

Tris(trimethylsilyl)methyl Functionalized 4-Chloromethyl Styrene Polymers: Effects of Side Chain Modification on Polymer Structure and Glass Transition Temperature

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ABSTRACT: 4-Chloromethyl styrene was copolymerized with various molar ratio of methyl methacrylate or ethyl methacrylate by solution free radical polymerization method, at $70 \pm 1^\circ\text{C}$ using α, α' -azobis(isobutyronitrile) as an initiator. Then, very highly sterically hindered tris(trimethylsilyl)methyl substituent was covalently linked to the obtained copolymers with liberation of chlorine atoms. The structure of all polymers was characterized and confirmed by FT-IR, ^1H and ^{13}C NMR spectroscopy techniques. The average molecular weight and glass transition temperature of polymers were determined using gel permeation chro-

matograph and differential scanning calorimeter instruments, respectively. Study of differential scanning calorimetry analyses showed that chemical modification of 4-chloromethyl styrene copolymers with tris(trimethylsilyl)methyl substituents leads to an increase in the rigidity and glass transition temperature of polymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 633–639, 2006

Key words: 4-chloromethyl styrene; methyl methacrylate; ethyl methacrylate; tris(trimethylsilyl)methyl ligand; glass transition temperature

INTRODUCTION

4-Chloromethyl styrene (CMS) or *p*-vinylbenzyl chloride (VBC) is an important dual functional monomer that can be polymerized before or after chemical functionality reactions on the benzyl chloride group. The CMS polymers are reactive to react with various nucleophilic reagents at fairly high yields. The numerous physical and chemical properties of the functionalized CMS polymers and their applications in various industries have been reported in many articles and patents.¹ The functionalized CMS polymers have been widely used in different processes as bactericide polymers,² photo-sensitizers,³ solar energy storages,⁴ photo-resists,⁵ nonlinear optics,⁶ cholesterol trapping of human serum⁷ and polymeric prodrugs in drug delivery systems.⁸

Chemical modification of polymer structures is an important route for modification of polymer properties such as mechanical, thermal and surface properties. In recently years, modification of polymer properties has been studied by attachment of various silyl groups to macromolecular chains.^{9–12} The properties of CMS polymers are modified by nucleophilic substitutions of the chlorine atoms, which yields depend on the steric hindrance.

The very bulky tris(trimethylsilyl)methyl group, $(\text{Me}_3\text{Si})_3\text{C}-$, in which three organosilyl groups are attached to the central carbon atom, is one of the largest substituents. This group is greater than *t*-Bu, or 2,4,6-*i*-Pr₃C₆H₂ and close to 2,4,6-*t*-Bu₃C₆H₂. The various organometallic compounds containing tris(trimethylsilyl)methyl group have been synthesized and studied in recent years.^{13–18} The prototype tris(trimethylsilyl)methyl group is referred to as the trisyl and commonly denoted by "Tsi."

Since the preparation of polymers containing very bulky Tsi groups and studying of their modified properties is a new field in polymer and silicon chemistry,¹⁹ the synthesis and studying of trisylated polymers properties have been reported in a few articles.^{20,21}

In this research work, CMS was first copolymerized with methyl methacrylate (MMA) or ethyl methacrylate (EMA) in various molar ratios by the free radical polymerization method. The very bulky Tsi groups were then attached to the resulted copolymers by reaction between tris(trimethylsilyl)methyl lithium (trisyllithium = TsiLi) as a nucleophilic reagent and benzyl chloride group of CMS units. The differential scanning calorimetry (DSC) analyses of trisylated polymers showed that with increase of CMS mole in copolymer structures, incorporation of the bulky Tsi groups is increased. Increasing of the Tsi ligands in polymer structures leads to an increase in the glass transition temperature (T_g).

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EXPERIMENTAL

Materials and measurements

For preparation of TsiLi, chloroform (Merck), THF (Merck) and diethyl ether (Merck) were dried by standard methods. Also, Me₃SiCl (Merck), MeI (Merck), Li (Merck) used as received. The monomers of CMS (Aldrich, 90%), MMA (Merck), EMA (Merck) were distilled under reduced pressure to remove inhibitors before use. Toluene (Merck) was dried over sodium wire and distilled before use. α,α' -azobis(isobutyronitrile) (AIBN; Merck) was purified by crystallization from methanol. All the reactions were carried out under dry argon to exclude oxygen and moisture from the reaction systems.

Infrared spectra were recorded with a 4600 Unicam FT-IR spectrophotometer as KBr pellets. ¹H and ¹³C NMR spectra were run on a Bruker 400 MHz spectrometer at room temperature using CDCl₃ as a solvent. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph (GPC) fitted with 10² and 10³ nm Waters Styragel columns. THF was used as an elution solvent at a flow rate of 1 mL/min and polystyrene standards were employed for calibration. The glass transition temperature was determined with a Perkin-Elmer DSC7 differential scanning calorimeter at a heating rate of 10°C/min in air. T_g 's were taken at the mid-points of the heat flow changes.

Copolymerization of CMS with MMA or EMA

Copolymerization reactions were carried out in dried toluene solutions at (70 ± 1)°C, in Pyrex glass ampoules sealed off under vacuum. AIBN was used as initiator ([CMS] + [comonomer] = 40 mmol, [AIBN] = 0.4 mmol). The sealed ampoules were vigorously shaken by shaker machine and immersed in a water bath held at the mentioned temperature of polymerization about 30 h. After the reaction time, the ampoules were removed from the bath and at once the contents were poured into a large excess of cooled proper nonsolvent (methanol). The precipitate samples were washed with the precipitant and dried under vacuum until constant weight was attained.

Preparation of tris(trimethylsilyl)methyl lithium (TsiLi)

Typically for preparation of TsiLi (about 20 mmol), a solution of 5.75 g (25 mmol) of tris(trimethylsilyl)methane (TsiH) in dried THF (30 mL) was added to a solution of MeLi generated from 3.54 g (25 mmol) of MeI and 0.35 g (50 mmol) of Li in dried diethyl ether (20 mL). Then, the diethyl ether was distilled from the reaction mixture for reducing reaction time, and the reaction mixture was boiled under reflux about 2 h. The color of the mixture changed to reddish brown during reflux time.

Addition of the bulky Tsi groups to copolymer chains

In a 100 mL two-necked flask equipped with a dropping funnel and a reflux condenser, 0.5 g of each synthesized copolymer was dissolved in dried THF (30 mL). A gas-inlet is attached to the top of the dropping funnel and the system is maintained under a slight pressure of argon. A solution of TsiLi (20 mmol) in dried THF (30 mL) was prepared as described earlier and transferred into dropping funnel under argon. Then, TsiLi was added dropwise with stirring to a solution of copolymer into flask at room temperature. The reaction mixture was refluxed for about 3 h. Then, the solution was poured into an excess methanol and the yellow precipitate filtered and washed with methanol. The resulted polymer was dissolved in THF (10 mL) for removing LiCl from the polymer. Then the remaining solution was poured into cooled methanol (50 mL) and the precipitate washed with methanol for several times. The white obtained polymer containing Tsi substituents in the side chains was collected and dried under vacuum at room temperature.

Determination of solubility

The solubility of all the copolymers was tested by mixing of 20 mg of the copolymer with 2 mL of different solvents in a test tube. After setting aside the closed tubes for 1 day the solubility was noticed.

TABLE I
The Preparation Conditions of Copolymers at (70 ± 1)°C

Copolymer	Monomer of 1	Monomer of 2	[1] (mmol)	[2] (mmol)	Time (h)	Conversion (%)
PCM1	CMS	MMA	10	30	30	75.2
PCM2	CMS	MMA	20	20	30	69.2
PCM3	CMS	MMA	30	10	30	73.5
PCE1	CMS	EMA	10	30	30	79.5
PCE2	CMS	EMA	20	20	30	80.2
PCE3	CMS	EMA	30	10	30	77.3

TABLE II
The Solubility of the Synthesized Copolymers

Solvent	PCM1	PCM2	PCM3	PCE1	PCE2	PCE3
Chloroform	++	++	++	++	++	++
Dichloromethane	++	++	++	+	+	+
Water	-	-	-	-	-	-
Acetone	+	+	+	±	±	±
Benzene	++	++	++	+	+	+
Toluene	++	++	++	+	+	+
THF	++	++	++	++	++	++
DMF	++	++	++	+	+	+
DMSO	++	++	++	+	+	+
Methanol	-	-	-	-	-	-
<i>n</i> -Hexane	-	-	-	-	-	-

++, soluble; +, soluble on heating; ±, partially soluble on heating; -, insoluble.

RESULTS AND DISCUSSION

Synthesis of copolymers

The monomer of CMS was copolymerized with MMA or EMA (in various molar ratios) at $(70 \pm 1)^\circ\text{C}$ using AIBN as the radical initiator. The reaction conditions are shown in Table I. The conversion of monomers to copolymers was determined gravimetrically after exhaustive drying of the isolated copolymer samples.

Characterization of copolymers

The resulted copolymers are white solids and amorphous. The solubility of the copolymers is reported in Table II.

The FT-IR spectra of copolymers showed a peak at 3030 cm^{-1} due to C—H stretching of the aromatic ring. The peaks at 2990 and 2950 cm^{-1} were attributed to the asymmetrical and symmetrical C—H stretching of methylene and methyl groups. The ester carbonyl stretching was observed at 1735 cm^{-1} . The ring stretching vibrations of the aromatic nuclei were observed at 1600 and 1485 cm^{-1} . The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1453 and 1380 cm^{-1} , respectively. The peaks at

1273 and 1160 cm^{-1} were due to C—O stretching. The C—H out of plane bending vibrations due to the aromatic nuclei was observed at 883 , 750 , and 690 cm^{-1} .

In the ^1H NMR spectra of the copolymers, two methylene protons of benzyl chloride appeared at 4.5 ppm . The proton signals of the aryl group were seen between 6.7 and 7.2 ppm . The resonance signal at 4.0 ppm was attributed to two methylene protons of $-\text{COOCH}_2$ in copolymers PCE1, PCE2, and PCE3. Three methyl protons of $-\text{COOCH}_3$ in copolymers PCM1, PCM2, and PCM3 appeared at 3.7 ppm . The broad signal at 0.6 – 2.5 ppm was due to the methylene groups of backbone and other alkyl groups. A typically ^1H NMR spectrum of the copolymer PCE1 is shown in Figure 1.

In the ^{13}C NMR spectra, the resonance signal at 176 ppm was due to the ester carbonyl carbon in copolymers. The aromatic carbons gave signals at 127 , 128 , 135 , and 145 ppm . The signal at 46 ppm was attributed to the methylene carbon of benzyl chloride. The attached methyl and methylene carbons to the oxygen of ester appeared at 52 ppm . The backbone carbon signals were observed at 40 – 45 ppm . A series of reso-

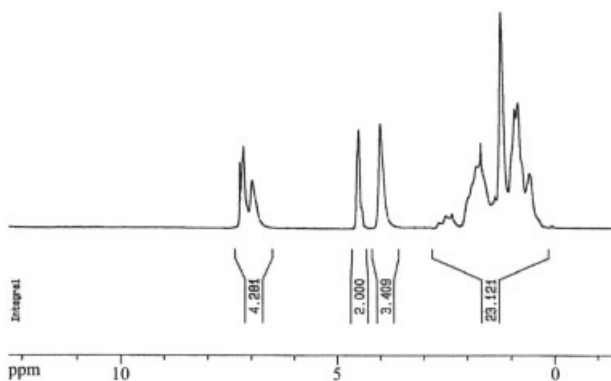


Figure 1 ^1H NMR spectrum of PCE1 in CDCl_3 .

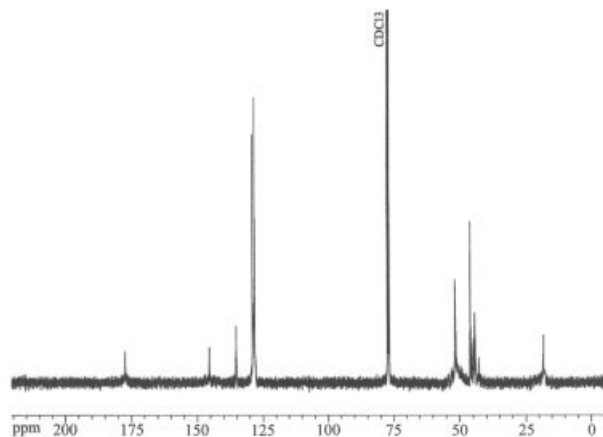


Figure 2 ^{13}C NMR spectrum of PCM1 in CDCl_3 .

TABLE III
Molecular Weights and Mole Fractions of the Synthesized Copolymers

Copolymer	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	CMS (%)	MMA (%)	EMA (%)
PCM1	37.2	24.8	1.5	33	67	–
PCM2	32.6	19.1	1.7	48	52	–
PCM3	31.8	15.9	2.0	65	35	–
PCE1	34.6	20.3	1.7	27	–	73
PCE2	30.3	16.8	1.8	45	–	55
PCE3	35.1	18.4	1.9	68	–	32

nance peaks between 13 and 25 ppm was due to α -methyl group and other alkyl groups. A typically ^{13}C NMR spectrum of copolymer PCM1 is given in Figure 2.

The number and weight-average molecular weights of synthesized copolymers were determined by GPC and are presented in Table III.

The copolymer compositions were determined from the corresponding ^1H NMR spectra. In the past few decades ^1H NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity, and sensitivity.^{22–24} The assignment of the resonance peaks in the ^1H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Thus, the mole fraction of CMS in the copolymer chain was calculated from measuring of the integrated peak of 4.5 ppm, corresponding to two protons of the $\text{CH}_2\text{—Cl}$ in CMS units and integrated peak of 3.8 ppm, corresponding to three protons of the OCH_3 in MMA units or 4.0 ppm corresponding to two protons of OCH_2 in EMA units. Table III gives the mole fractions of copolymers.

The glass transition temperature (T_g) is an important intrinsic characteristic that influences the material properties of a polymer and its potential applications. Furthermore, polymers with high glass-transition

temperatures are attractive for industrial polymer science because of strong economic rewards that may arise from their potential applications.²⁵

The T_g value of the copolymers was determined by DSC and the resulted data are presented in Table IV. All the synthesized copolymers show a single T_g , showing the absence of formation of a mixture of homopolymer or the formation of a block copolymer. The observed T_g value for all the copolymers is approximately according to Fox and Pochan equations, where T_{g1} and T_{g2} are the glass transition temperatures ($^\circ\text{K}$) of CMS homopolymer and comonomer homopolymer.²⁶ Also, w_1 and w_2 are weight fractions of CMS and comonomer in the feed, respectively.

Fox's equation is

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

and Pochan's equation is

$$\ln T_g = w_1 \ln T_{g1} + w_2 \ln T_{g2}$$

The obtained T_g value from Fox and Pochan equations is compared with observed T_g value from DSC curves in Table IV.

TABLE IV
Comparison of Observed T_g Value of the Copolymers with Calculated T_g Value from Fox and Pochan Equations

Copolymer	w_1^a	w_2^b	T_{g1}^c ($^\circ\text{C}$)	T_{g2}^d ($^\circ\text{C}$)	T_g^e ($^\circ\text{C}$)	T_g^f ($^\circ\text{C}$)	T_g^h ($^\circ\text{C}$)
PCM1	0.34	0.66	105	103	103.6	103.6	104
PCM2	0.60	0.40	105	103	104.2	104.2	105
PCM3	0.82	0.18	105	103	104.6	104.6	104
PCE1	0.30	0.70	105	65	76.0	76.5	78
PCE2	0.56	0.43	105	65	90.1	66.5	85
PCE3	0.80	0.20	105	65	96.2	96.6	97

^a Weight fraction of CMS in the feed.

^b Weight fraction of second monomer in the feed.

^c T_g of homopolymer of CMS.

^d T_g of homopolymer of second monomer.

^e Calculated by Fox equation.

^f Calculated by Pochan equation.

^h Observed in relating DSC curve.

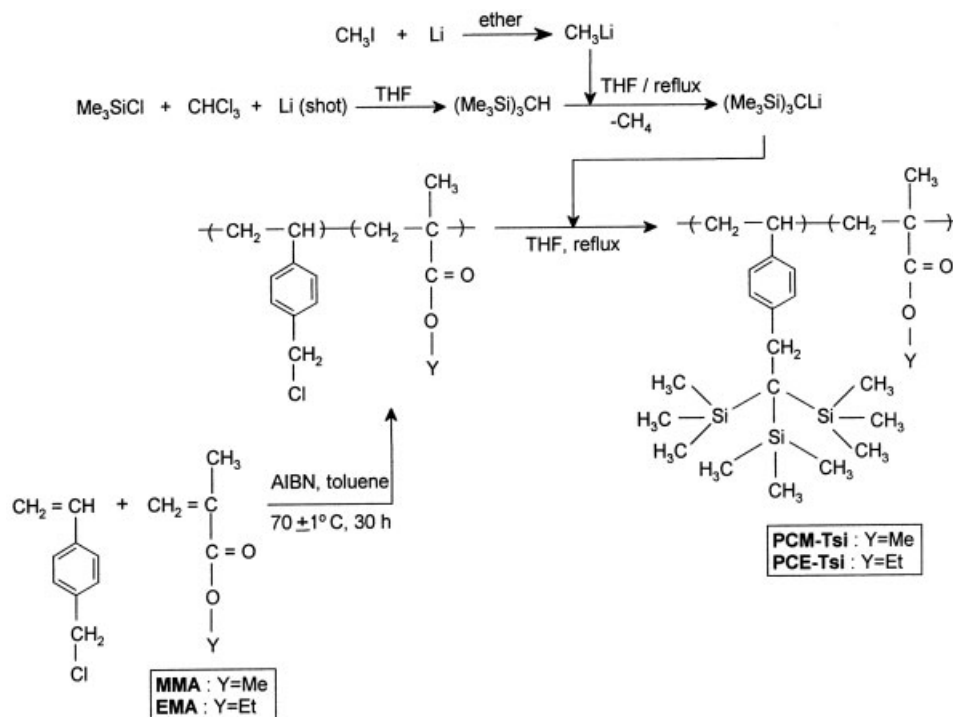


Figure 3 Preparation route of trisylated copolymers.

Synthesis of trisylated copolymers

TsiLi as a nucleophilic reagent was prepared from the reaction of TsiH and MeLi.^{16–18} As shown in Figure 3, this reagent is able to react with benzyl chloride groups of copolymers. Therefore, 0.5 g of each copolymer was reacted with 20 mmol of TsiLi in THF and the resulted ¹H NMR spectrum showed that all the chlorine atoms were replaced with Tsi groups. The solubility of trisylated polymers was same mentioned solubility in Table II. The yield of trisylated copolymers is given in Table V.

Characterization of trisylated copolymers

The replacement of chlorine atom by Tsi group is easily followed by ¹H NMR. The peak around 4.6 ppm corresponding to two protons of methylene of benzyl

chloride in CMS disappeared and two new peaks, one at 3.0 ppm corresponding to two protons of methylene containing Tsi group and other at about 0.1 ppm corresponding to 27 protons of —C[Si(CH₃)₃]₃ appeared (Fig. 4).

Also, in ¹³C NMR spectra, carbon absorption around 46.0 ppm corresponding to one carbon of methylene of benzyl chloride disappeared and three new peaks, one at 35.0 ppm corresponding to one carbon of methylene containing Tsi substituent, the second at about 9.0 ppm corresponding to one central carbon of —C(SiMe₃)₃ and the latter at 2.6 ppm corresponding to nine carbons of methyl in —C[Si(CH₃)₃]₃,

TABLE V
The Yield of Trisylated Copolymers

Trisylated copolymer	Weight (g)	Yield (%)
PCM1-Tsi	0.61	79
PCM2-Tsi	0.72	81
PCM3-Tsi	0.84	86
PCE1-Tsi	0.60	85
PCE2-Tsi	0.65	78
PCE3-Tsi	0.82	84

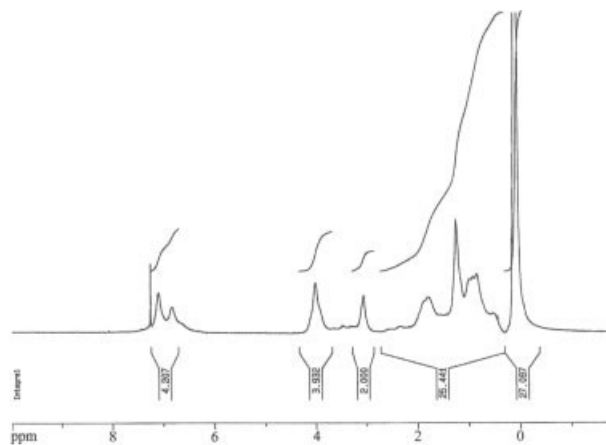


Figure 4 ¹H NMR spectrum of PCE1-Tsi in CDCl₃.

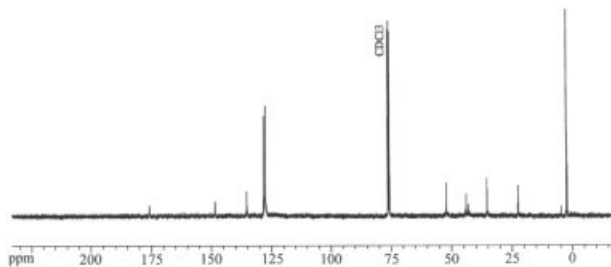


Figure 5 ^{13}C NMR spectrum of PCM1-Tsi in CDCl_3 .

were observed (Fig. 5). Since the electronegativity of silicon atom is lower than the electronegativity of chlorine atom, the chemical shifts of new bonds in both ^1H and ^{13}C NMR spectra are logically shifted towards lower frequency.

Determination of the T_g value of trisylated polymers was carried out by DSC. There is only one T_g peak in the DSC curves. As shown in Figure 6, the T_g values of PCM1-Tsi, PCM2-Tsi, and PCM3-Tsi are 240, 255, and 273°C, respectively. Also, the T_g values of PCE1-Tsi, PCE2-Tsi, and PCE3-Tsi are 200, 220, and 251 °C, respectively, (Fig. 7).

Study of these DSC curves resulted that incorporation of Tsi substituents in polymer side chains increases the rigidity of polymers and the T_g value is subsequently increased. In addition, with increase of CMS moles in the copolymer structures, the bulky trisyl groups are incorporated in high yields. Increasing of functionalized side chains in polymers decreases the free volume of the macromolecules chains.

CONCLUSIONS

The various CMS copolymers with MMA and EMA were prepared by radical polymerization method. The

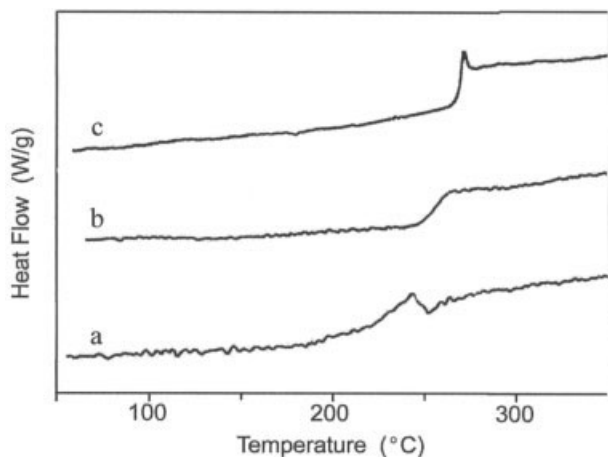


Figure 6 DSC curves of (a) PCM1-Tsi; (b) PCM2-Tsi; (c) PCM3-Tsi

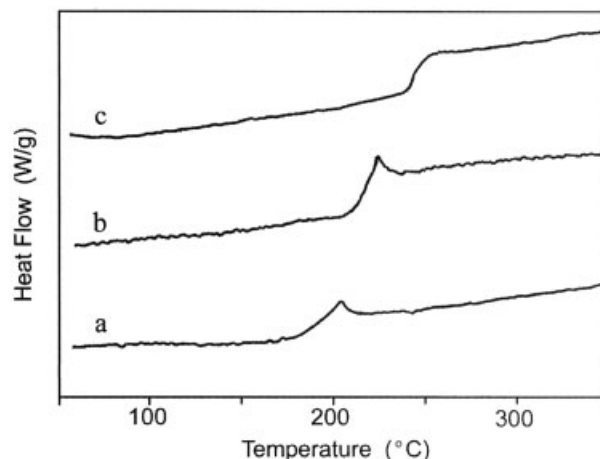


Figure 7 DSC curves of (a) PCE1-Tsi; (b) PCE2-Tsi; (c) PCE3-Tsi

incorporation of highly sterically hindered trisyl groups took place from the reaction between TsiLi and benzyl chloride bonds in the copolymers to yield the novel modified copolymers. Very bulky Tsi substituents were linked to the aromatic rings via a methylene group. The DSC analyses showed that the presence of bulky Tsi groups leads to an increase in the glass transition temperature. The incorporation of the Tsi group into polymer structure creates macromolecules with novel architecture that could be used as membranes for gas or fluid separation.

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