

Synthesis of Well-defined Telechelic *Trans*-1,4-polyisoprene by Oxidative Cleavage^{*}

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Abstract Synthesis of telechelic *trans*-1,4-polyisoprenes (TPI: *trans*-structure > 95%) was evaluated based on two different methods of oxidative cleavage (indirect cleavage: first epoxidation of TPI, then the selective cleavage of epoxidized units in epoxidized *trans*-1,4-polyisoprene (ETPI) and direct cleavage of isoprene units in TPI). The influence of solvents and the ratio of oxidative agents was investigated by ¹H-NMR and ¹³C-NMR. A series of well-defined telechelic TPI with double terminated functional groups and less side reaction (molecular weight distribution range: 1.96–2.26) were synthesized by indirect cleavage in chloroform. Telechelic TPI showed similar crystallization behavior with TPI and interesting cold crystallization behavior characterized by DSC.

Keywords: *Trans*-1,4-polyisoprene; Telechelic polymers; Degradation; Epoxidization.

INTRODUCTION

Chemical modifications of polydiene are always an attractive field since they may give materials some special performances in the practical application. It is the scientists' target to tailor-make materials in accordance to requirements for new applications. Nowadays, polymer materials are known for great versatility of their macroscopic properties promoted by the precise control of their primary structures^[1]. Telechelic polymers are one of the important research fields due to the reactive functional end groups, which are widely used as precursors for a great variety of polymer materials, such as star^[2], block^[3] and graft copolymers^[4].

Currently, a large variety of methods have been developed for synthesis and characterization of telechelic polymers, such as anionic polymerization^[5], ring-opening polymerization^[6] and the selective cleavage of polymers with synchronous functionalization, especially polydienes^[7]. Thereof, telechelic *cis*-1,4-polyisoprenes (CPI) including natural rubber and synthetic rubber derivatives have been reviewed^[8] by oxidation degradation (such as ozonolysis, RuO₄ oxidation *etc.*)^[9–13], photochemical methods^[14], as well as metathesis polymerization^[15]. A variety of polymer materials derived from telechelic CPI showed potential application in the field of biological materials^[16], foaming^[17, 18] and elastomers^[19, 20].

Trans-1,4-polyisoprene (TPI) with the same chemical “building block” as natural rubber (*cis*-1,4-polyisoprene) but special configuration, is a crystalline polymer at room temperature with a melting point (*T*_m) of 60 °C^[21], which was widely used as medical materials, golf ball covers, electrical insulated materials, shape

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memory materials, and so on^[22–24]. TPI also attracted much attention as a high-performance tire stock due to its distinct dynamic properties, including excellent anti-fatigue properties, low rolling resistance, low heat buildup, and low abrasion loss^[25–29]. However, rare reports based on synthesis of telechelic TPI were shown, only Ni^[30, 31] reported the synthesis of TPI-polyurethane shape memory material using hydroxyl-terminated functionalization TPI prepared by light catalytic cleavage of TPI. Thereof telechelic TPI with relatively controllable chain lengths, chain length distributions and end groups efficiency have not been systematically checked. Block copolymers based on telechelic TPI will be expected to show new performances different from those based on CPI. One of the key factors was synthesis of well-defined telechelic TPI. Here synthesis of telechelic TPI was discussed based on different oxidation cleavage methods in order to obtain well-defined telechelic TPI with narrow molecular weight distribution and high end functionality.

EXPERIMENTAL

Materials

Periodic acid (H_5IO_6 , 98%, Kelon Co.Ltd, Chengdu, China), *m*-chloroperbenzoic acid (MCPBA, 85%, Flute Parker Co. Ltd, Shanghai, China) were used as received; similar procedure for synthesis of TPI was carried out according to previous reports^[32]. Other reagents were commercialized chemicals and used as received.

Synthesis of TPI

The polymerization of isoprene was carried out in a 50 mL round-bottomed flask which was dried thoroughly by the cycle of evacuation and purging with nitrogen several times before use. Then, isoprene, $\text{Al}(i\text{-Bu})_3$, the third component and supported TiCl_4 catalyst were introduced into the round-bottomed flask at certain temperatures. The reaction was terminated with ethyl alcohol solution which contains 1% hydrochloric acid. The products were washed by ethyl alcohol, and then dried under vacuum for 24 h at 40 °C.

Direct Cleavage of TPI with H_5IO_6

TPI (0.5g, double bond 7.35 mmol) was dissolved in 50 mL CHCl_3 and THF at 30 °C respectively; H_5IO_6 (17.1 mg, 0.0735 mmol; 34.2 mg, 0.147 mmol; 68.4 mg, 0.294 mmol) dissolved in 5 mL THF was added dropwise, and the reaction proceeded for 6 h; Then the combined organic solution was extracted with 0.3 mol/L NaOH solution twice (for THF solution, mixed with plenty of CHCl_3 before extraction with NaOH solution), then was dried over anhydrous NaSO_4 , and then the solvent was evaporated to give a viscous liquid. The polymer was precipitated in a large amount of ethanol and dried in a vacuum at 45 °C.

Indirect Oxidative Degradation of TPI with H_5IO_6

Preparation of epoxidized TPI ($E_\chi\text{TPI}$)

TPI (1.1 g, double bond 16.2 mmol) was dissolved in 150 mL CHCl_3 at room temperature, and then transferred to ice water bath; MCPBA (32.8 mg, 0.162 mmol; 65.6 mg, 0.324 mmol; 131.2 mg, 0.648 mmol) dissolved in 10 mL CHCl_3 was added dropwise. The reaction solution was stirred at 0 °C for 6 h, then the combined organic solution was extracted twice with 0.3 mol/L NaOH solution, $E_\chi\text{TPI}$ was precipitated in a large amount of ethanol and dried in a vacuum at 45 °C.

Selective oxidative degradation of epoxide units of $E_\chi\text{TPI}$

$E_\chi\text{TPI}$ (0.5 g, 7.35 mmol) was dissolved in 50 mL CHCl_3 and THF at 30 °C respectively; H_5IO_6 (17.1 mg, 0.0735 mmol; 34.2 mg, 0.147 mmol; 68.4 mg, 0.294 mmol) dissolved in 5 mL THF was added dropwise, the reaction proceeded for 6 h; Then the combined organic solution was extracted with 0.3 mol/L NaOH solution two times (for THF solution, mixed with plenty of CHCl_3 before extraction with NaOH solution), then was dried over anhydrous NaSO_4 , and the solvent was evaporated to give a viscous liquid. The polymer was precipitated in a large amount of ethanol and dried in a vacuum at 45 °C.

Characterization

^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C with a Bruker 500 MHz spectrometer with samples in CDCl_3 containing tetramethylsilane as standard. Weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) (HLC-8320GPC) fitted with a refractive index detector with samples in tetrahydrofuran at 40 °C calibrated by polystyrene standards. Fourier transform infrared (FTIR) spectra of the samples were recorded on a TENSOR27 FTIR spectrometer (Bruker, Germany). The samples were dissolved in CHCl_3 at 45 °C, then the dissolved polymers were coated on the potassium bromide salt tablet to prepare thin films. Thermal analysis of the telechelic polyisoprene was made by using a NETZSCH DSC-204 differential scanning calorimeter under N_2 atmosphere. About 5 mg of sample was sealed in aluminum sample pan, the sample was heated from room temperature to 100 °C at a heating rate of 10 K/min to eliminate the thermal history, and then cooled to -100 °C at 10 K/min. Then the samples were heated from -100 °C to 100 °C at 10 K/min.

RESULTS AND DISCUSSION

Direct Cleavage of TPI

The reaction of TPI direct oxidative degradation with H_5IO_6 was performed in CHCl_3 and THF respectively, the mole ratio of double bond of isoprene with H_5IO_6 was 100:1, 100:2 and 100:4; ^1H -NMR analysis was used to check the expected chain end in the resulting carbonyl telechelic TPI and quantitative analysis of the reaction process.

As shown in Fig. 1, the signals at $\delta = 9.75$ and 2.12 were assigned for A_1 ($-\text{CHO}$) and K_1 ($-\text{COCH}_3$) respectively, which indicated telechelic TPI was synthesized *via* direct oxidation reaction with H_5IO_6 . The chain ends were also characterized by the signals A_2 ($-\text{CH}_2\text{CHO}$) and A_3 ($-\text{CCH}_2\text{CH}_2-$) of the methylene groups in the neighborhood of the aldehyde group and by K_2 ($-\text{CH}_2\text{CH}_2\text{COCH}_3$) and K_3 ($-\text{CH}_2\text{CH}_2\text{CH}-$) of the methylene groups in the neighborhood of the ketone group. Therefore, it was clear that H_5IO_6 was a good reagent for the scission of double bonds. Besides the signals of carbonyl end groups, the signals C ($\delta = 2.71$) of residual epoxide was detected, which was reasonable to propose that the cleavage is a two-step mechanism. In the first step, H_5IO_6 reacted with a double bond to give an epoxide group, in the second step, the epoxide group was cleaved by further reaction with H_5IO_6 .

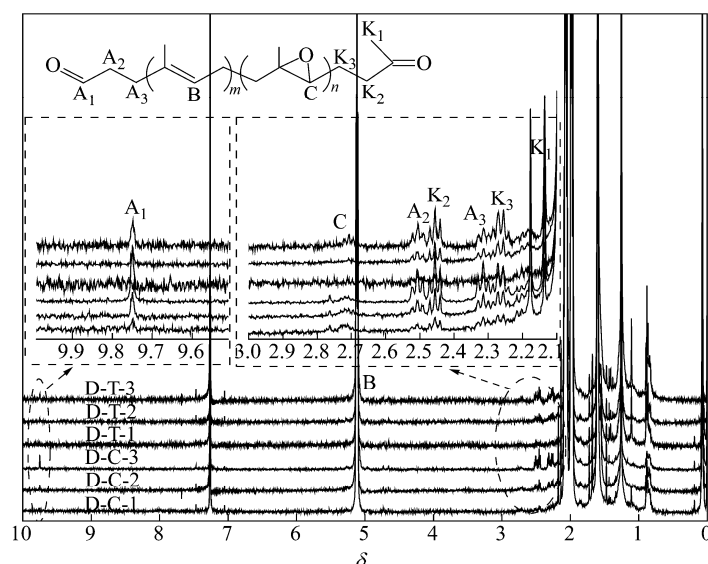


Fig. 1 ^1H -NMR spectra of telechelic TPIs by direct cleavage

The molecular weights and polydispersity indices were calibrated by polystyrene standards and are collected in Table 1. Moreover, the molecular weights were also determined by the area ratio between the characteristic peaks of isoprene groups (peak B, $\delta = 5.14$) and the aldehyde proton (peak A₁, $\delta = 9.75$) from ¹H-NMR in Fig. 1. Thus, the obtained molecular weights by ¹H-NMR were well-fitted to the data determined by GPC as shown in Table 1 and Fig. 2. As shown in Fig. 2, the molecular weights gradually reduced with the increase of reaction molar ratio of double bond of isoprene with H₅IO₆. Additionally, the telechelic TPI prepared from TPI oxidative degradation had relatively narrow molecular weight distribution (about 2.30). Also the result obtained with CHCl₃ ($A_{9.7}/A_{5.1}$) showed high efficiency of end group functionalization.

Table 1. Quantitative analysis of direct degradation of TPI with H₅IO₆

Samples	Isoprene/H ₅ IO ₆ molar ratio	$A_{2.7}/(A_{5.1}+A_{2.7})$	$A_{9.7}/A_{5.1}$	$M_n^{(NMR)^c}$ ($\times 10^4$)	$M_n^{(GPC)}$ ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
TPI	—	—	—	—	18.08	40.76	2.26
D-C-1 ^a	100:1	1.08%	0.0023	2.96	2.80	6.52	2.33
D-C-2 ^a	100:2	0.99%	0.0044	1.55	1.59	3.63	2.28
D-C-3 ^a	100:4	0.94%	0.0107	0.63	0.80	1.91	2.38
D-T-1 ^b	100:1	0.59%	0.0025	2.72	4.69	11.23	2.40
D-T-2 ^b	100:2	0.66%	0.0030	2.27	2.66	6.22	2.34
D-T-3 ^b	100:4	1.38%	0.0062	1.10	1.41	2.94	2.08

^a TPI dissolved by CHCl₃; ^b TPI dissolved by THF; ^c the M_n calculated by $(A_{5.1}/A_{9.7}) \times 68$

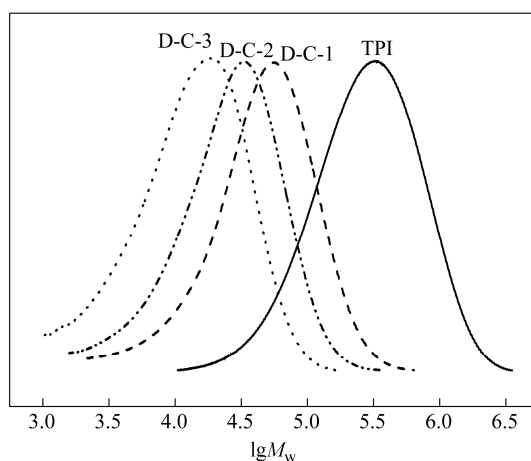
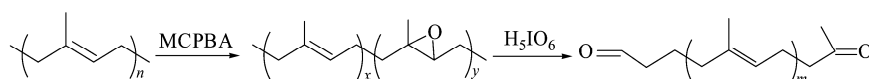


Fig. 2 GPC curves of telechelic TPIs by direct cleavage

Indirect Oxidative Degradation with H₅IO₆

According to two-step mechanism of TPI oxidative degradation with direct method, the consumption of H₅IO₆ in the two processes can not be controlled well. It was imagined that the epoxidation process and chain scission process of TPI were operated respectively in order to precisely control the structure of telechelic TPI with less residue of epoxide groups. As shown in Scheme 1, MCPBA was chosen for quantitative epoxidization of TPI, and then H₅IO₆ was used for selective degradation of epoxide groups.



Scheme 1 Synthesis of telechelic TPI with indirect method

Synthesis of E_x TPI

The E_x TPI was prepared with the mole ratio (double bond with MCPBA = 100:1, 100:2 and 100:4) under ice water bath. The structure and the degree of epoxidization of E_x TPI were characterized by $^1\text{H-NMR}$.

As shown in Fig. 3, the signals B at $\delta = 2.71$ were assigned for epoxide groups, and no other signals of ring-opening side reaction were observed. The degree of epoxidization (E_x TPI) was determined from $^1\text{H-NMR}$ data with $E\% = A_{2.71}/(A_{2.71} + A_{5.14})$ (where $A_{2.71}$ and $A_{5.14}$ represented the integral area of $\delta = 2.71$ and 5.14). The molar percentages of epoxide groups ($E\%$) were 0.85, 1.72 and 3.55 in E_1 TPI, E_2 TPI, and E_4 TPI, corresponding to MCPBA/TPI molar ratio of 1, 2, and 4 respectively.

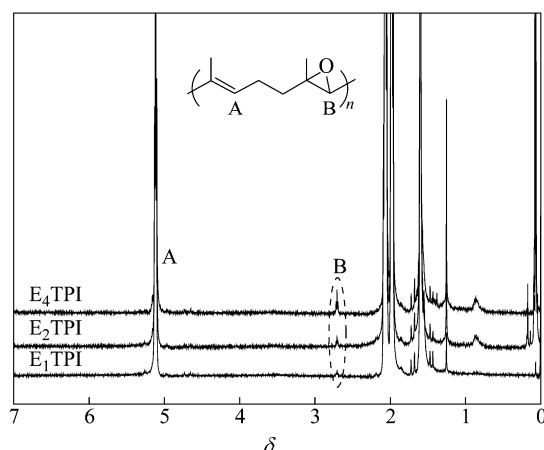


Fig. 3 $^1\text{H-NMR}$ spectra of E_x TPI

Selective degradation of epoxide units of E_x TPI

The selective cleavage of the epoxide groups of E_x TPI with H_5IO_6 was performed in CHCl_3 and THF. Typical signals in Fig. 4 for the aldehydic and ketonic chain ends were the same with that obtained by direct cleavage in TPI with H_5IO_6 . Specially, the signals of epoxide groups at about $\delta = 2.7$ became weaker comparing with those in direct TPI oxidative degradation. The same result was shown that the specific data of $A_{2.71}/(A_{5.14} + A_{2.71})$ to CHCl_3 system (to S-C as shown in Table 2) reduced more obviously than those obtained by direct degradation of TPI. The signals at $\delta = 202.3$ and 208.7 ($^{13}\text{C-NMR}$ in Fig. 5) were assigned to aldehydic (C_8) and ketonic (C_9) chain ends respectively, moreover typical *trans*-1,4-polyisoprene structure ($-\text{CH}_3$, $\delta = 16.1$; $-\text{CH}_2\text{CH}_2\text{CH}-$, $\delta = 26.6$; $-\text{CH}_2\text{CH}_2\text{C}-$, $\delta = 39.8$; $-\text{CH}_2\text{CHC}-$, $\delta = 124.2$; $-\text{CHCH}_3\text{CCH}_2-$, $\delta = 135.0$) was identified, and the calculated content of *trans*-1,4 structure to telechelic TPI by $^{13}\text{C-NMR}$ still kept above 95%. As shown in Fig. 6, the characteristic bands at 1722 cm^{-1} to telechelic TPI (S-C-2 and S-C-3) were observed representing the stretching vibration of carbonyl groups, respectively.

The data of residual epoxide groups, molecular weight and molecular weight distribution with different reaction conditions are listed in Table 2. The molecular weight was also determined by the area ratio between the characteristic peaks of isoprene groups (peak B, $\delta = 5.14$) and the aldehyde protons (peak A₁, $\delta = 9.75$) from $^1\text{H-NMR}$ in Fig. 4, which was well-fitted to that determined by GPC. The results of carbonyl telechelic TPI (CTTPI) prepared from selective cleavage of ETPI in THF and CHCl_3 are also listed in Table 2. With the increase of H_5IO_6 , the molecular weight of telechelic TPI reduced and the functionality efficiency of end groups increased according to the data of $A_{9.75}/A_{5.14}$. The reaction preformed in CHCl_3 led to lower residual epoxide groups (the data of $A_{2.71}/(A_{5.14} + A_{2.71})$) and lower molecular weight (as shown in Fig. 7), which was the same as that in direct method. Therefore, it is clear that CHCl_3 was the better solvent for oxidation degradation of TPI in direct and indirect methods. Moreover, the polydispersity index of the CTTPI prepared from selective cleavage was nearly 2.2, which was narrower than that obtained by direct method. All these results suggested the method of selective oxidation degradation allowed us to better control the structure of CTTPI.

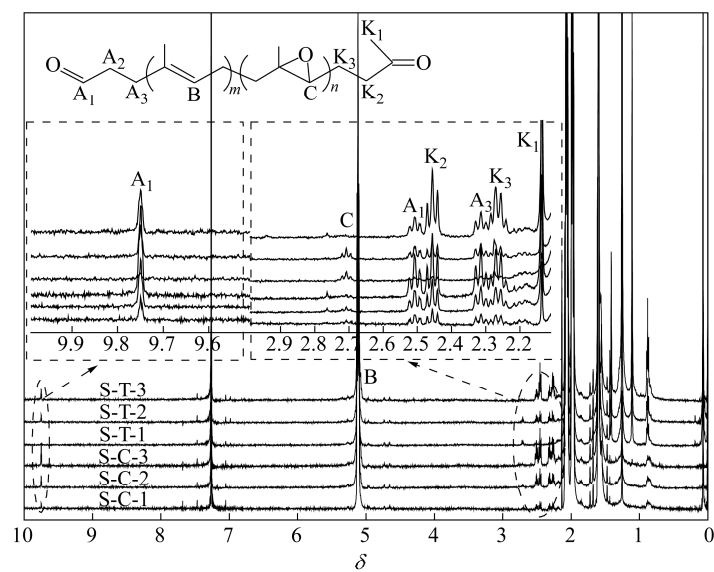


Fig. 4 ^1H -NMR spectra of selective degradation of E_χTPI

Table 2. Quantitative analysis of selective degradation of E_χTPI

Samples	ETPI (E%)	$A_{2.7}/(A_{5.1} + A_{2.7})$	$A_{9.7}/A_{5.1}$	M_n (NMR) ^c ($\times 10^4$)	M_n (GPC) ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
TPI	—	—	—	—	18.08	40.76	2.26
S-C-1 ^a	0.85	0.50%	0.0065	1.05	1.85	4.07	2.20
S-C-2 ^a	1.72	0.73%	0.0115	0.59	0.98	2.15	2.19
S-C-3 ^a	3.55	0.38%	0.0284	0.24	0.44	0.89	2.03
S-T-1 ^b	0.85	0.83%	0.0013	5.23	5.43	12.26	2.26
S-T-2 ^b	1.72	0.99%	0.0076	0.89	1.26	2.72	2.17
S-T-3 ^b	3.55	0.71%	0.0106	0.65	0.56	1.09	1.96

^a E_χTPI dissolved by CHCl_3 ; ^b E_χTPI dissolved by THF; ^c the M_n calculated by $(A_{5.1}/A_{9.7}) \times 68$

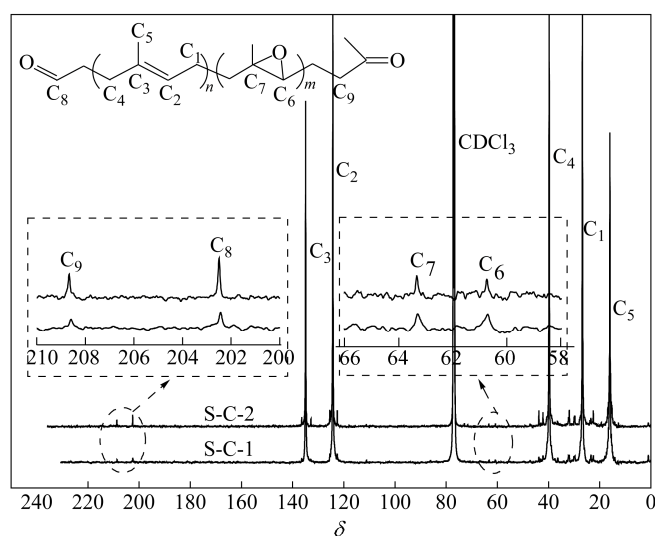


Fig. 5 ^{13}C -NMR spectra of selective degradation of E_χTPI

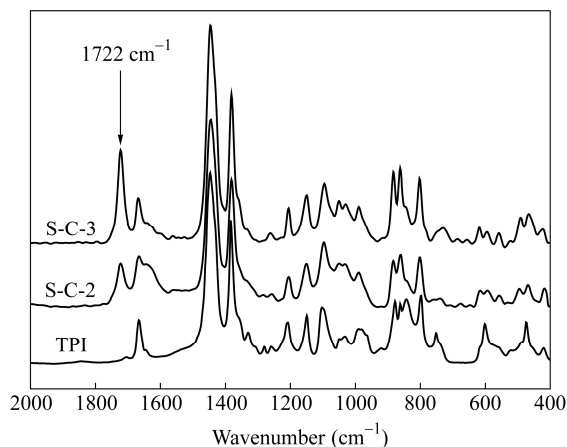
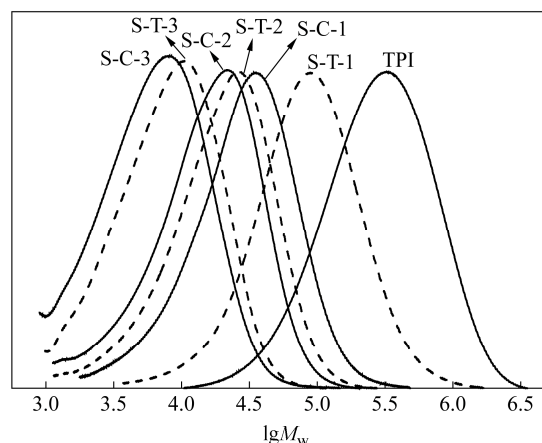


Fig. 6 FTIR spectra of telechelic TPI

Fig. 7 GPC curves of selective degradation of E_{χ} TPI

Thermal Properties of CTTPI

Thermal analysis was conducted to verify the crystallization behavior of CTTPI by DSC. As shown in Fig. 8 and Table 3, the glass transition temperature (T_g) of CTTPI was lower than that of TPI. Melting temperature (T_m) and the crystallization temperature (T_c) of CTTPI were similar with those of TPI indicating the chain structure kept well. The ability of crystallization increased perhaps due to the reduction of molecular weight and the contribution of end functional groups. It was worth mentioning that CTTPI showed a cold crystallization in DSC curves, and further work is ongoing.

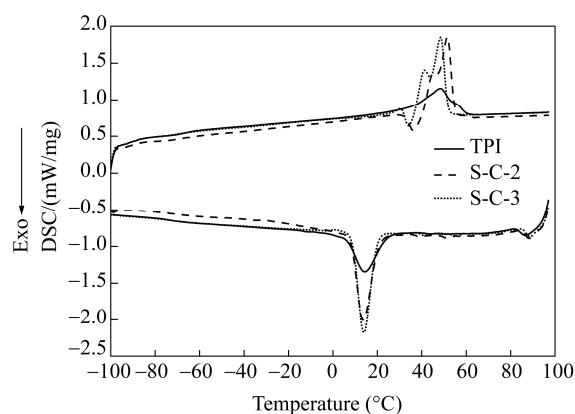


Fig. 8 DSC curves of CTTPI

Table 3. DSC data of different CTTPI and TPI

Samples	T_c (°C)	T_g (°C)	T_{cc} (°C)	T_m (°C)		ΔH_m (J/g)	ΔH_c (J/g)
				1	2		
TPI	14.3	-66.7	—	—	48.4	40.3	-40.3
S-C-2	13.6	-68.3	36.2	45.5	51.5	58.7	-58.7
S-C-3	14.0	-69.9	34.0	41.4	48.4	57.8	-57.9

CONCLUSIONS

Carbonyl telechelic TPIs were prepared by direct cleavage and selective oxidation degradation methods, respectively. According to the data by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and GPC, carbonyl telechelic TPI obtained by selective oxidation degradation in CHCl_3 had lower residual epoxide groups and high efficiency of end functional groups. The results by DSC indicated the chain structure of TPI was not destroyed after selective scission and the ability of crystallization kept well.

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