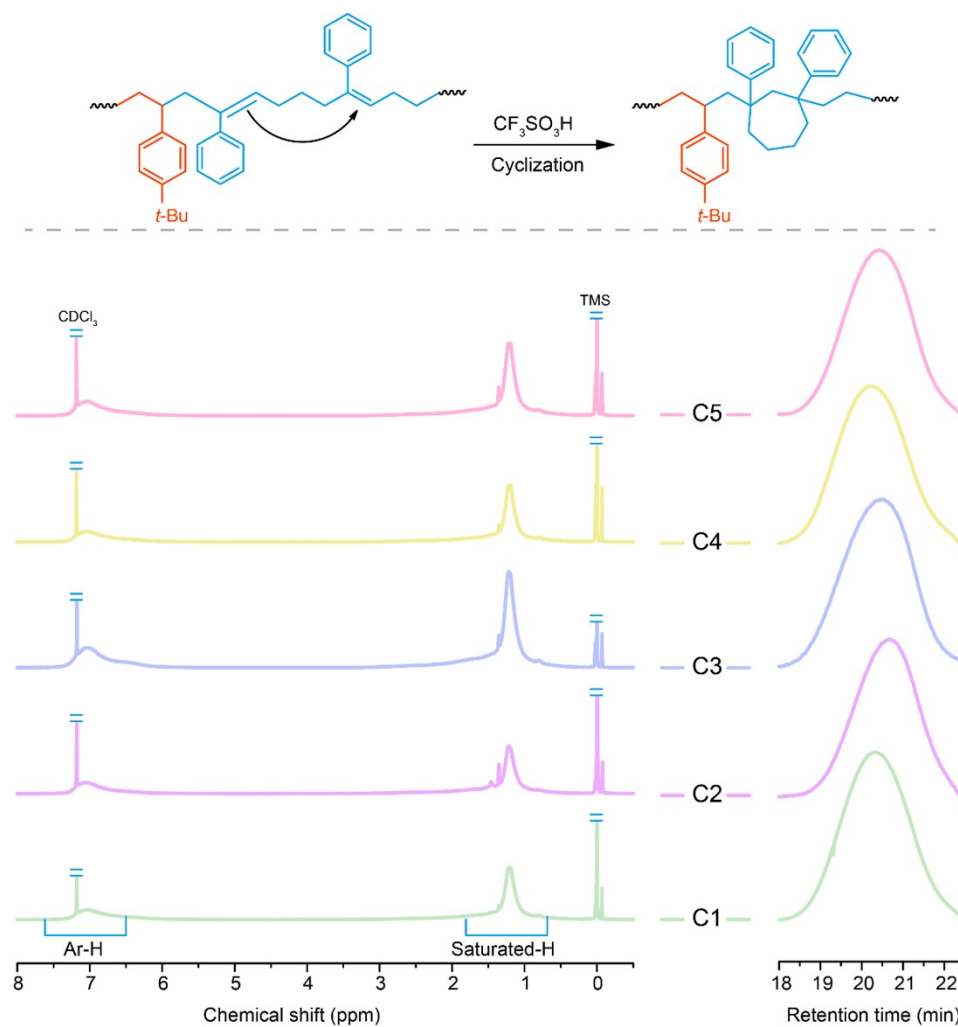


Figure S7. The  $^1\text{H}$  NMR spectra and GPC curves of the cyclized copolymers for C1-5.

### Diagram showing $T_g$ values and the DSC curves of the resulting products

Table S2. The characterization results of the ultimate obtained multi-block copolymers.

Sample	$M_n^{\text{a)}$ (kg/mol)	$D^{\text{a)}$	Comp. CPVB <sup>b)</sup>	Block numbers	$T_g^{\text{c)}$ ( $^{\circ}\text{C}$ )
PTS	23.0	1.07	0	1	150.0
PCPVB <sup>3</sup>	8.6	1.18	1.000	1	-4.5
Run 1	27.0	1.13	0.204	1	134.0
Run 2	30.0	1.29	0.353	1	109.0
Run 3-2	34.0	1.18	0.292	2	126.2
Run 4-3	22.7	1.22	0.242	3	117.4
Run 5-6	28.0	1.51	0.335	6	111.1

a)  $M_n$  and  $D$  values of the copolymers that were determined using SEC with PS as a standard, and the corresponding results were shown in Figure 3; b) the composition ratio of CPVB in chain for multi-block copolymers  $[N_{CPVB}/(N_{CPVB}+N_{t-st})]$ ; c) glass transition temperature and the DSC curves of the polymers were showed in Figures S8-10.

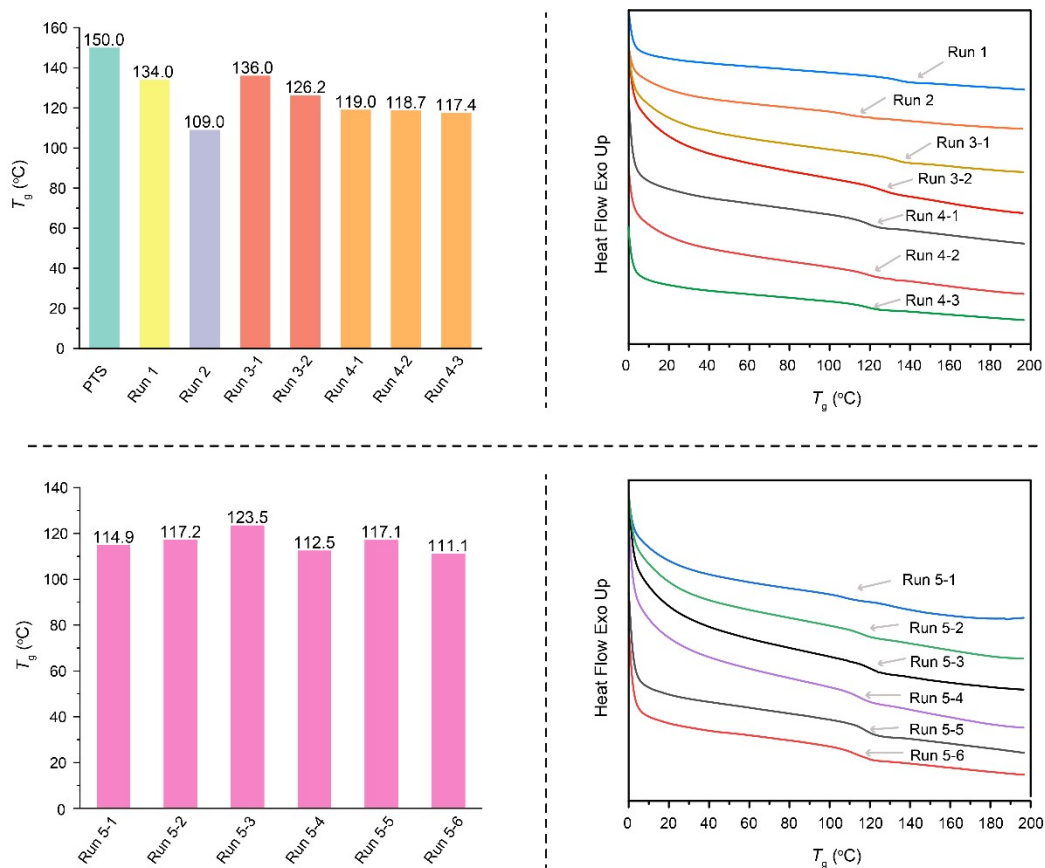


Figure S8. Diagram showing  $T_g$  values and the DSC curves of the resulting products.

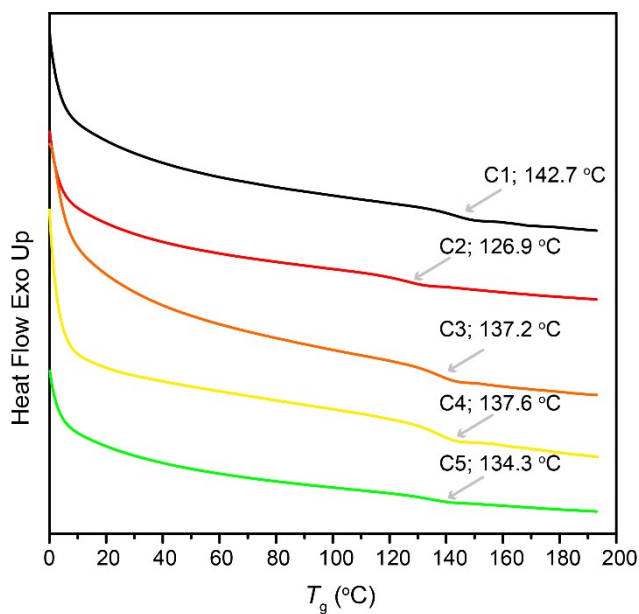


Figure S9. The DSC curves of the cyclized products for C1-C5.

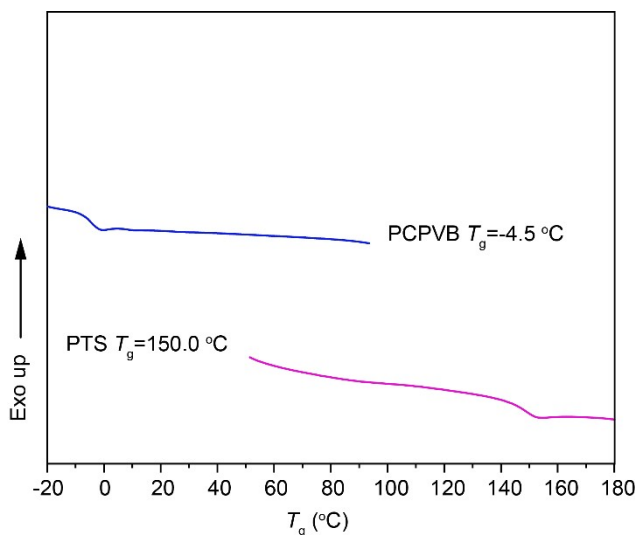


Figure S10. The DSC curves of the homopolymers.

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