

## Supporting information for

### Poly(trimethylene monothiocarbonate) from Alternating Copolymerization of COS and Oxetane: A Semicrystalline Copolymer

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**Materials and Methods.** Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in a nitrogen-filled glovebox. Following purification, materials were stored in a nitrogen-filled glovebox prior to use unless otherwise specified. Oxetane (OX) purchased from J&K Scientific LTD and distilled over  $\text{CaH}_2$  for use. Carbonyl sulfide (99.9%, ACS Grade, Alfa Aesar) was purchased from the APK (Shanghai) Gas Company LTD and used directly. (*R,R*)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride, (salen)CrCl, was purchased from Strem and used as received. Bis(triphenylphosphoranylidene) ammonium chloride (PPNCl), 4-dimethylaminopyridine (DMAP); 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from Aladdin Reagent Company (Shanghai) and used as received.. Trichlorobenzene (TCB), chloroform, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) was purchased from Aladdin Reagent Company (Shanghai) and distilled over  $\text{CaH}_2$ .

**Nuclear Magnetic Resonance (NMR).**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the resultant copolymers were performed on a Bruker Advance DMX (500 MHz) spectrometer. Chemical shift values were referenced to  $\text{CDCl}_3$  at 7.60 ppm for  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectra of the  $\text{CH}_2\text{Cl}_2$ -soluble part of the samples were recorded for estimating the polymer selectivity and the alternating degree. High-temperature  $^{13}\text{C}$  NMR spectra of the polymers were recorded on a Varian Mercury plus 300 spectrometer operating at 100 MHz in the pulse Fourier transform mode. 3.0 wt% Chromium(III) acetylacetonate of polymer solution was used as relaxation reagent, and relaxation delay of 3s was adopted. The spectra were recorded at 130 °C using the peak at downfield of *o*-dichlorobenzene- $d_4$  (132.60, 130.52 and 127.68 ppm) or  $d_6$ -DMSO (39.52 ppm) as internal references. Typically, 10000 scans were collected.

**Gel Permeation Chromatography (GPC).** Molecular weight and molecular weight distribution of the samples were measured by a PL 220 GPC instrument (Polymer

Laboratories Ltd.) at 150 °C in 1,2,4-trichlorobenzene. Universal calibration against narrow polystyrene standards was adopted.

**Differential Scanning Calorimetry (DSC).** The melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ) of the resultant copolymers were determined by using a TA Q200 instrument. The samples were heated from room temperature to 150 °C at a rate of 10 °C/min, kept for 2 min, and then cooled to -80°C in a cooling rate of -10 °C/min, finally heated from -80 °C to 150 °C at a heating rate of 10 °C/min. Before DSC test, samples were held at 140°C for 10 min and then at 110°C for 8 h under N<sub>2</sub> atmosphere.  $T_m$  and  $\Delta H_m$  were determined from the second heating curves. The crystalline point ( $T_c$ ) was from the first cooling curve.

**Wide X-ray Diffraction (XRD).** XRD profiles of the resultant copolymers were measured by using an Ultima IV instrument. Before test, samples were held at 140°C for 10 min and then at 110°C for 8 h under N<sub>2</sub> atmosphere to remove the heat history. The sample was scanned with the degree of angle from 2 $\theta$  equal to 5° to 60° at a rate of 3 °/min. The degree of crystallinity was calculated by the Jade 6.5 with XRD curve. During analysis, the result is credible when the residual error of fit is less than 9%, otherwise the peak should be found manually for adjusting the residual error of fit to less than 9%.

**Copolymerization of Carbonyl Sulfide and Oxetane.** A typical synthetic procedure of copolymerization is described as follows: The copolymerization of COS and OX was performed in a 10 mL autoclave equipped with a magnetic stirrer and a barometer. The autoclave was firstly dried at 110 °C in oven for at least 8 hours and transferred into the glovebox. The (Salen)CrCl complex, cocatalyst and OX were added into the autoclave successively. The autoclave was pressurized to appropriate pressure with COS. Afterwards, the autoclave was put into an oil bath with the preset temperature (e.g., 120°C). The reaction mixture was magnetically stirred for 4 hours at the preset reaction temperature. After copolymerization, COS was vented and the crude product was precisely weighted (W) and

then immersed in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The soluble part was characterized by  $^1\text{H}$  NMR spectroscopy in order to determine the mole ratio of the cyclic product (cyclic%) in the soluble part; The insoluble part was dried in vacuum over overnight and its weight ( $W_i$ ) recorded.

The mole ratio of cyclic product as well as copolymer selectivity could be estimated by the formula:

$$\begin{aligned} & \text{Mole ratio of cyclic product/copolymer} \\ &= \text{Mass fraction of cyclic product/copolymer} \\ &= (\text{cyclic}\% \times (W - W_i - W_c)) / W \end{aligned}$$

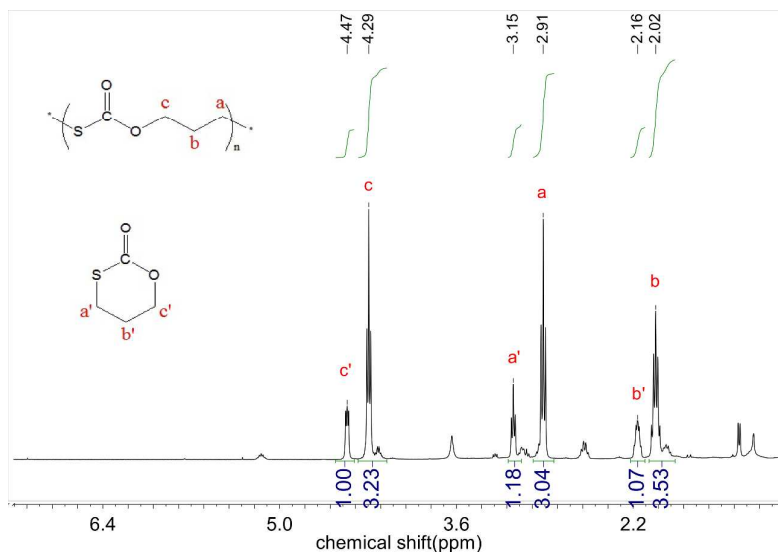
( $W_c$  is the total weight of the catalyst and catalyst promotor)

Subsequently, the insoluble part was dissolved in hot DMSO (ca.  $120^\circ\text{C}$ ) and precipitated in methanol. The white precipitate was collected and dried in vacuum at  $40^\circ\text{C}$  overnight. The obtained copolymer was analyzed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, GPC, DSC and XRD.

**Taking the sample of entry 1 in table 2 as example:**

$W = 0.2464$  g,  $W_i = 0.1931$ g,  $W_c = 0.0179$  g;

The  $^1\text{H}$  NMR spectrum of the  $\text{CH}_2\text{Cl}_2$ -soluble part of entry 1 in Table 2:



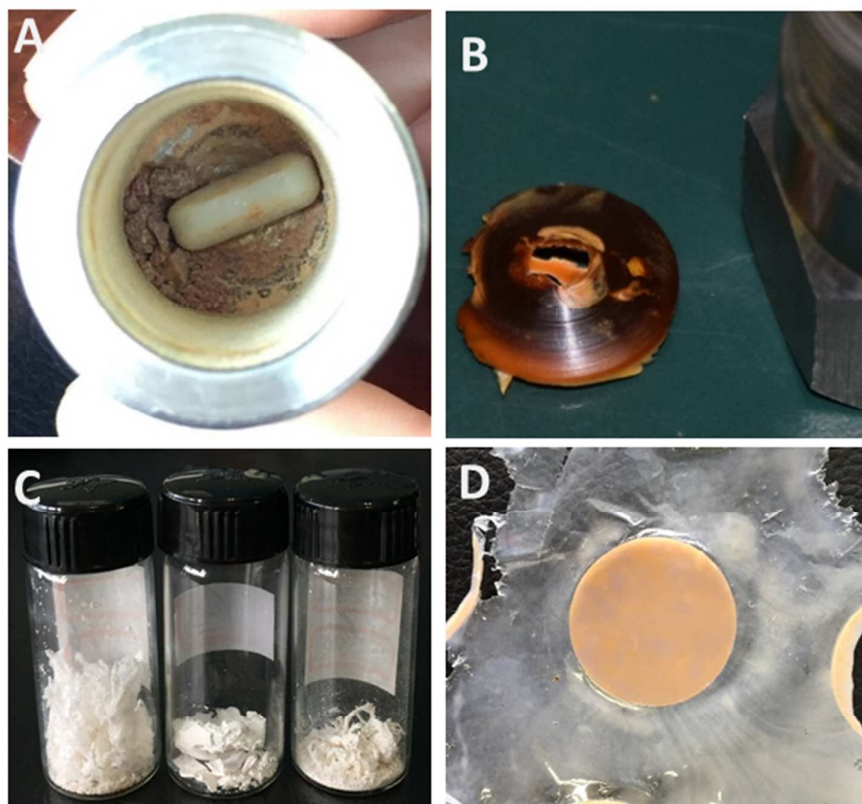
According to the integral area:

$$\text{cyclic\%} = (1 + 1.18 + 1.07) / ((1 + 1.18 + 1.07) + (3.23 + 3.04 + 3.53)) \times \% = 24.90\%$$

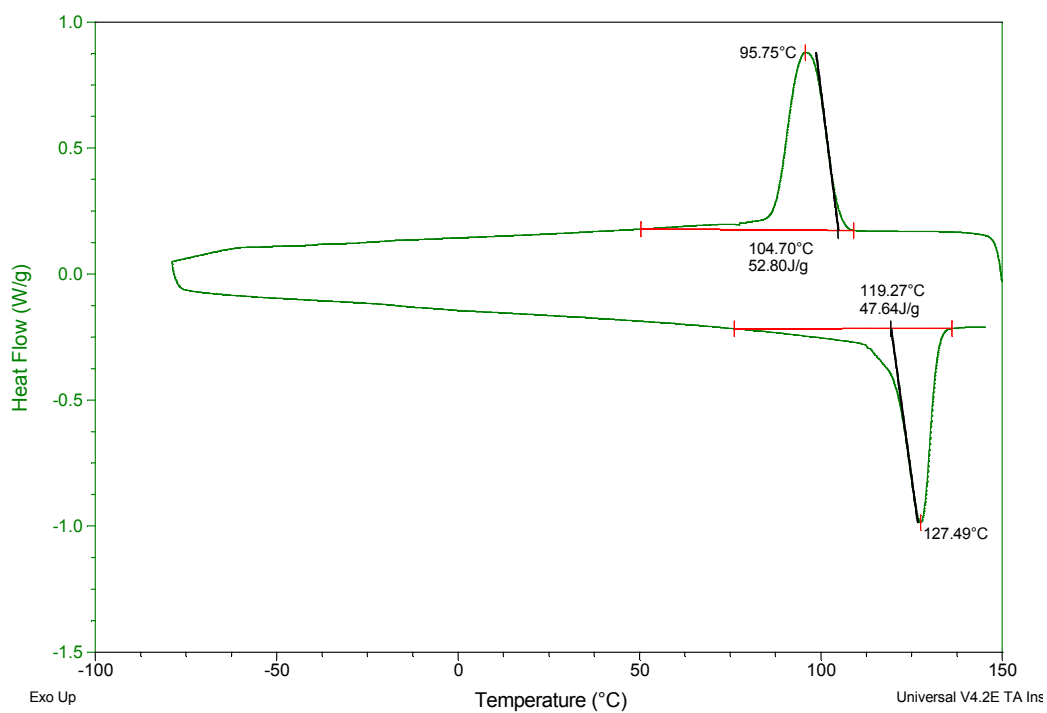
Hence,

Mole ratio of cyclic product = Mass fraction of cyclic product

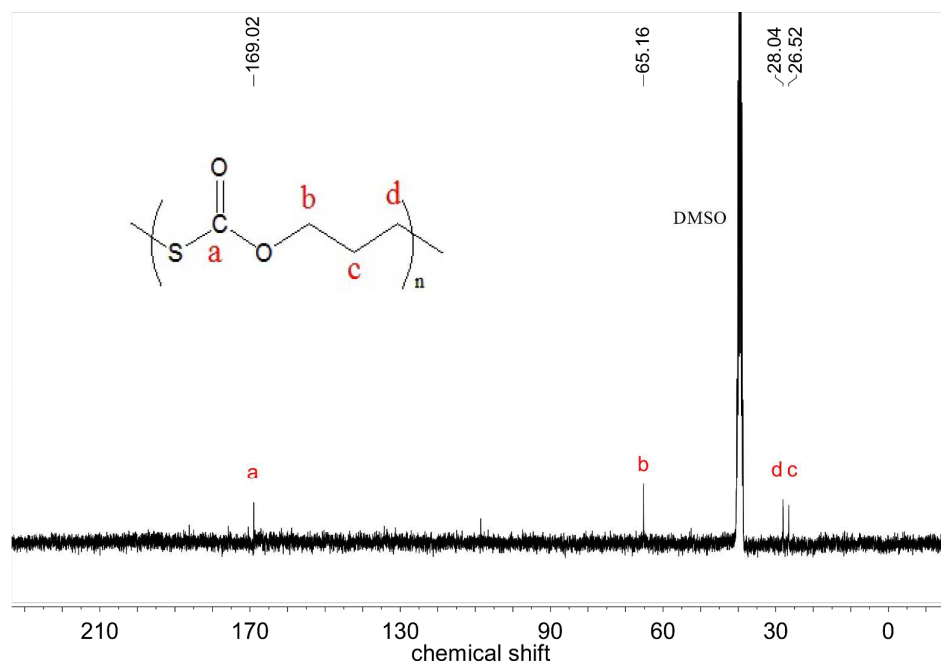
$$\begin{aligned} &= (\text{cyclic\%} \times (W - W_i - W_c)) / W \\ &= (24.90\% \times (0.2464 - 0.1931 - 0.0179)) / 0.2464 \\ &= 0.04 \text{ (4\%)} \end{aligned}$$



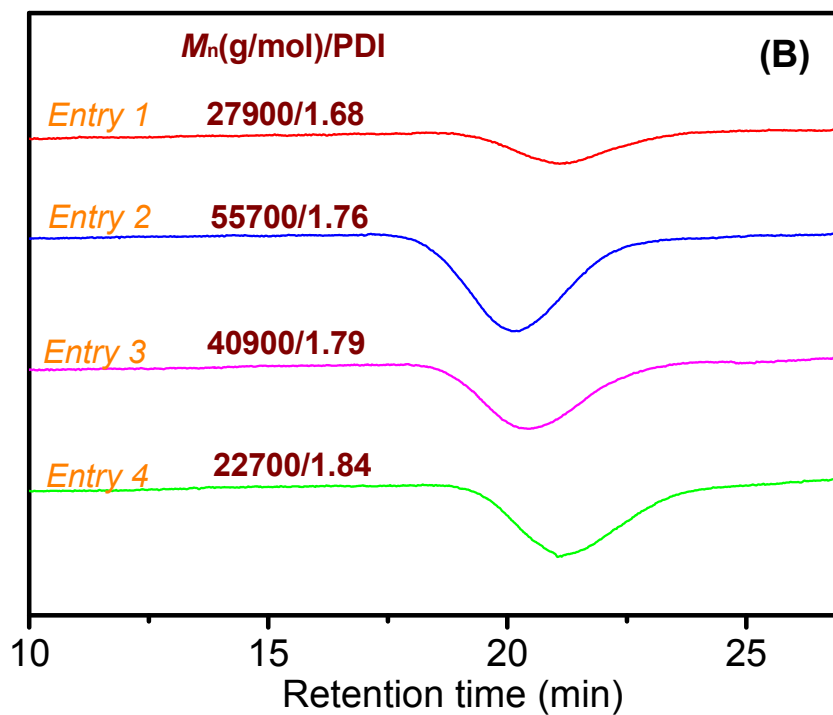
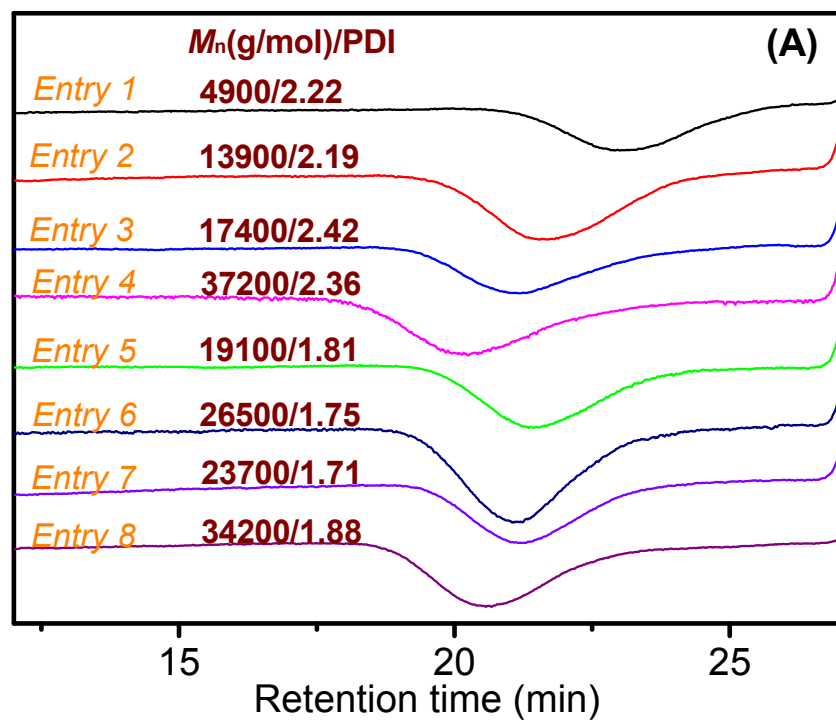
**Figure S1.** Photos of: (A) the crude product of COS/OX copolymerization with relative low  $M_n$  (entry 1, Table 1), (B) the crude product of COS/OX copolymer with high  $M_n$  (entry 4, Table 1); (C) the purified PTMMTCs (entries 2-4, Table 1); (D) PTMMTC wafer prepared by hot-press of the mixed purified copolymers (photographed by iPhone 6).



**Figure S2.** DSC curves of PTMMTC with a  $M_n$  of 4900 g/mol (entry 1, Table 1). Samples were annealed at 140°C for 10 min and decreased to and kept at 110°C for 8 h under  $N_2$  atmosphere to remove their thermal history.

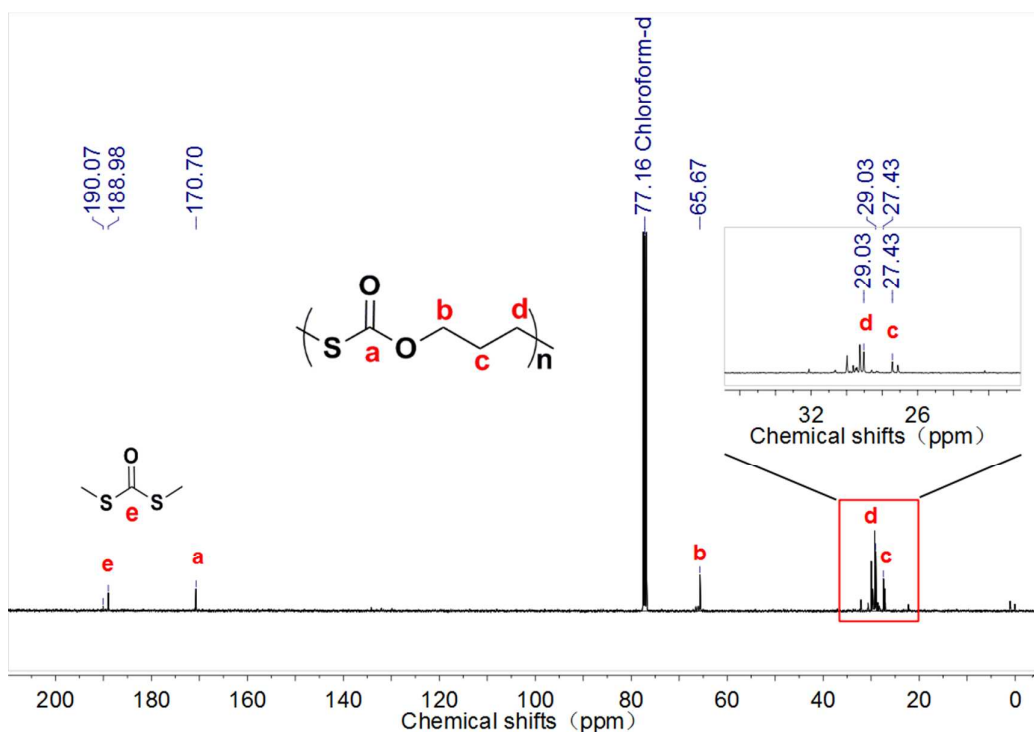


**Figure S3.** Selected  $^{13}C$  NMR spectrum of sample (entry 5, Table 1), 100 MHz, High-temperature using  $d_6$ -DMSO as the solvent, 130°C.

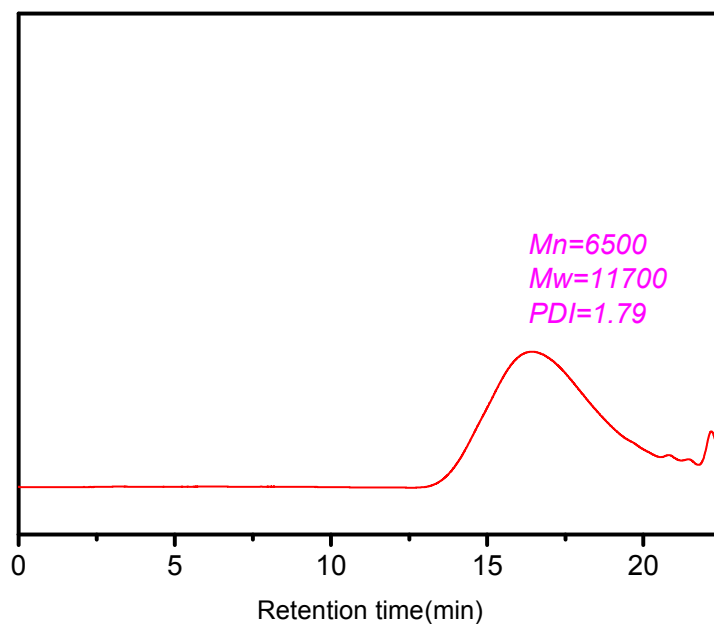


**Figure S4.** GPC curves of PTMMTCs in Table 1(A) and Table 2 (B).

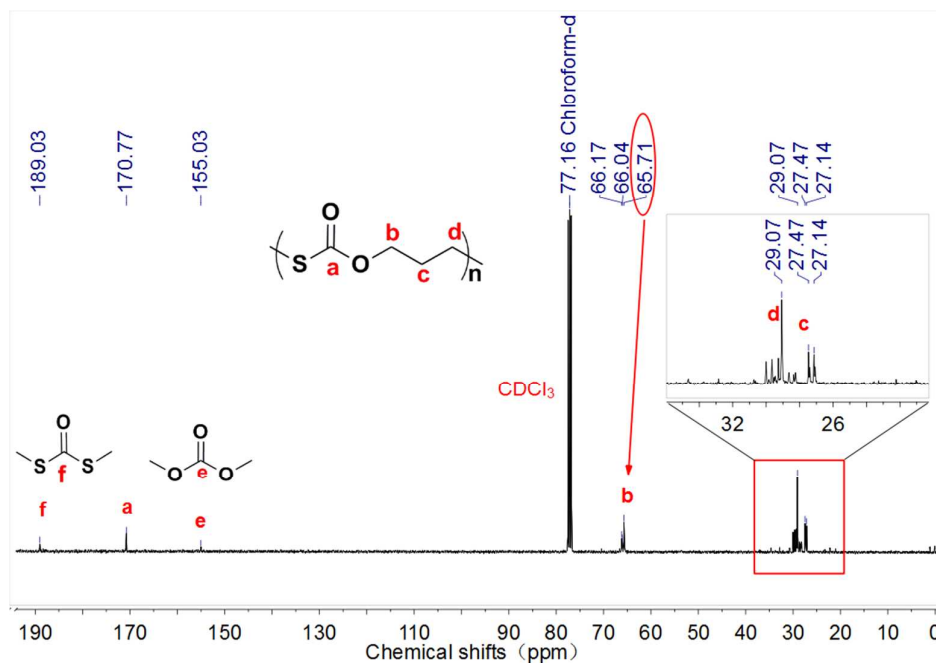




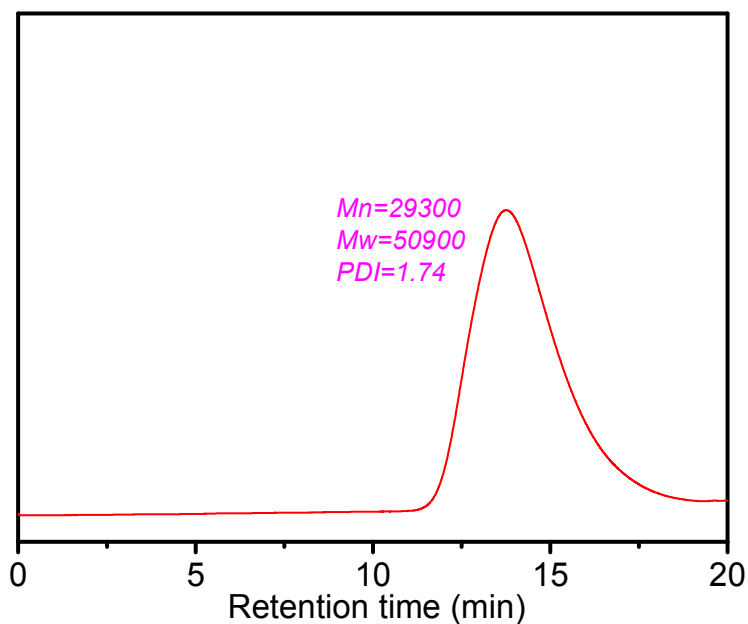
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of the soluble part in  $\text{CH}_2\text{Cl}_2$  (74wt% of the crude product, entry 8 in Table 1) (500 MHz,  $\text{CDCl}_3$ ). O/S ER occurred because the unit e generated, which was proposed from the coupling of COS with trimethylene sulfide.



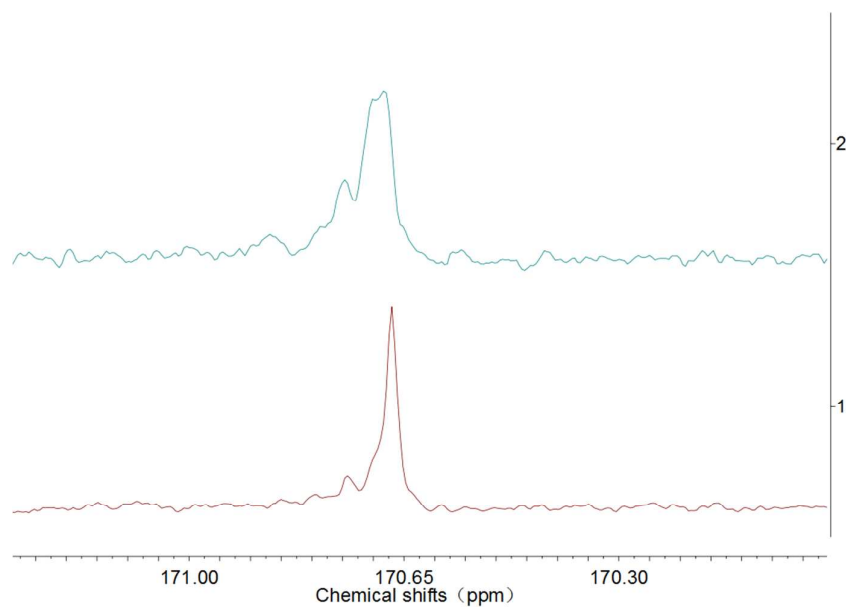
**Figure S6.** GPC curve of the soluble part of entry 8 in Table 1 (74% of the crude product,), THF was used as a solvent for GPC test, monodispersed polystyrene used as the standard.



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of the soluble part (entry 5 in Table 2) (500 MHz,  $\text{CDCl}_3$ ). O/S ER occurred because the generation of unit **e** which was proposed from the coupling of  $\text{CO}_2$  with trimethylene oxide, and unit **f** that which was proposed from the coupling of COS with trimethylene sulfide.



**Figure S8.** GPC curve of the copolymer of entry 5 in Table 2, THF was used as a solvent for GPC test, monodispersed polystyrene used as the standard.



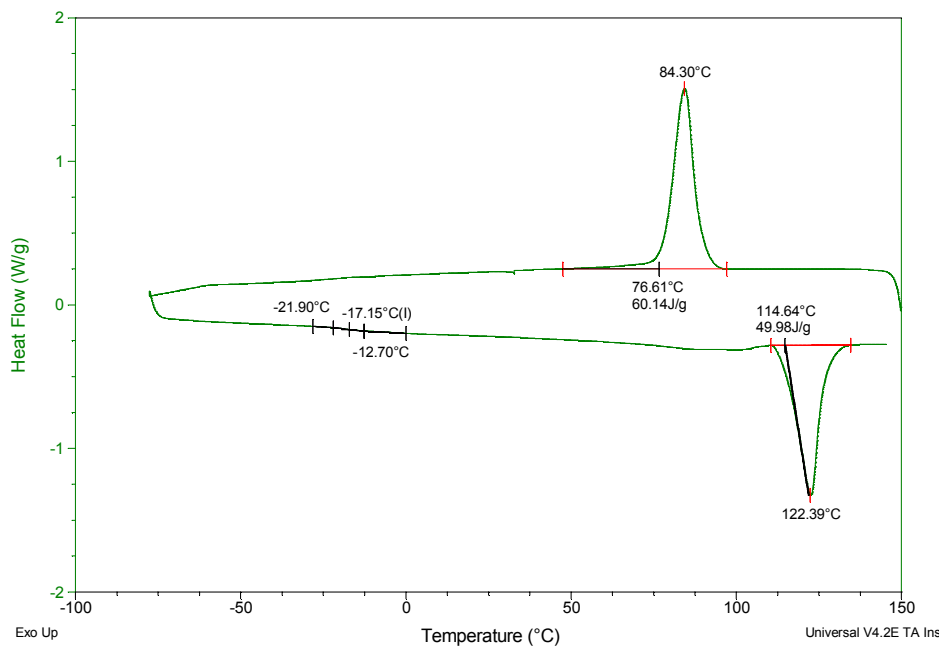
**Figure S9.** Carbonyl region of  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ) of (1) soluble part of entry 8 in Table 1 and (2) entry 5 in Table 2. The split of carbonyl region of two samples indicated the occurrence of O/S ER.

**Figure S10.** DSC curves of PTMMTC in Table 1, determined by DSC in a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. Samples were annealed at  $140^\circ\text{C}$  for 10 min and kept at

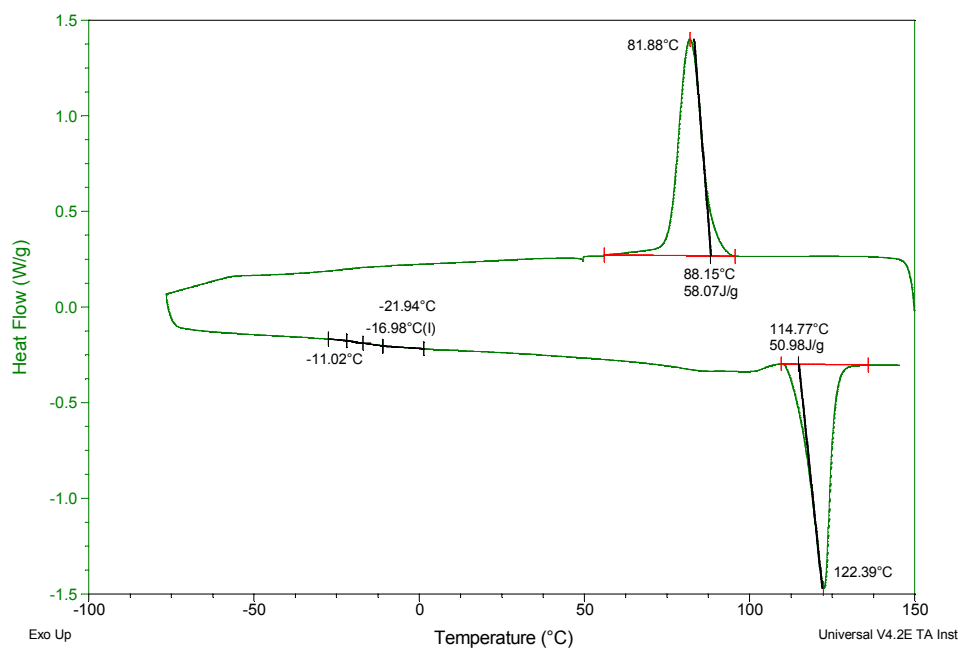
110°C for 8 h under N<sub>2</sub> atmosphere to remove their thermal history.

**Entry 1:** see Figure S2.

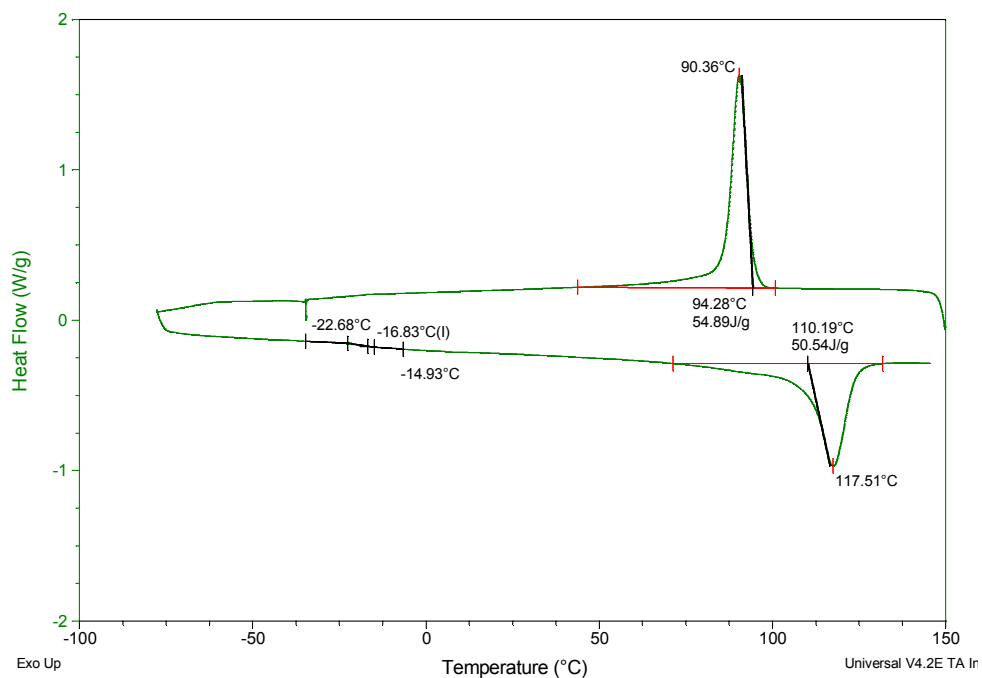
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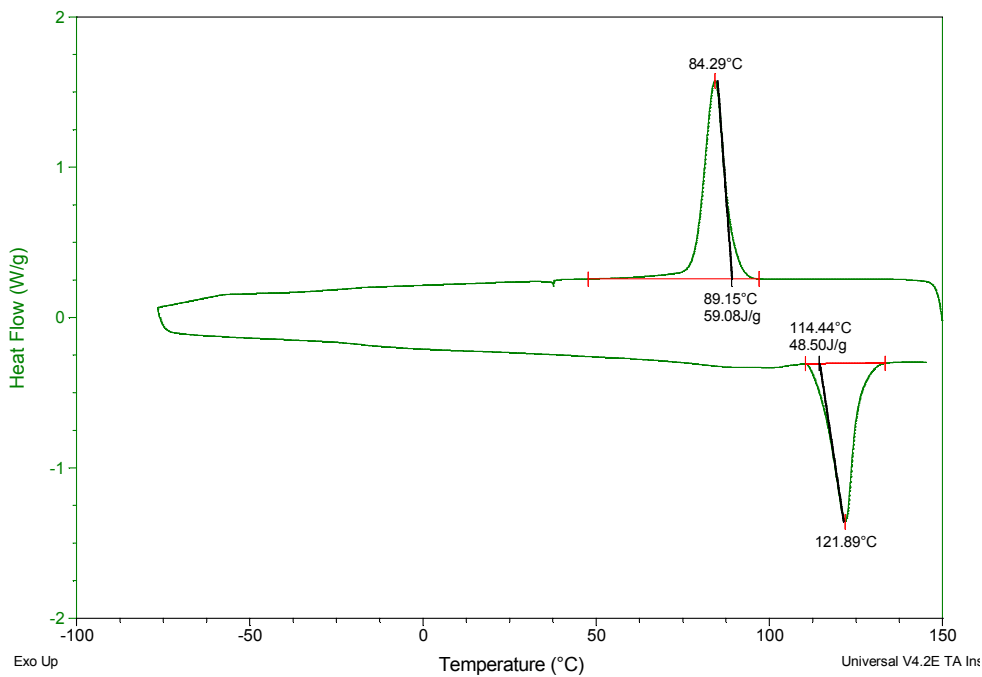
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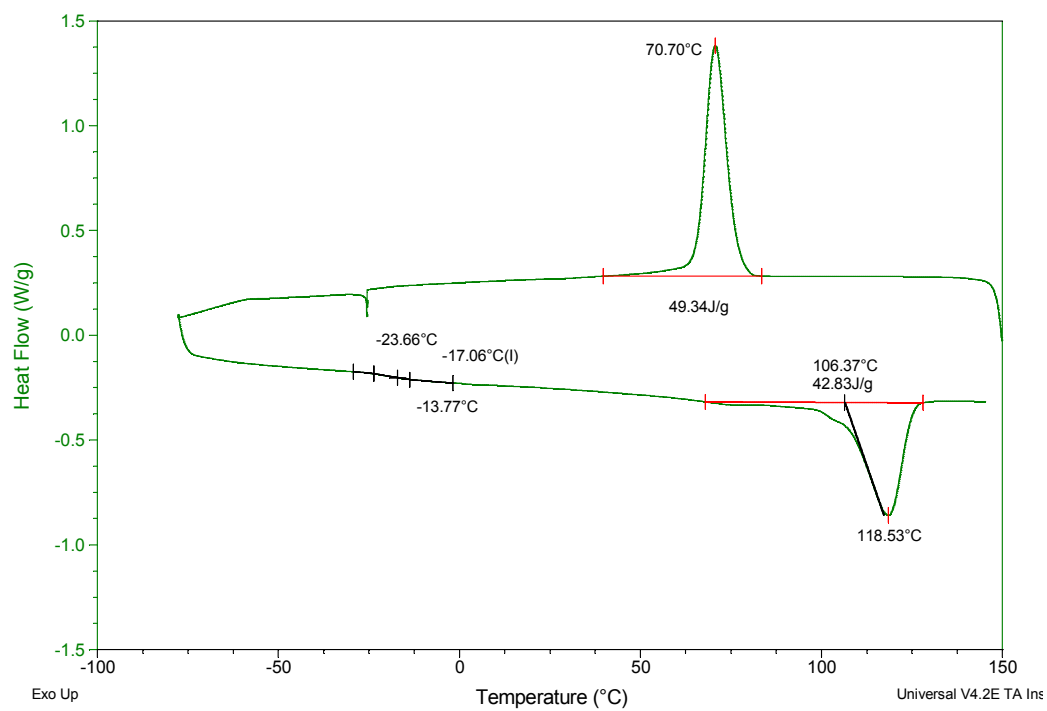
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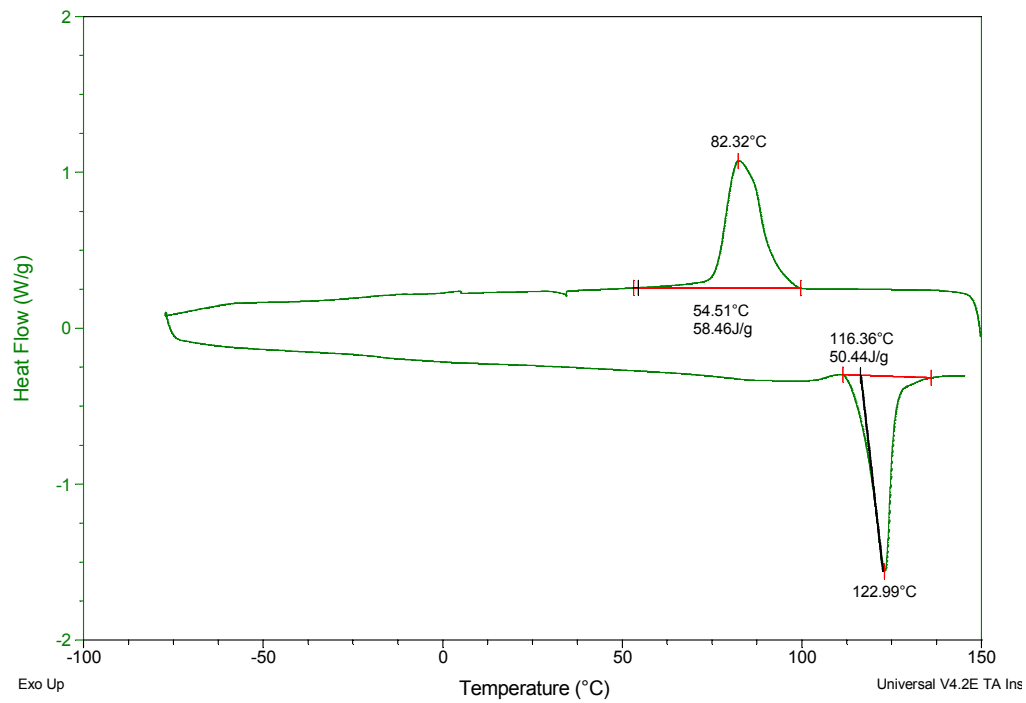
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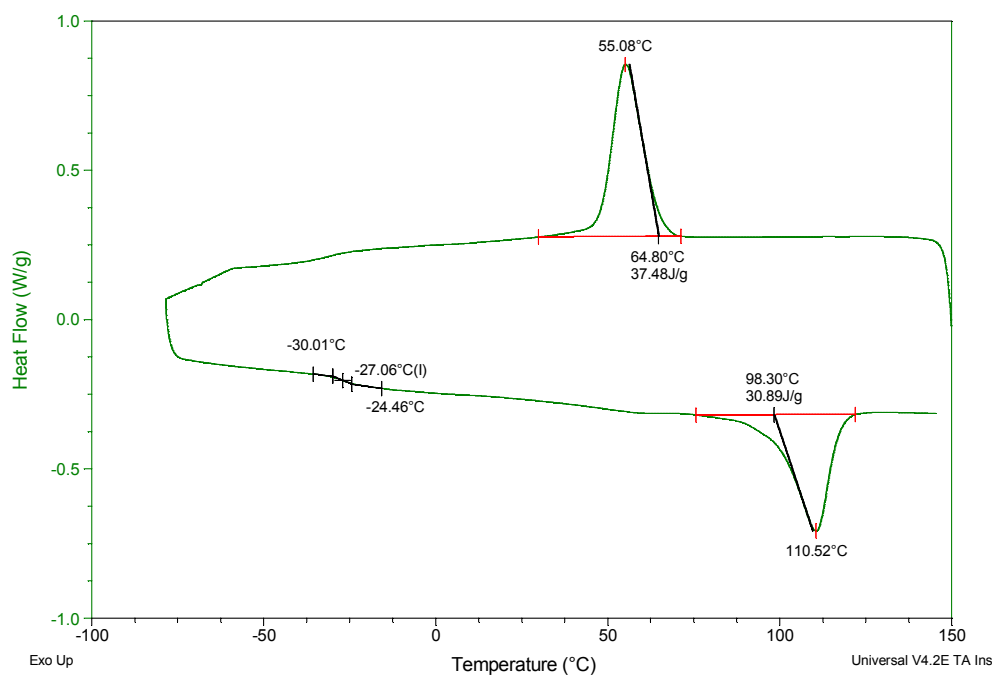
**Entry 6:**



### Entry 7:

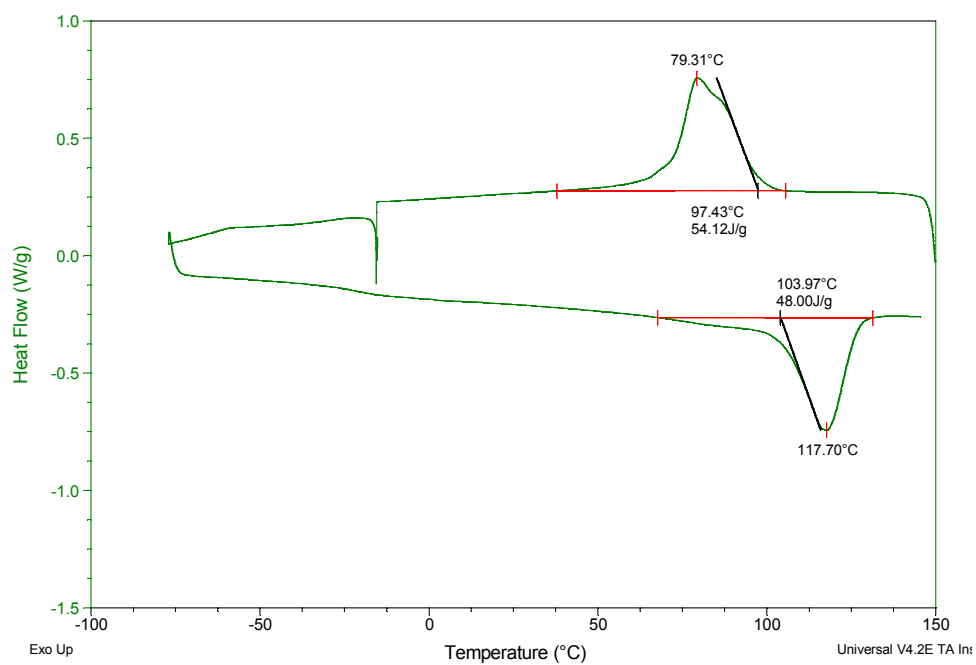


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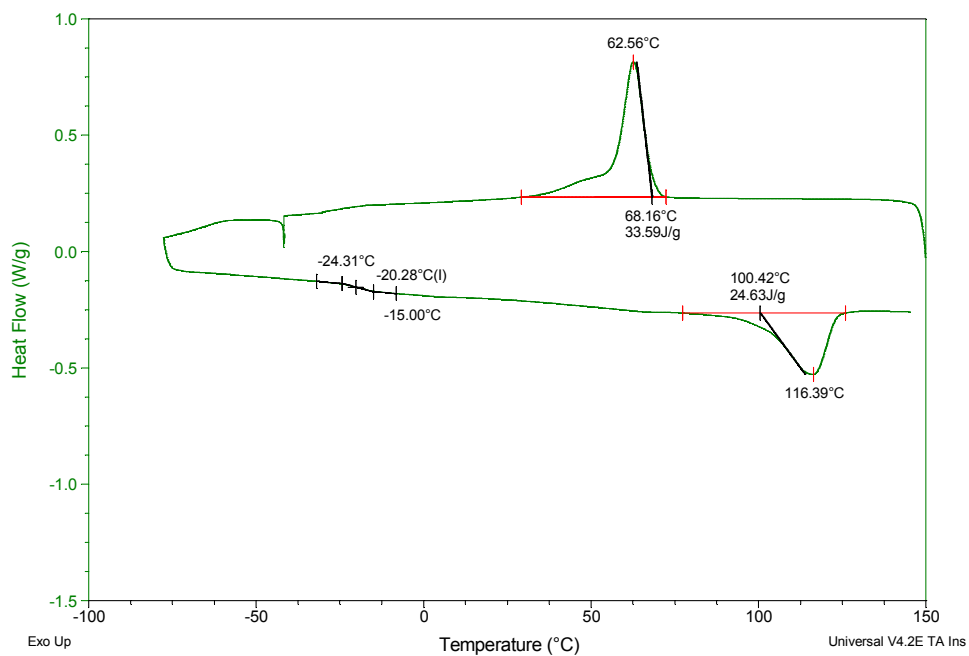


**Figure S11.** DSC curves of PTMMTC in Table 2, determined by DSC in a heating rate of 10°C/min under N<sub>2</sub> atmosphere. Samples were annealed at 140°C for 10 min and kept at 110°C for 8 h under N<sub>2</sub> atmosphere to remove their thermal history.

### Entry 1:

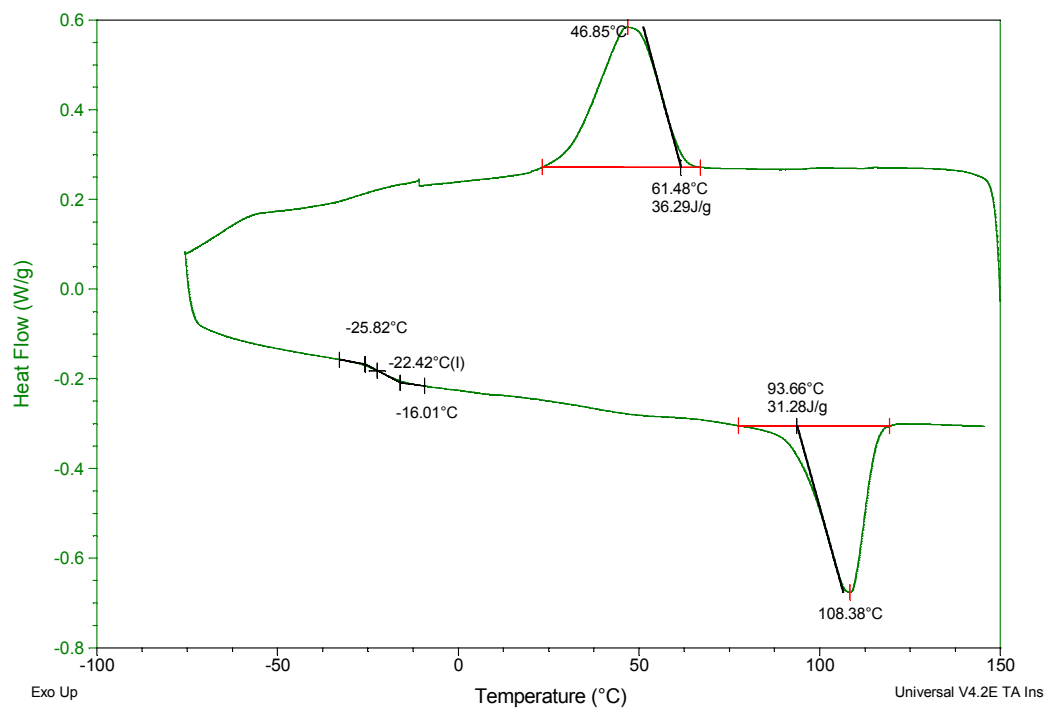


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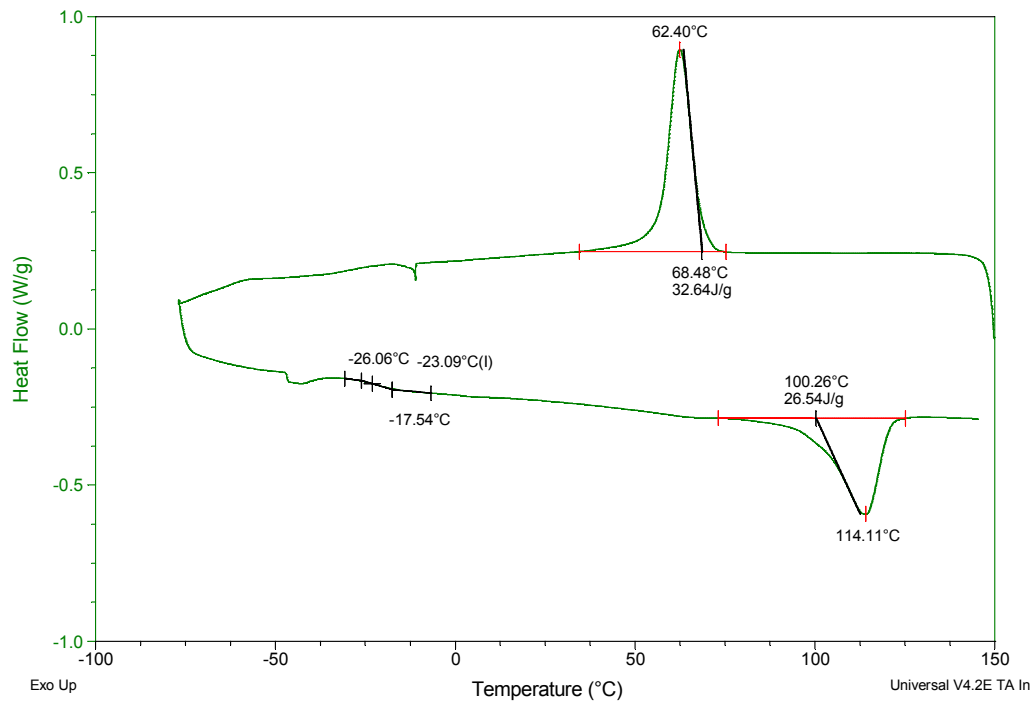


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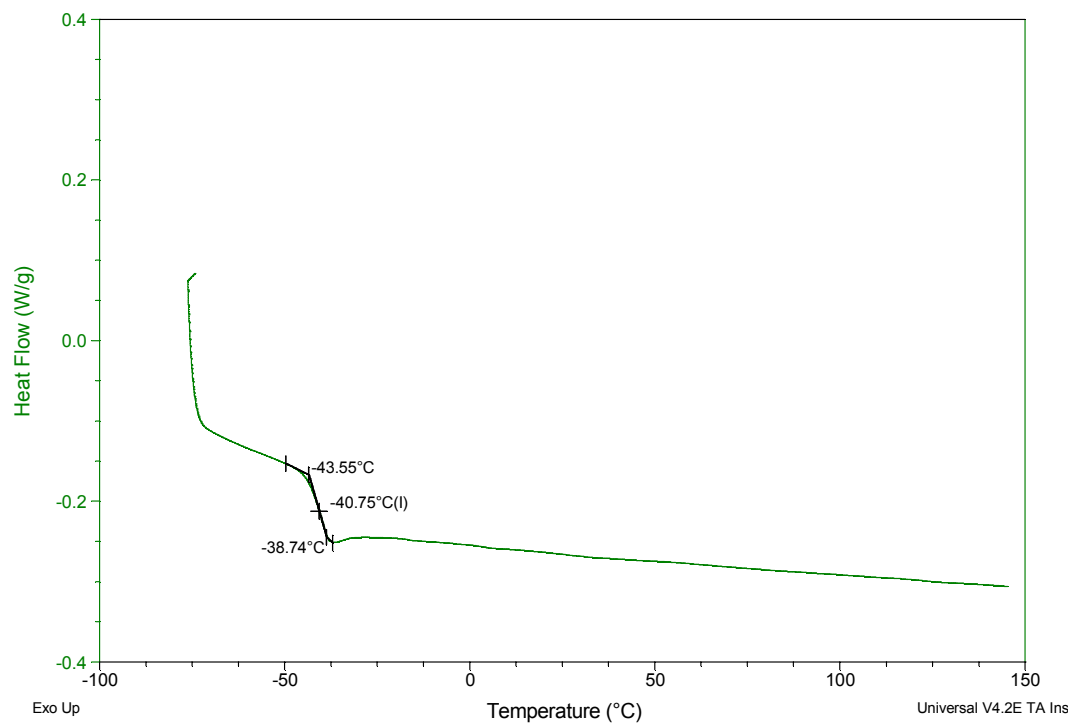




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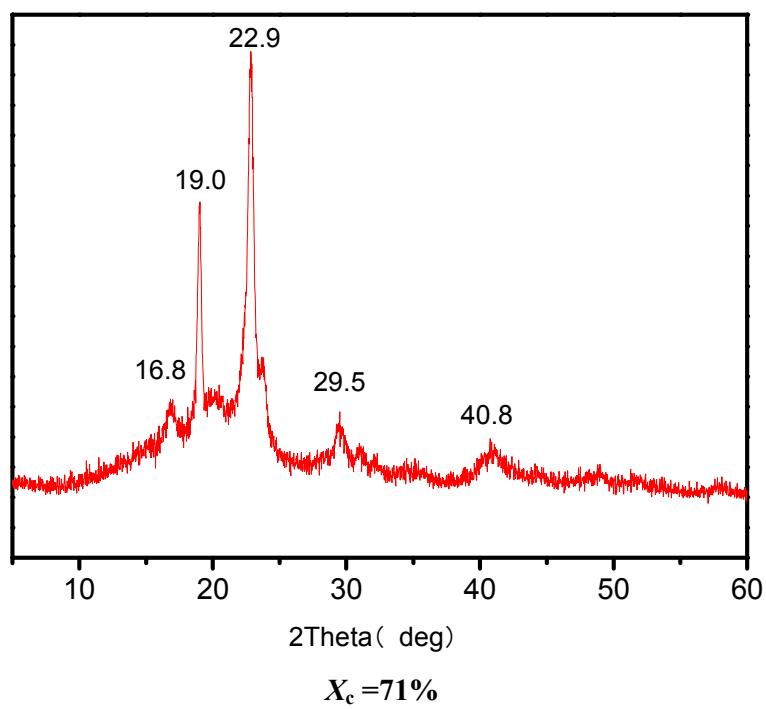


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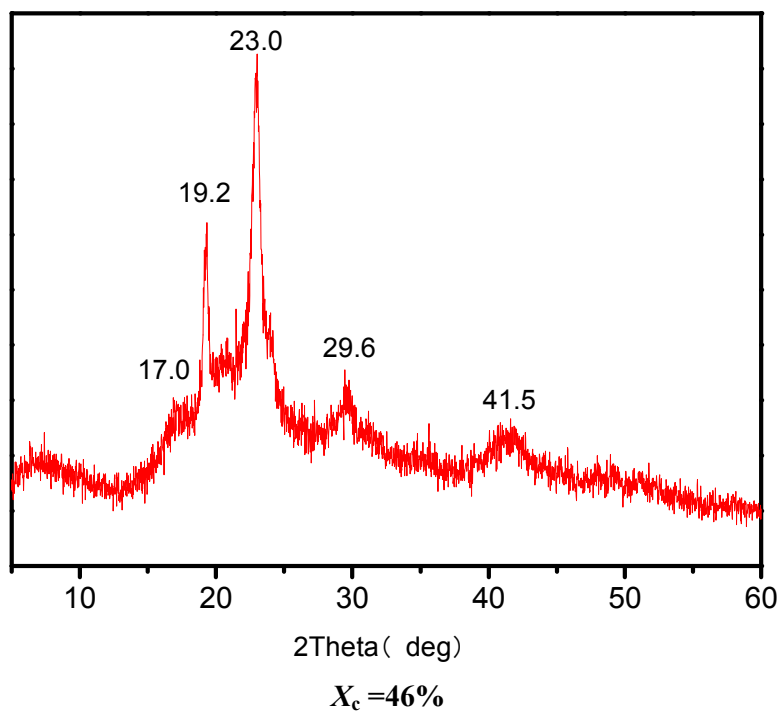


**Figure S12.** Powder XRD profiles of annealed PTMMTCs in Tables 1 and 2.

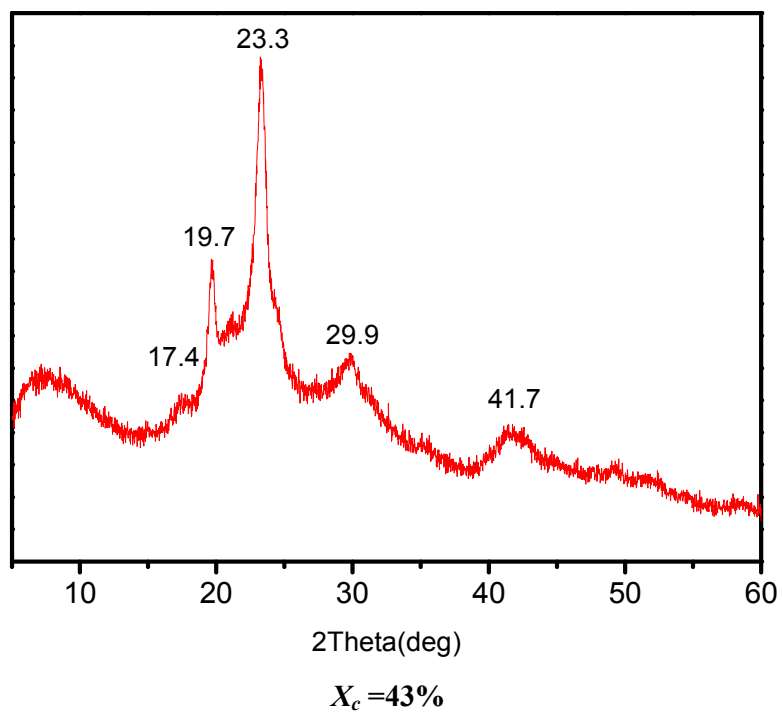
**Entry 1 in Table 1:**



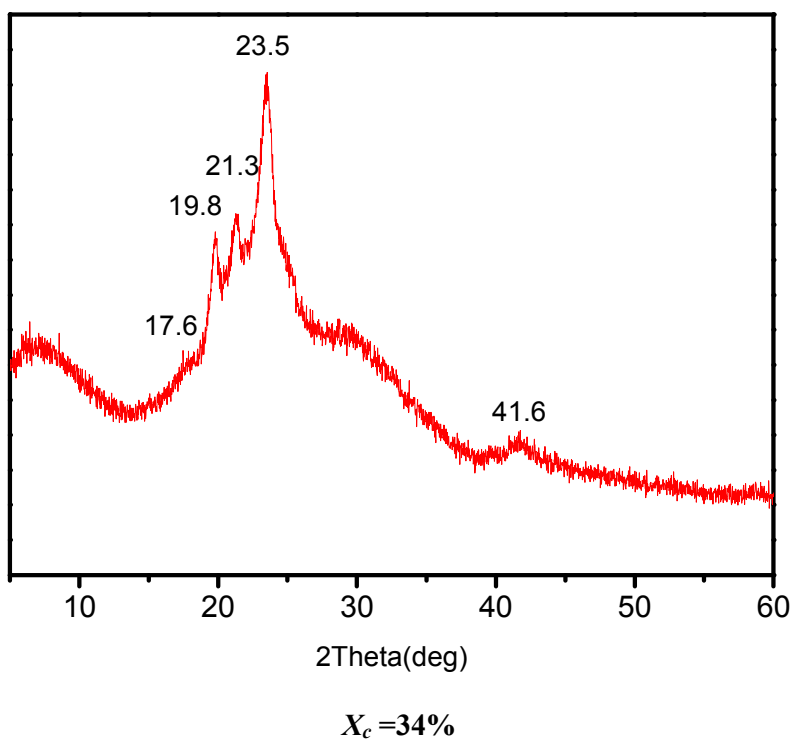
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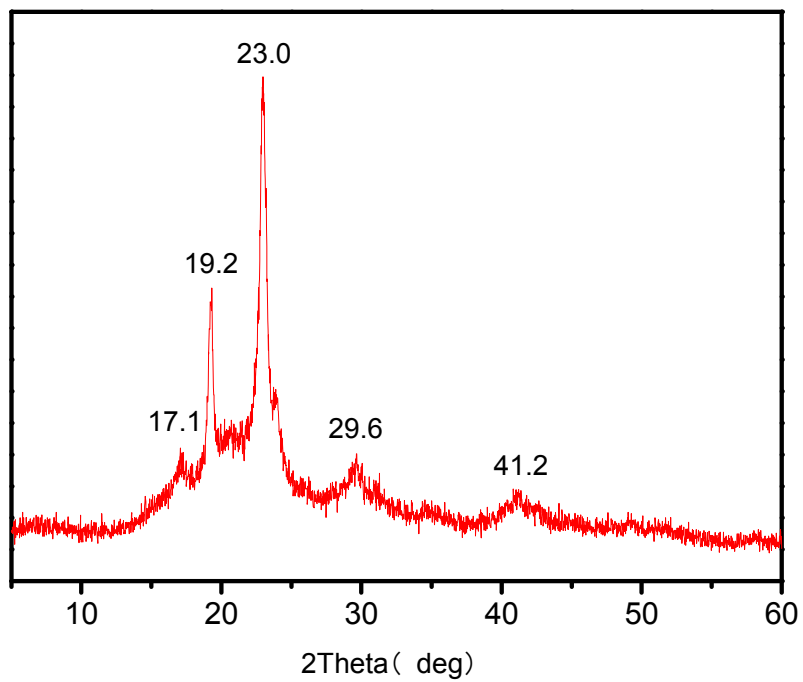
**Entry 3 in Table 1:**



**Entry 4 in Table 1:**

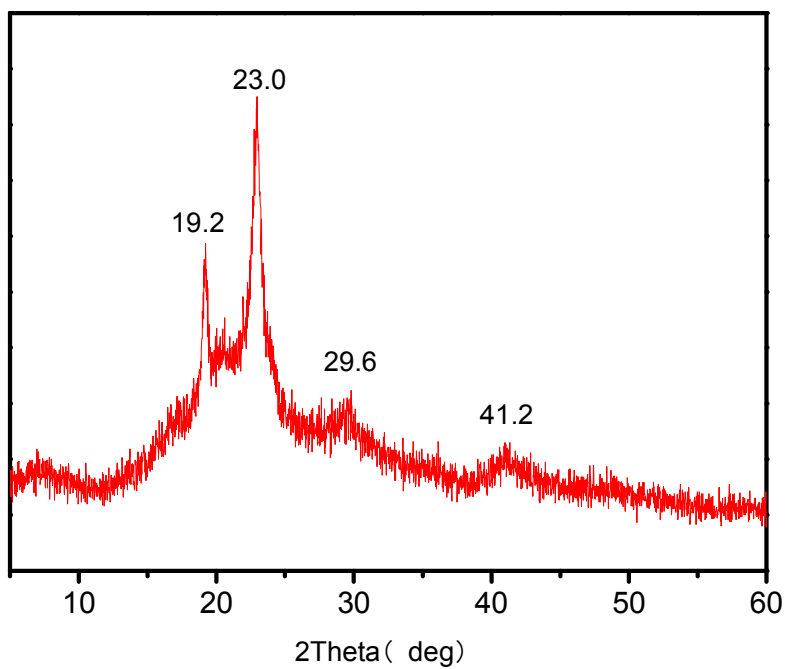


**Entry 5 in Table 1:**



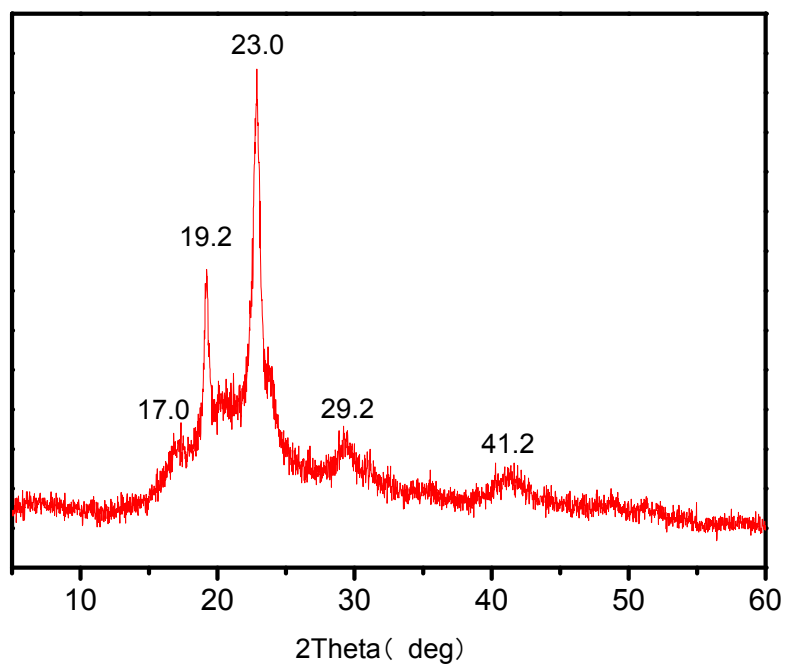
$X_c = 35\%$

Entry 6 in Table 1:



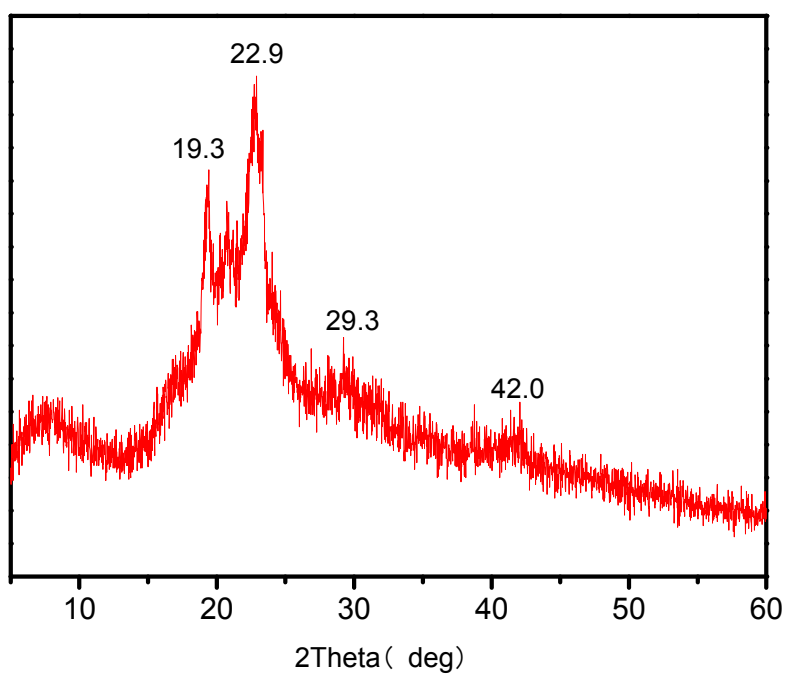
$X_c = 39\%$

Entry 7 in Table 1:



$X_c = 35\%$

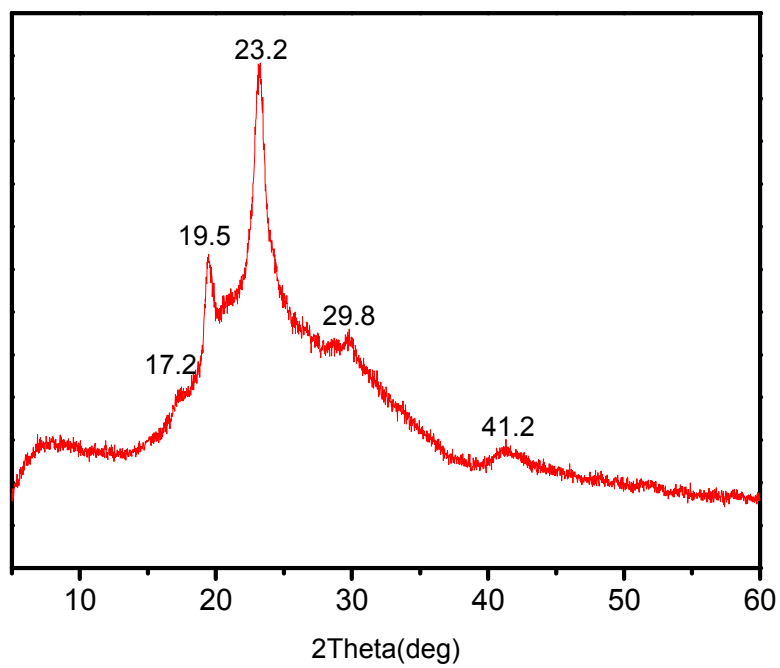
Entry 8 in Table 1:



$X_c = 13\%$

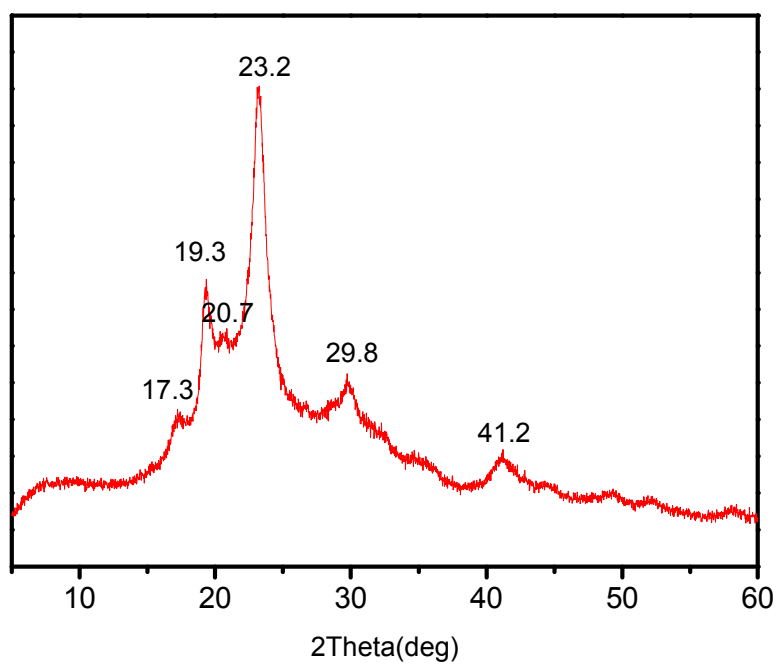
Table 2

**Entry 1 in Table 2:**



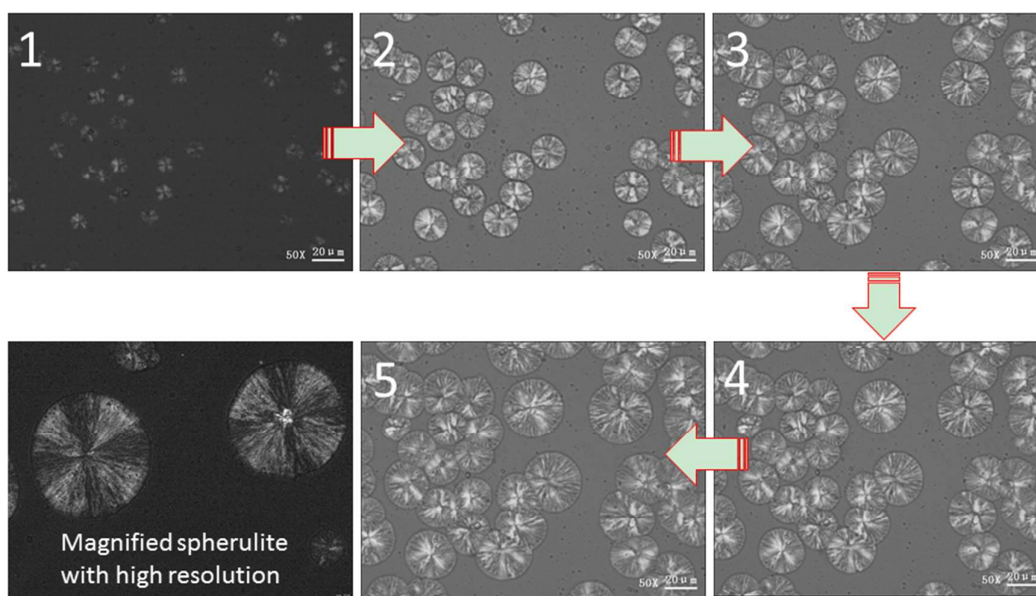
$X_c=37\%$

**Entry 2 in Table 2:**

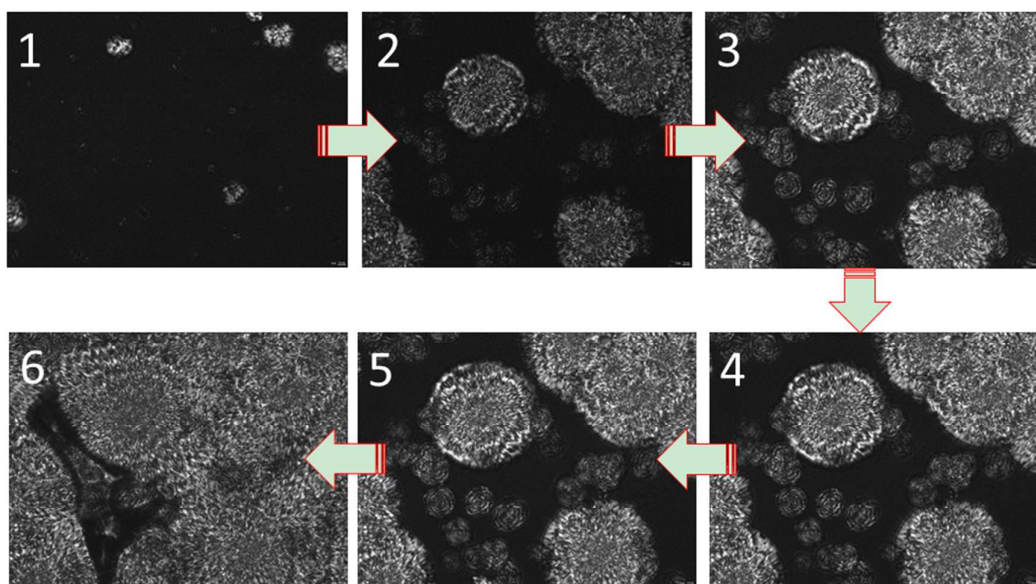


$X_c=44\%$

Entries 3-5: Not determined.



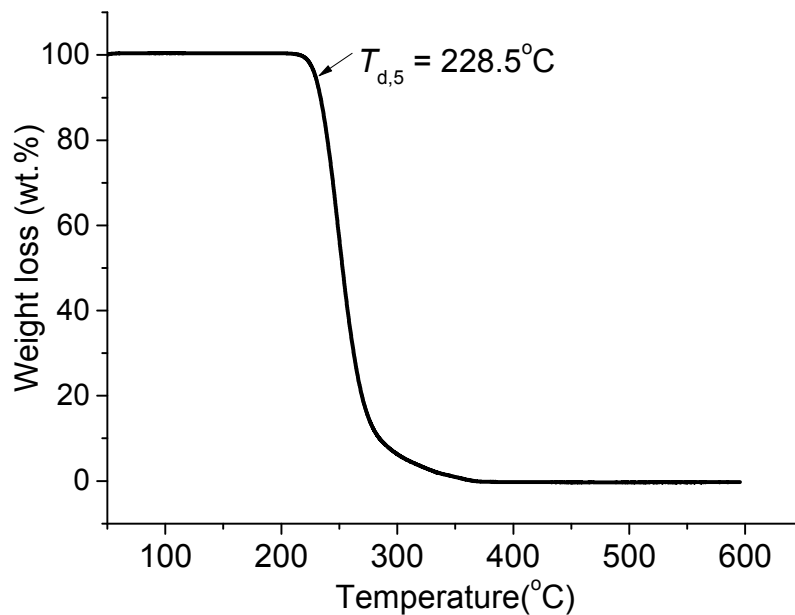
(A)



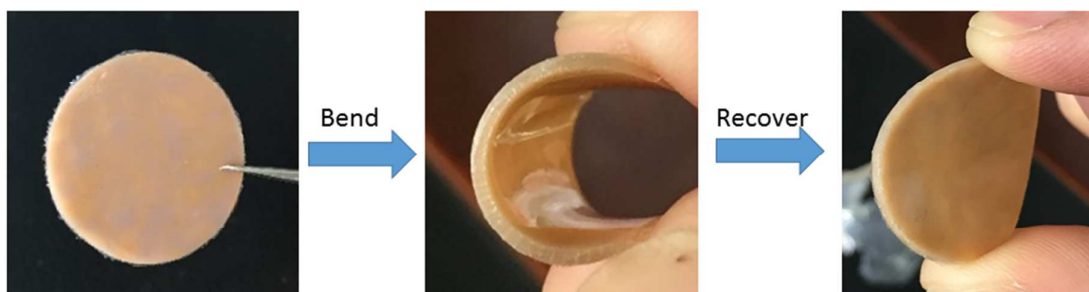
(B)

**Figure S13.** POM images of the crystal growth of the molten PTMMTC observed at: (A) 96°C (entry 1 in Table 1) and (B) 110°C (entry 4 in Table 1) with increasing time. Each scale bar shows 20 μm.





**Figure S14.** The 5 % initial weight loss temperature ( $T_{d,5\text{wt}\%}$ ,  $228.5^{\circ}\text{C}$ ), determined by TG in a heating rate of  $10^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere.



**Figure S15.** PTMMTC (the copolymers from entries 4, 6 in Table 1, and entries 1, 3 in Table 2 were mixed by solution method) was hot pressed at  $150^{\circ}\text{C}$  for 8 min and then cool pressed at room temperature for 8 min (similar to PE processing)