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Ring-opening polymerization of γ-glycidoxypropyltrimethoxysilane catalyzed by multi-metal cyanide catalyst

Jingxia Wang · Xiaodong Fan · Wei Tian · Yanli Wang · Juanli Li

Abstract Ring-opening polymerizations of γ-glycidoxypropyltrimethoxysilane (GPTMS) were carried out by using multi-metal cyanide (MMC) catalyst and the synthesized homopolymer was a comb-shaped polymer with regular structure. The structure of the polymer obtained (P-GPTMS) was characterized by FTIR, ^{1}H-NMR, and ^{29}Si-NMR spectroscopy, and the molecular weight and its distribution were analyzed by size-exclusion chromatography with multi-angle laser light scattering (SEC-MALLS). The thermal behavior of P-GPTMS was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). P-GPTMS with high molecular weight (M_n=18,000–80,000) and narrow molecular weight distribution (1.10–1.35) were synthesized when the dosage of MMC catalyst was 0.1% and polymerization temperature was 130 °C. The molecular weight of the product could be adjusted by controlling the polymerization time. The T_g of P-GPTMS is in the range of −34 to −30 °C. On the basis of the TGA data, the decomposition rate of P-GPTMS reached its peak at 374.14 °C and the entire decomposition stopped at 600 °C.

Keywords Ring-opening polymerizations · γ-Glycidoxypropyltrimethoxysilane (GPTMS) · Multi-metal cyanide catalyst · DSC · TGA

J. Wang (✉) · X. Fan · W. Tian · Y. Wang
Key laboratory of Physics and Chemistry in Space,
Ministry of Education, School of Science,
Northwestern Polytechnical University,
127 Youyi xilu,
Xi'an 710072, China
e-mail: wjx@nwpu.edu.cn

J. Li
Electro-Optical Materials Department,
Xi'an Modern Chemistry Research Institute,
Xi'an 710065, China

Introduction

Multi-metal cyanide (MMC) is a well-known catalyst for the ring-opening polymerization of epoxides such as propylene oxide and ethylene oxide [1]. MMC is an efficient multicomponent catalyst comprising $Zn_3[Co(CN)_6]_2$ as the main component, $Ni_3[Co(CN)_6]_2$, $Fe[Co(CN)_6]$, $Ni_3[Fe(CN)_6]_2$, and/or $Zn_3[Fe(CN)_6]_2$, along with organic complexing agent and functional polymer as ligand. MMC catalysis allows the efficient polymerization of epoxides, and the resulting polyethers have low unsaturation and high molecular weights [2, 3].

In the past few years, many researches have focused on the polymerization of propylene oxide catalyzed by MMC. Some researches indicated that this catalyst could only be used to catalyze copolymerization of epoxide and carbon dioxide [4], cyclohexene oxide and carbon dioxide [5], propylene oxide and cyclic acid anhydride [6], and propylene oxide and carbon dioxide [7], etc.

As a silane coupling agent, γ-glycidoxypropyltrimethoxysilane (GPTMS) is mostly used in the modification of composite material and its interface [8–10]; ring-opening polymerization of GPTMS is widely used in the surface modification of polymer or monomer, graft modification of polymer microspheres, and preparation of organic-inorganic composite materials.

At present, P-GPTMS was mostly synthesized by polycondensation of alkoxy groups in GPTMS. Due to the fact that catalysts used at present, such as triethylamine [11, 12], diethanolamine [13], BF_3OEt_2 [14, 15], and so on [16–19], can initiate the hydrolytic cross-linking of silane methoxy groups in GPTMS to form a three-dimensional cross-linked elastomer, there is little reported research on preparing linear P-GPTMS by ring-opening polymerization of epoxy groups in GPTMS.

In this paper, a new synthetic method was introduced for ring-opening polymerization of GPTMS, in which MMC was selected as catalyst. A linear, comb-shaped homopolymer, i.e., P-GPTMS, was synthesized. The structure of the synthesized P-GPTMS was characterized by FTIR, ^{1}H-NMR, and ^{29}Si-NMR spectroscopy. The molecular weight and its distribution of P-GPTMS were analyzed by size-exclusion chromatography with multi-angle laser light scattering (SEC-MALLS) and the polymerization conditions were determined. The glass-transition temperature (T_g) and thermal weight loss of P-GPTMS were assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively.

Experimental

Material

MMC catalyst was purchased from Nanjing Jinglin Petrochemical Co. Ltd. (Nanjing, China) and was dried for 24 h at 60 °C under vacuum before use. Its formula is $Zn_3[Co(CN)_6]_2 \cdot Ni_3[Co(CN)_6]_2 \cdot Fe_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot wH_2O \cdot yTBA \cdot jP \cdot zA$, where $Zn_3[Co(CN)_6]_2$ is the main component of the metal cyanides. The masses of $Ni_3[Co(CN)_6]_2$ and $Fe_3[Co(CN)_6]_2$ are each 5% of that of $Zn_3[Co(CN)_6]_2$. TBA is *tert*-butyl alcohol, P is polyether, and A is organosiloxane.

GPTMS (97%) was purchased from Alfa Aesar and used as received. Petroleum ether was analytical grade, purchased from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjing, China), and dried before use.

Ring-opening polymerization of GPTMS

The ring-opening polymerization of GPTMS was carried out according to the following procedure: 16 g of GPTMS and 16 mg of MMC catalyst were put into a 50-mL dried flask equipped with a magnetic stirrer. The flask was purged for 30 min with nitrogen gas and then sealed. The system was allowed to polymerize at 130 °C for 15 h with magnetic stirring. A white viscous liquid was obtained. The product was extracted several times with petroleum ether to remove the residual monomer GPTMS, and then dried to

constant weight in vacuum at 45 °C. Finally P-GPTMS was obtained.

Characterizations

The ^{1}H-NMR and ^{29}Si-NMR spectra were conducted on a Bruker Avance 300 spectrometer (Bruker BioSpin,Switzerland), with dimethyl sulfoxide (DMSO) as the solvent, and tetramethylsilane (TMS) as the internal standard.

The FTIR spectrum was acquired with a Nicolet iS10 FTIR (USA, KBr film).

The molecular weight and the molecular weight distribution of P-GPTMS were determined by SEC-MALLS in SEC/DAWN EOS/Optilab rEX/QELS model (Wyatt Technology Corporation, USA) using an HPLC pump (Waters 515) and a column (300 mm×0.8 mm, MZ-Gel SDplus 500 Å 5 μm). The mobile phase was tetrahydrofuran (THF), the flow rate was 0.5 mL min^{-1} and the injection volume was 0.2 mL. The differential refractive index (dn/dc) value of P-GPTMS was measured using an Optilab rEX differential refractometer (Wyatt Technology). Sample concentration was 5, 10, 15, 20, and 25 mg mL^{-1}, respectively. ASTRA software (Version 5.1.3.0, Wyatt Technology) was utilized for data acquisition and analysis.

The glass-transition temperature of P-GPTMS was obtained by using a TA-2910 differential scanning calorimeter (USA) under nitrogen protection. The heating rate was 10 °C min^{-1}.

TGA was conducted on a TA Hi-Res TGA2950 (USA) under nitrogen protection. The heating rate was 10 °C min^{-1}.

Result and discussion

Ring-opening polymerization of GPTMS

As shown in Scheme 1, ring-opening polymerization of GPTMS can occur under the action of MMC catalyst and forms a linear polymer P-GPTMS. The polymerization was influenced by several factors such as polymerization time, polymerization temperature, and the amount of MMC used.

In order to investigate the effect of polymerization time on the product's molecular weight, polymerization was

Scheme 1 Synthesis of P-GPTMS by MMC-catalyzed ring-opening polymerization of GPTMS
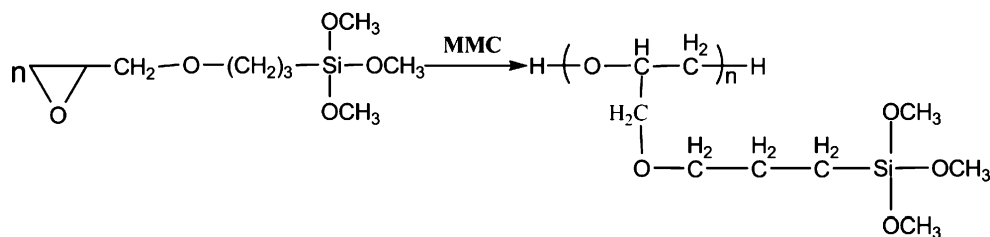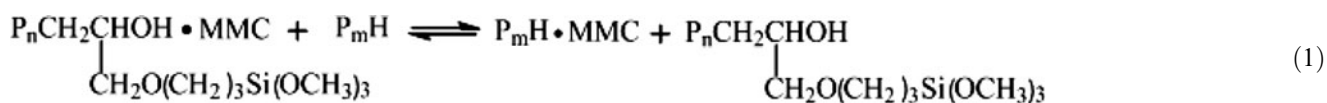
carried out in the time period from 1 to 25 h and the results are shown in Table 1. The molecular weight of P-GPTMS increased from 18,000 to 80,000 with increasing polymerization time. In the reaction period 1–15 h, the molecular weight and the monomer conversion increased significantly with the polymerization time, whereas they increased slowly after 15 h reaction. The polymerization was therefore considered to be almost finished after 15 h reaction and the molecular weight could be modified by controlling the polymerization time. In contrast to the effect of polymerization time on the molecular weight, the molecular weight distribution decreased with the polymerization time in the period 1–15 h and increased in the period 15–25 h. Because we used a large excess of monomer (16 g) in comparison with catalyst (0.016 g), monomer-to-catalyst molar ratios as high as 10^3 were reached. Accordingly, it is impossible to assume that all chains grow in a living mode like in controlled anionic polymerization. It is therefore reasonable to assume that a rapid exchange between the non-active and active centers

Table 1 Results of ring-opening polymerization of GPTMS

Polymerization time (h)	M_n (g/mol)	M_w/M_n	Monomer conversion (wt%)
1	18,160	1.341	33.7
2	27,020	1.333	42.9
3	32,940	1.331	52.3
5	43,400	1.305	59.8
8	52,940	1.202	69.3
11	66,640	1.195	79.1
15	75,900	1.147	85.3
20	76,100	1.209	86.9
25	77,250	1.244	87.2

MMC 16 mg, GPTMS 16 g, temperature 130 °C

accounts for the control of the molecular weight distribution (shown as reaction Eq. 1; P represents a chain segment of $CH_2CH(CH_2O(CH_2)_3Si(OCH_3)_3)O$ and P_mH is a non-active chain element).

$$P_nCH_2CHOH \cdot MMC \ + \ P_mH \ \rightleftharpoons \ P_mH \cdot MMC \ + \ P_nCH_2CHOH$$
$$CH_2O(CH_2)_3Si(OCH_3)_3 \qquad\qquad\qquad CH_2O(CH_2)_3Si(OCH_3)_3$$

(1)

During the reaction procedure, if the exchange reaction rate is greater than the chain propagation rate, P-GPTMS could possess a narrow molecular weight distribution. At prolonged reaction times, the exchange reaction rate decreased. When the exchange reaction rate is slightly less than the chain propagation rate, the molecular weight distribution gets slightly broader accordingly. However, the molecular weight distributions of all P-GPTMS in this study were narrow and in the range 1.10–1.35. So we concluded that the molecular weight distribution could also be modified by controlling the polymerization time.
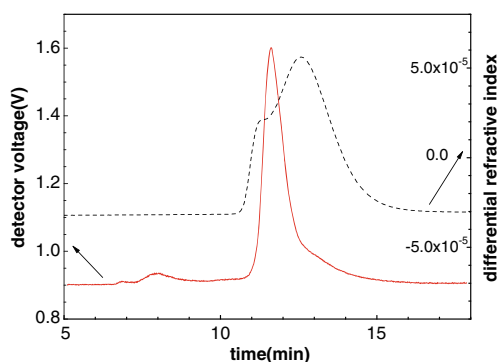
Figure 1 is the SEC-MALLS chromatogram of P-GPTMS. The obtained unimodal curve (the laser signal curve) indicated that the P-GPTMS molecular weight was monodisperse.

Polymerization temperature had significant effect on the ring-polymerization of GPTMS as demonstrated in Fig. 2, in which the percentage monomer conversion reflects the extent of polymerization. The polymerization did not occur within 15 h until the temperature reached 110 °C. Then the polymerization occurred and the
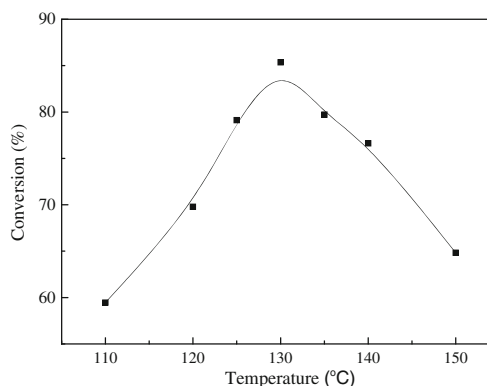

Fig. 1 SEC-MALLS chromatogram of P-GPTMS

Fig. 2 Effect of polymerization temperature on monomer conversion. Polymerization conditions: MMC 16 mg, GPTMS 16 g, polymerization time 15 h
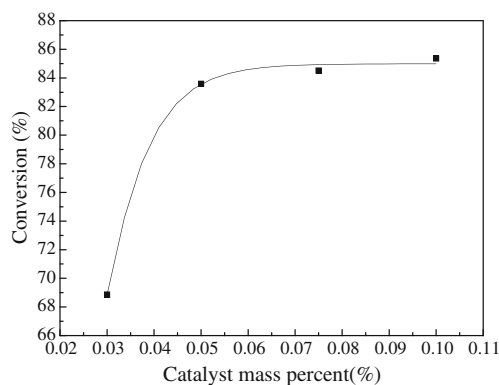
Fig. 3 Effect of catalyst amount on monomer conversion. Polymerization conditions: temperature 130 °C, GPTMS 16 g, polymerization time 15 h

Fig. 4 FTIR spectra of GPTMS and P-GPTMS

monomer conversion increased with temperature within the range 110–130 °C, and decreased when the temperature was above 130 °C. The reason for these results was that the catalyst MMC was activated at 110–130 °C, so the monomer conversion increased at first. However, when temperature was above 130 °C, the color of the product became darker possibly as a result of some side reactions occurring which could slow down the polymerization. On the basis of the above results, the optimum temperature of ring-polymerization of GPTMS catalyzed by MMC was 130 °C.

The dosage of MMC catalyst is another important factor that influences the polymerization as shown in Fig. 3. The polymerization did not occur until the dosage of MMC
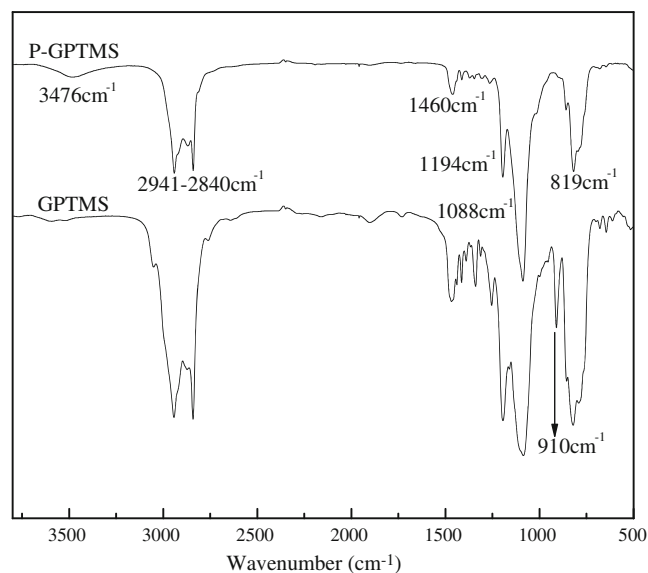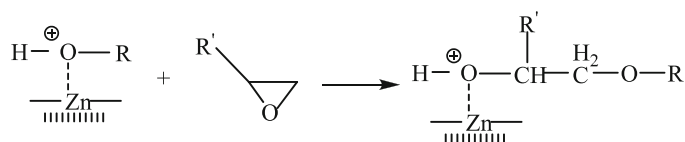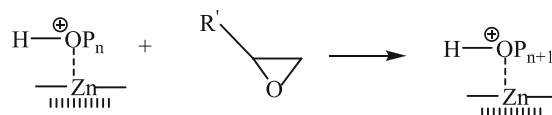
catalyst reached 0.03% (weight percent). Then the monomer conversion increased rapidly when the dosage of MMC catalyst was 0.03–0.05%. After the dosage reached 0.05%, the monomer conversion increased slowly. This result was due to the efficiency of the catalyst increasing with its dosage and then reaching a stable level when the dosage reached a certain amount. Excess catalyst was not only unable to improve its efficiency, but also worsened the
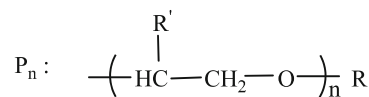
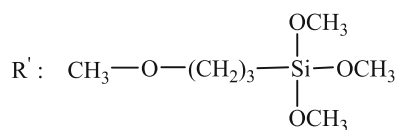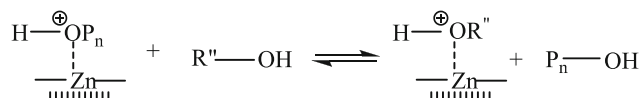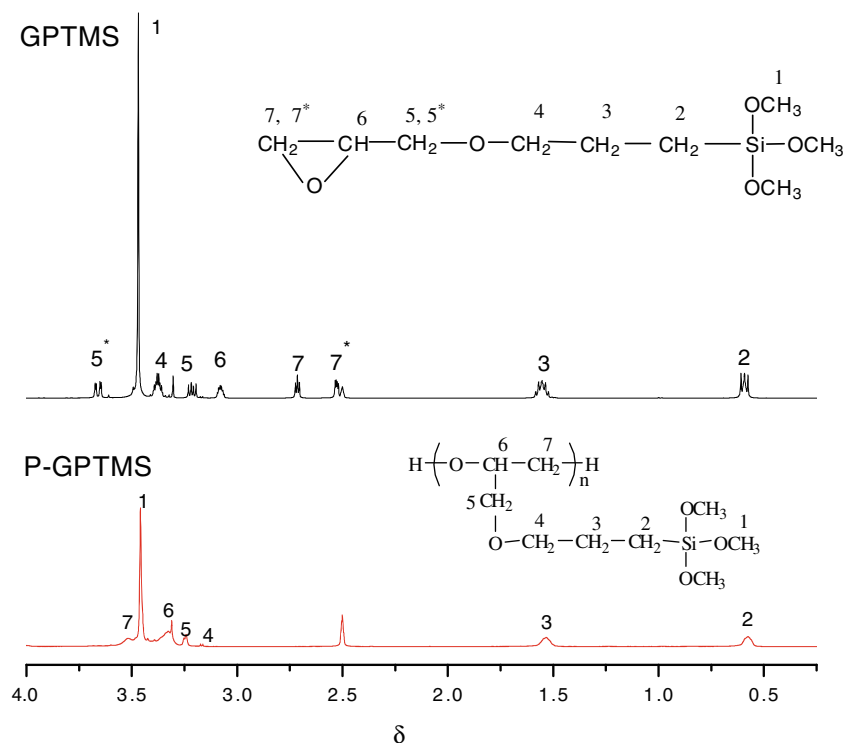Scheme 2 Proposed mechanism of GPTMS polymerization

Fig. 5 ^{1}H-NMR spectra of P-GPTMS and GPTMS

purity and the performance of the final product. Taking all these factors into consideration, the optimum dosage of MMC catalyst was selected to be 0.05–0.1%.

On the basis of our epoxide polymerization results and reports in the literature [20–24], the catalytic mechanism of MMC can be postulated as shown in Scheme 2. Firstly, a

Zn–O active site, which has cationic character, coordinates with GPTMS to form a monomer active site. Then another GPTMS coordinates with the monomer active site to form a propagation center. In addition, the chain propagation is usually accompanied by an exchange reaction between a dormant site and active site.

Fig. 6 ^{29}Si-NMR spectrum of P-GPTMS
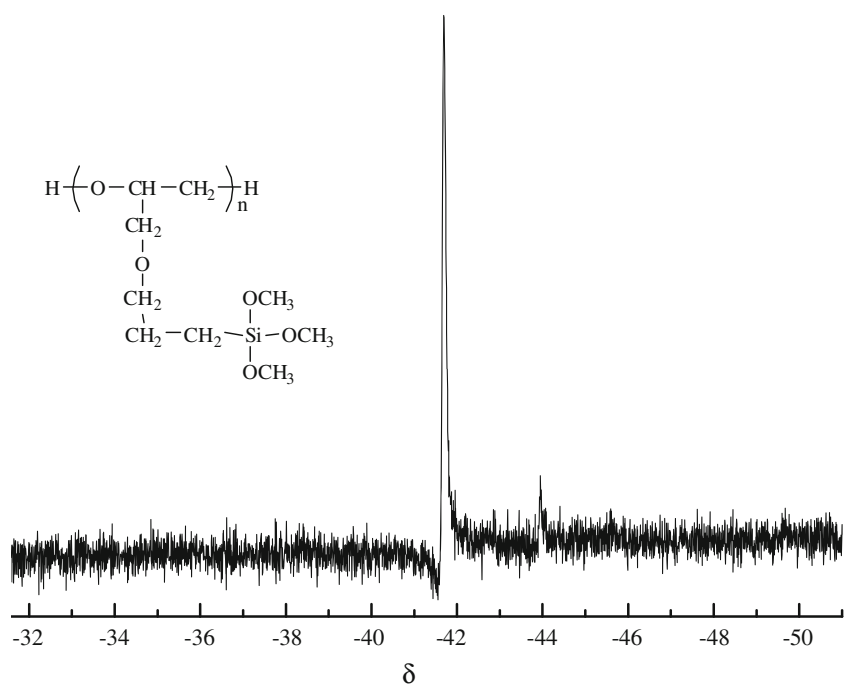
Characterizations

FTIR spectroscopy

The FTIR spectra of GPTMS monomer and P-GPTMS polymer are shown in Fig. 4. The characteristic absorption peak of the epoxy group can be seen at around 910 cm^{-1} in the spectrum of monomer disappeared completely after polymerization of GPTMS. This indicated the great possibility of ring-opening polymerization of GPTMS monomer. The FTIR spectrum of P-GPTMS was assigned as follows [25]: 819 cm^{-1} ($\nu_{Si–C}$, s), 1,088 cm^{-1} ($\nu_{C–O\ (Si–O–CH3)}$, s), 1,194 cm^{-1} ($\nu_{C–O(C–O–C)}$, s), 2,941–2,840 cm^{-1} (ν_{CH3} and ν_{CH2}, s), 1,460 cm^{-1} ($\delta_{sC–H}$, s) 3,476 cm^{-1} ($\nu_{O–H}$, s). The characteristic absorption peak of the C–O bond from the Si–O–CH$_3$ group was retained at around 1,088 cm^{-1} after polymerization of GPTMS; in addition, there was no absorption peak at 1,020–1,070 cm^{-1}, the region in which the characteristic absorption peak of the Si–O–Si group would occur. So, hydrolytic cross-linking reactions of the Si–O–CH$_3$ group did not occur. Such results proved that P-GPTMS was indeed a ring-opening polymerization product other than a hydrolytic cross-linking product.

NMR characterizations

The ^{1}H-NMR spectra of polymer P-GPTMS and monomer GPTMS are shown in Fig. 5, in which the chemical shifts of hydrogen protons are assigned accordingly. Note that the signal at δ 2.501 is the characteristic absorption peak of the solvent. It can be seen that the GPTMS signals at δ 2.705–2.724 and δ 3.081, which are due to the epoxy group, were shifted to around 3.4 ppm after ring-opening polymerization, which is in good agreement with literature data [17, 26]. The P-GPTMS signal at δ 3.459, which is due to the –SiOCH$_3$ group, still existed; this observation also proved that P-GPTMS was a ring-opening polymerized polymer other than a hydrolytic cross-linked polymer. Figure 6 shows the ^{29}Si-NMR spectrum of polymer P-GPTMS. The dominant signal at δ 41.7 is due to the –SiOCH$_3$ group.
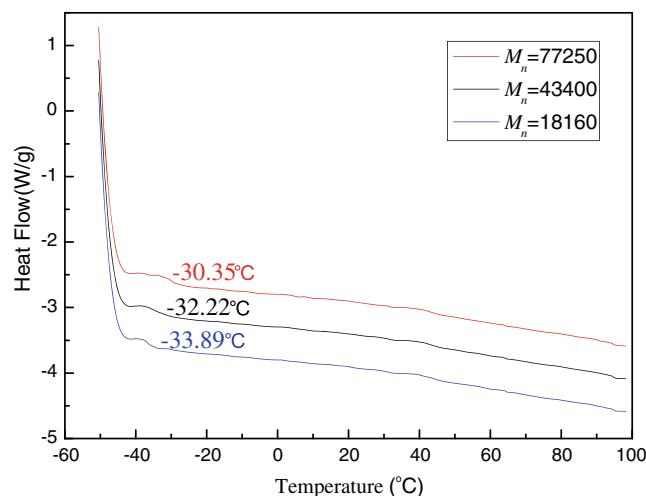

Fig. 7 DSC curves of P-GPTMS

This indicated again that no significant hydrolytic cross-linking reaction of the Si–O–CH$_3$ group occurred. However, it should be noted that a few Si–O–Si groups evidenced by the signal at δ 44 could still be found; these groups might be produced by the epoxy group of P-GPTMS reacting with water in air during the P-GPTMS reprocessing procedure. Therefore, the ^{29}Si-NMR spectrum confirmed the conclusions drawn from the ^{1}H-NMR spectra.

In summary, the results of FTIR, ^{1}H-NMR, and ^{29}Si-NMR spectroscopy all supported that P-GPTMS could be synthesized by MMC-catalyzed ring-opening polymerization of GPTMS with no accompanying hydrolytic cross-linking reaction. In accordance with this ring-opening polymerization of GPTMS, the structure of P-GPTMS must have a comb-shaped regular structure, i.e., a macromolecular chain with long side chains, according to the Scheme 1.

DSC analysis

Table 2 lists the glass-transition temperature of P-GPTMS with different molecular weight. The glass-transition tem-
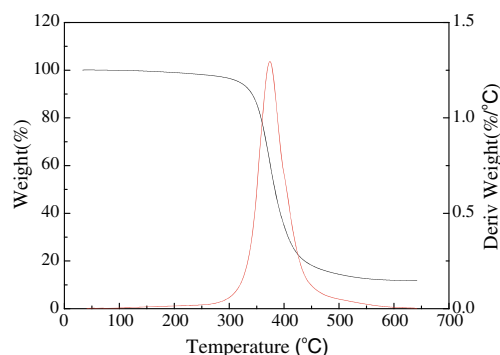
Table 2 T_g data of P-GPTMS

M_n (g/mol)	T_g (°C)
18,160	−33.89
27,020	−33.79
32,940	−32.89
43,400	−32.22
52,940	−31.72
66,640	−31.09
75,900	−30.91
77,250	−30.35

Fig. 8 TGA curve of P-GPTMS

peratures of P-GPTMS were all below −30 °C and increased gradually with the molecular weight. This result is in accordance with the relation between glass-transition temperature and molecular weight of the common polymer.

Figure 7 shows the DSC curves of P-GPTMS with a molecular weight of 18,160, 43,400, and 77,250, respectively. By using the data processing software, the corresponding glass-transition temperatures were determined to be −33.89, −32.22, and −30.35 °C, respectively.

TGA analysis

The TGA curve of P-GPTMS is shown in Fig. 8. The mass of the P-GPTMS sample remained constant at the beginning of the heating run below 150 °C, but after reaching 150 °C, the sample started to lose weight. With increasing temperature, the degradation rate of P-GPTMS increased. At 374.14 °C, the degradation rate reached the maximum value and then gradually decreased and reached zero at 600 °C, which indicated that the entire decomposition stopped.

Conclusions

Ring-opening polymerizations of GPTMS were carried out by using MMC catalyst, and P-GPTMS with different molecular weight was prepared. The results of FTIR, ^{29}Si-NMR, and ^{1}H-NMR spectroscopy illustrated that the synthesized P-GPTMS was a ring-opening polymerized product with a comb-shaped structure other than a hydrolytic cross-linking product. The molecular weight and its distribution (M_{w}/M_{n}=1.10–1.35) could be modified by controlling the range of polymerization time from 1 to 25 h. The optimum temperature for synthesizing P-GPTMS was 130 °C and the optimum dosage of MMC catalyst was 0.05–0.1%. The glass-transition temperature of P-GPTMS was all below −30 °C and increased gradually with the molecular weight. On the basis of the TGA data collected, the decomposition of P-GPTMS started at 150 °C, the decomposition rate reached its peak at 374.14 °C, and the entire decomposition stopped at 600 °C.

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