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A novel and facile method for direct synthesis of cross-linked polysiloxanes by anionic ring-opening copolymerization with Ph_{12}-POSS/D_4/Ph_8D_4

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Abstract

The cross-linked polysiloxanes were directly synthesized by anionic ring-opening copolymerization of Ph_{12}-POSS as multifunctional monomer with D_4 and Ph_8D_4 under KOH or Me_4NOH siloxanolate. And the influences of the polar additive DMAc on gelation time were investigated. The results of gel content and swelling ratio, GPC, solid-state ^{29}Si and ^{13}C NMR, FT-IR, WAXD showed that Ph_{12}-POSS was reacted and most of the product was cross-linked. The DSC and TG results indicated that the cross-linked polysiloxanes exhibited distinct glass transition temperatures (T_g) and excellent thermal stability. Compared to that with KOH siloxanolate, the cross-linked polysiloxane synthesized with Me_4NOH siloxanolate has more preferable thermal stability.

Keywords: POSS; Cross-linked polysiloxane; Anionic ring-opening copolymerization

1. Introduction

The superior thermal stability and the good resistance to oxidative degradation of polysiloxanes have made them attractive candidates for applications at elevated temperatures [1–5]. But polysiloxanes must be cross-linked partially or extensively to prevent from flowing and give themselves strength before used whether as silicone rubbers or silicone resins. Cross-linked polysiloxane networks can be formed in numerous approaches such as condensation, transition-metal-catalyzed addition and free radical initiation cross-linking techniques [1,6–11], which are all two-step methods to give cross-linked polysiloxanes, that is to say, the prepolymers are prepared first and then cross-linked. Condensation cross-linking technique requires an enough high temperature and highly effective catalytic agents to form extensively cross-linked polysiloxanes. Moreover, considerable amount of small molecules such as water or alcohol are spilt out to form ever-larger molecules during the condensation process, leaving cracks and voids. These drawbacks influence the performance of cross-linked polysiloxanes and their applications. The others develop slowly due to expensive cost or inconvenient use. Therefore, it is a challenge to search a novel and facile method for directly producing cross-linked polysiloxanes.

Polyhedral oligomeric silsesquioxane (POSS) [12–20], a cage structure with Si–O–Si framework and its empirical formula $(RSiO_{1.5})_n$, where R is an organic substituent or a cap, is a novel class of relatively large molecules containing organic and inorganic components and has recently been developed for incorporation into synthetic polymer systems due to its designable hybrid nanostructure. Marsmann et al. have observed that the octa-silsesquioxanes were rearranged to produce the greater frameworks deca- and dodeca-silsequioxanes under the influences of the catalysts such as sodium acetate, sodium cyanate, sodium sulfite, sodium hydroxide and potassium carbonate in acetone as solvent [21]. Feher et al. have reported that the POSS frameworks were cleaved to afford functionalized products by either strong acids or strong bases [22–24].

Based on the considerations above, the objective of this research is to investigate the anionic ring-opening copolymerization of dodecaphenyl-POSS (Ph_{12}-POSS) as multifunctional monomer with octamethylcyclotetrasiloxane

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(D_4) and octaphenylcyclotetrasiloxane (Ph_8D_4) by using the base catalysts such as potassium hydroxide (KOH) or tetramethylammonium hydroxide (Me_4NOH) siloxanolate. Furthermore, this method can directly produce excellently thermally stable and cross-linked polysiloxanes under relatively mild conditions (Scheme 1).

2. Experimental section

2.1. Materials

All reagents were commercially obtained, unless otherwise stated. D_4 was dried over calcium hydride (CaH_2) and purified by distillation. Ph_{12}-POSS, Ph_8D_4, KOH, *N*,*N*-dimethylacetamide (DMAc) and toluene were all used without further purification. Me_4NOH, 10% water solution, was concentrated by removal of the water under vacuum before use.

2.2. Siloxanolate synthesis

KOH or Me_4NOH siloxanolate were synthesized by the reaction of D_4 and an amount of base (KOH for 3 h at 130 °C; Me_4NOH for 3 h at 90 °C) with weight ratio 50:1 under nitrogen atmosphere. Then the reactions were allowed to remove trace amounts of water under vacuum for 1 h [25] and the obtained clearly transparent oils were stored dryly at low temperature until use.

2.3. Cross-linked polysiloxanes polymerization

Cross-linked polysiloxanes were synthesized by anionic ring-opening copolymerization of D_4, Ph_8D_4 and Ph_{12}-POSS at presence of the polar additive DMAc with siloxanolate catalyst (KOH siloxanolate at 100 °C; Me_4NOH siloxanolate at 90 °C) under nitrogen atmosphere. When the reaction mixture became too viscous to stir, stopped the stirring and kept the reaction temperature for different times depending on the catalysts (KOH siloxanolate for 3 h; Me_4NOH siloxanolate for 3 h, then the temperature was quickly raised to about 160 °C for 0.5 h to isolate the Me_4NOH). The resulting white solid was dried under vacuum for more 24 h at 60 °C to remove thoroughly the small molecules. The obtained polymers were insoluble in usual organic solvents.

2.4. Characterization

2.4.1. The determination of the gel content and swelling ratio

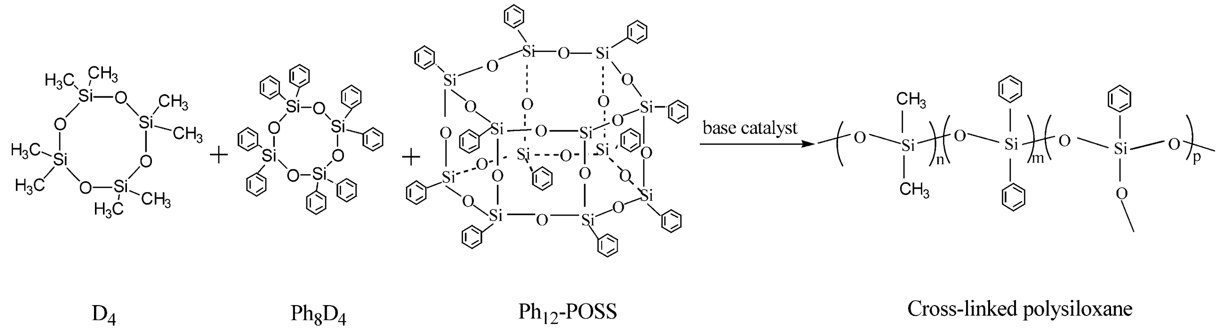
The gel content and swelling ratio of the products were measured through a 12 h soxhlet extraction with toluene. The extraction can thoroughly remove the uncross-linked polysiloxanes and the unreacted monomers, so the leavings are the completely cross-linked polysiloxanes. The gel content (GC) is the insoluble mass fraction and determined by taking the ratio of the mass of the thoroughly dried gel (W_1) after extraction to the mass of the starting polymer (W_0). The swelling ratio (SR) is a measure of the cross-link density and determined by placing the extracted sample (W_2) in a sealed container immediately after extraction and then taking the ratio of its mass to that of the thoroughly dried gel (W_1). So GC and SR are defined as

$$\mathrm{GC} = \left(\frac{W_1}{W_0}\right) \times 100\%$$

$$a\mathrm{SR} = \left(\frac{W_2}{W_1}\right) \times 100\%$$

2.4.2. Instruments

Polymer molecular weight was estimated using a Waters 515-2410 gel permeation chromatographer (GPC). Polystyrene standards were used for calibrating and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min. Solid-state (^{13}C, ^{29}Si) nuclear magnetic resonance (NMR) spectra measurements were recorded on a Bruker AV300 MHz spectrometer (4 mm specimen tube). Fourier transform infrared (FT-IR) spectra were performed using a Nexus 670 (FT-IR) instrument. All samples were prepared as pellets using spectroscopic grade KBr. Wide-angle X-ray diffraction (WAXD) was recorded with a D/Max 2500 VB2+/PC based analytical diffractometer using Ni-filtered Cu K_α radiation. Glass transition temperature (T_g) was determined at the inflection point of the



Scheme 1. Direct synthesis of cross-linked polysiloxane with Ph_{12}-POSS/D_4/Ph_8D_4.

endotherm with a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) with a heating rate of 20 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TG) was performed on a Perkin-Elmer TGS-2 with a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

3.1. The influence of the polar additive DMAc on gelation time

Because of the enormous cage frameworks and bulky substituents of Ph_{12}-POSS macromonomer, it is difficult to react by anionic ring-opening copolymerization for Ph_{12}-POSS, D_4 and Ph_8D_4 in the bulk. In this regard, no work has been yet reported on anionic ring-opening polymerization of POSS or with other monomers. Our experiments also demonstrated that it did not yet gel for 10 h in the reaction system above. But some polar additives can dramatically influence the anionic ring-opening polymerization. In this paper, the investigation is focused on the influence of the polar additive DMAc on gelation time. Fig. 1 shows that gelation time decreases distinctly with DMAc increase due to the formed ion pairs via active centers associated with the counterions in the system of anionic polymerization. The ion pairs are solvated by means of adding some polar substances in the bulk, resulting in extending the distance of the active centers and counterions. Therefore, Ph_{12}-POSS macromonomers are much easier to form new active species by inserting into the ion pairs. Consequently, the activity of the ion pairs increases, causing the rate of polymerization to enhance and the gelation time to decrease.

3.2. The determination of gel content and swelling ration

In our case, the cross-linking is confirmed by gel content and swelling ration. The lower the swelling ratio, the more is the cross-linking density.

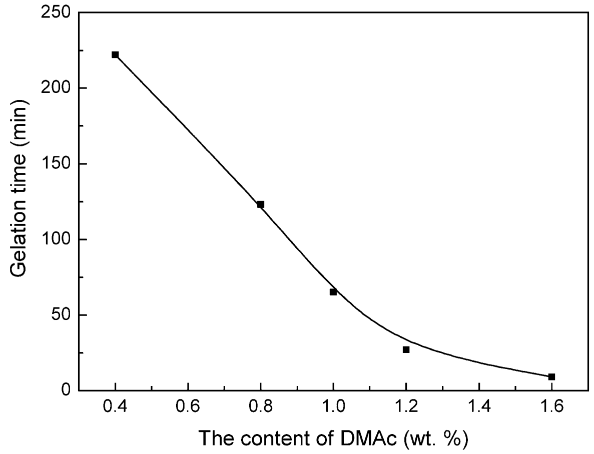


Fig. 1. The influence of the polar additive DMAc on gelation time; the Si mole ratio of D_4, Ph_{12}-POSS and Ph_8D_4 is 98:1.5:0.5, KOH siloxanolate catalyst, 100 °C.

Fig. 2 shows that the gel content is almost the same, approximately 80%, as the reactant of Ph_{12}-POSS (i.e. the Si mole fraction of Ph_{12}-POSS) increases. However, the swelling ratio decreases, indicating that the cross-linking density of the products increases, which is attributed to an equilibrium reaction of anionic ring-opening polymerization of cyclosiloxane with most strong bases [26,27]:

$$\boxed{[R_2SiO]_n} \rightleftharpoons [R_2SiO]_m + \boxed{[R_2SiO]_l}$$

At the same experimental conditions, the contents of cyclosiloxane are almost constant under the influence of the equilibrium reaction, so the gel content of the products is almost the same. Therefore, it is critical to control the equilibrium reaction and reduce the content of cyclosiloxane if the gel content of the products would be improved. However, with the Ph_{12}-POSS reactant increasing, the –O[(Ph)(O–)SiO]– units (i.e. T^{Ph} bonding) in polysiloxane chain increase. As a result, the cross-linking density of polysiloxane increases, embodying that the swelling ratio decreases.

The GPC analyses of the soluble part of the polymers show that the soluble polysiloxanes are mainly composed of the oligomers with lower molecular weight at hundreds to thousands and few polymers with higher molecular weight more than ten thousands. Therefore, it is believed that the polysiloxanes with higher molecular weight are almost cross-linked.

3.3. The characterization of cross-linked polysiloxanes

The solid-state ^{29}Si NMR spectrum of extracted cross-linked polysiloxane (Fig. 3) shows the detailed information about Si units present in the polymer chain. The signals at −19.0 and −22.4 ppm with a relatively high intensity are assigned to the silicon in the $–O[(CH_3)_2SiO]–$ units (D bonding); the signal at −47.7 ppm to the silicon in the $–O[(Ph)_2SiO]–$ units (D^{Ph} bonding) and the others at −78.9 and −80.4 ppm to the silicon in the –O[(Ph)(O–)SiO]– units (T^{Ph} bonding). The ratio of the three main types of resonances is 100:1.07:5.7, according with the designed value of 100:1.3:6.4, indicating not only that the polymer chains have the –O[(Ph)(O–)SiO]– units and is cross-linked polysiloxanes; but also that Ph_{12}-POSS is concerned with anionic ring-opening copolymerization nearly according to the designed value. It is noted that there are multisignals of the silicon in the $–O[(CH_3)_2SiO]–$ and –O[(Ph)(O–)SiO]– units because of the influence of different adjacent units. In addition, a relatively weak signal at −106.2 ppm is appointed to the silicon in the $–O[(O–)_2SiO]–$ units (Q bonding), which can be explained via the cleavage of Ph_{12}-POSS in base condition [19–21] and the subsequent condensation between the resulting Si–OH linkages.

The solid-state ^{13}C NMR spectrum of the extracted

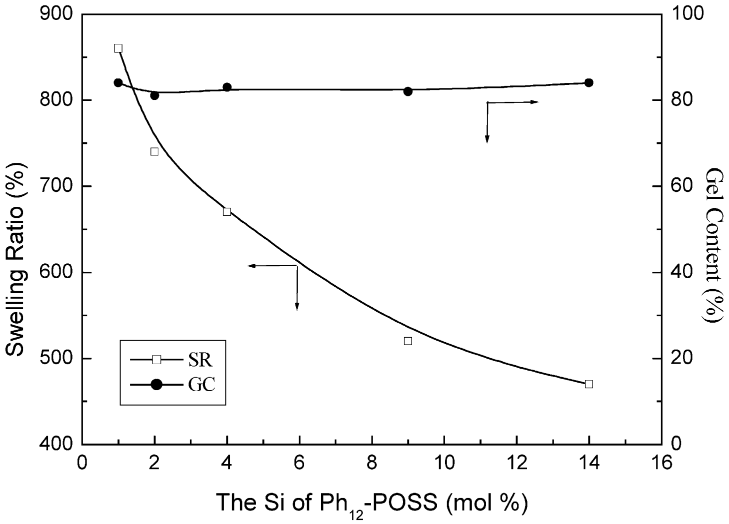


Fig. 2. Gel content and swelling ratio with different Si mole fraction of Ph_{12}-POSS; the Si of Ph_8D_4 is 1 mol%, KOH siloxanolate catalyst, 100 °C.

cross-linked polysiloxane is shown in Fig. 4, which shows that the principal signal at 1.2 ppm is appointed to the carbon in the $–O[(CH_3)_2SiO]–$ units and the other three signals at 130.0, 134.3 and 127.8 ppm to the phenyl carbon in the $–O[(Ph)_2SiO]–$ and $–O[(Ph)(O–)SiO]–$ units because of multiform carbon atoms in phenyl.

Fig. 5 is the FT-IR spectrum of the extracted cross-linked polysiloxane. The signals at 1077.43 and 1007.43 cm^{-1} with relatively high intensity are the characteristic of Si–O–Si stretching. And the signal at 2961.30 cm^{-1} is the characteristic of C–H stretching in the $Si–CH_3$ units. Additionally, the signal at 697.79 cm^{-1} may be the characteristic of C–H bending in the $Si–C_6H_5$ units.

Wide-angle X-ray diffraction methods are normally used to observe any evidence of POSS crystals in a polymer matrix. The WAXD patterns of containing POSS exhibit crystal reflections of POSS if any aggregations of POSS molecules are present in cross-linked polysiloxanes. Fig. 6 shows the WAXD profiles recorded for cross-linked polysiloxanes, the blend of Ph_{12}-POSS (5 wt%) and polydimethylsiloxane (PDMS). Curve *a*, recorded for extracted cross-linked polysiloxane, shows only a broad signal at $2\theta = 11.2°$, indicating that the polysiloxane is not highly crystalline. Curve *c* was recorded for the blend of Ph_{12}-POSS (5 wt%) and PDMS, which was fabricated using the similar solution-casting method, where we simply blended Ph_{12}-POSS with PDMS in toluene solution (0.5 wt%) and then evaporated the solvent to form a film. It shows a few distinct narrow POSS peaks at $2\theta = 8.2$, 17–22° and a broad PDMS signal at $2\theta = 12.0°$, which indicate that the Ph_{12}-POSS reprecipitated back into crystals in the polysiloxane upon solvent evaporation. However, curve *b* was recorded for the cross-linked polysiloxane without extraction, which had about 6 wt% Ph_{12}-POSS before the reaction. If Ph_{12}-POSS would not be reacted, it should reprecipitate back into crystals in the polymer, so its

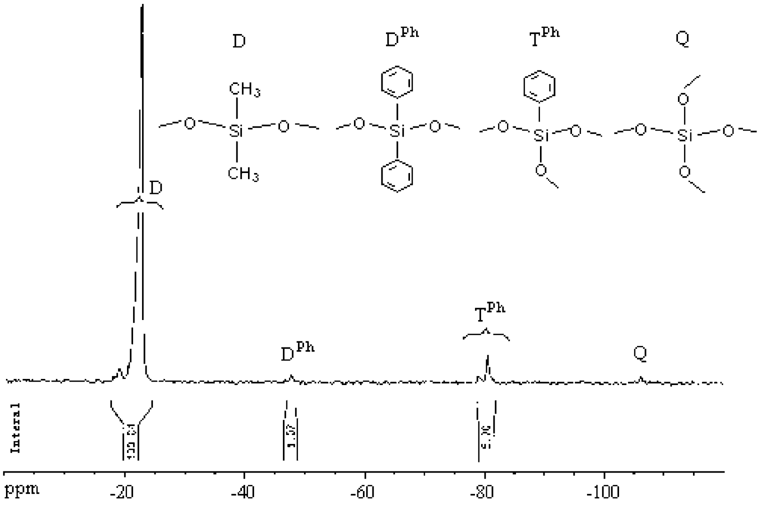


Fig. 3. Solid-state ^{29}Si NMR spectrum of the extracted cross-linked polysiloxane.

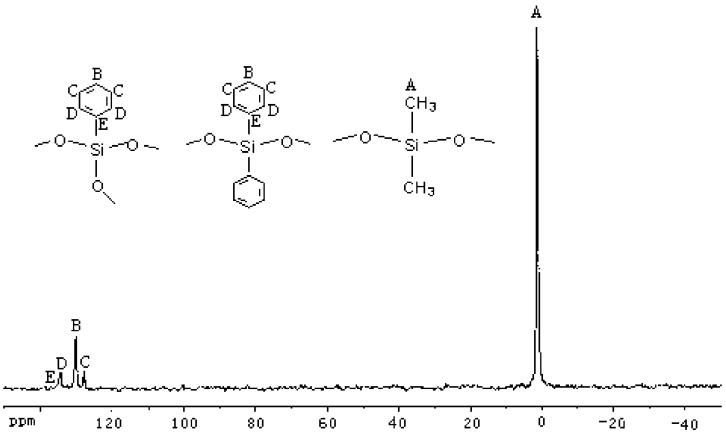


Fig. 4. Solid-state ^{13}C NMR spectrum of the extracted cross-linked polysiloxane.

WAXD curve, would be similar to curve *c* and show some evident narrow peaks at $2\theta = 8.2$, 17–22°. However, the strong similarity between the curve *b* and curve *a*, both only having a broad signal ($2\theta = 11.1°$), indicates that the polymer has few Ph_{12}-POSS aggregations, thus suggesting that most of Ph_{12}-POSS monomers had reacted.

3.4. The thermal analysis of cross-linked polysiloxanes

Fig. 7 is the DSC thermograms (A) and the TG curves (B) of cross-linked polysiloxanes. Curve *a* was recorded from the cross-linked polysiloxane synthesized with KOH siloxanolate, the swelling ratio 460%. Curves *b* and *c* were, respectively, recorded from the cross-linked polysiloxane and the extracted one synthesized with Me_4NOH siloxanolate, the swelling ratio 620%.

The DSC curves of *a*, *b* and *c* show that all the cross-linked polysiloxanes have distinct glass transition temperatures (T_g), −113.0, −115.2 and −113.3 °C (onset temperature), respectively. However, in comparison curve *a* and *b*, lower swelling ratio or higher cross-linking polysiloxanes has a little higher T_g, indicating that cross-linking can slightly increase T_g of the cross-linked polysiloxane. Additionally, the extracted cross-linked polysiloxanes (curve *c*) also has lightly higher T_g than that without extraction (curve *b*) because the extraction can thoroughly exclude the uncross-linked polymers and the unreacted monomers. But they are much higher than the T_g of PDMS at −123 °C [28]. The main reason for this is that the phenyl of pendent group is much more rigid and bulkier than methyl, which restricts the heat movement of chain conformation, causing one shift of T_g to a higher temperature.

The TG curves of cross-linked polysiloxanes under nitrogen atmosphere are shown in Fig. 7(B). The TG curves of *a*, *b* and *c* exhibit that the 10% weight loss temperature (T_{10d}) are 280, 338, 380 °C, respectively, indicating that all cross-linked polysiloxanes have excellent thermal stability. Although the swelling ratio of *b* and *c* is much higher than that of *a*, *b* and *c* have more preferable thermal stability because Me_4NOH siloxanolate catalyst decompounds thoroughly and loses easily its catalyst reactivity under high temperature at above 130 °C, but KOH not.

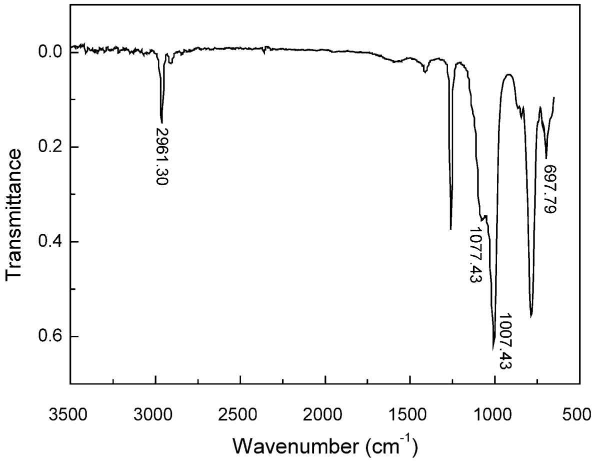


Fig. 5. The FT-IR spectrum of the extracted cross-linked polysiloxane.

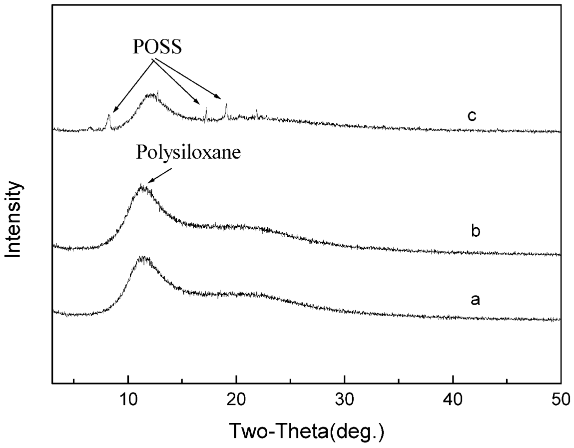


Fig. 6. The WAXD patterns; a, the extracted cross-linked polysiloxane; b, the cross-linked polysiloxane without extraction; c, the blend of Ph_{12}-POSS (5 wt%) and PDMS.

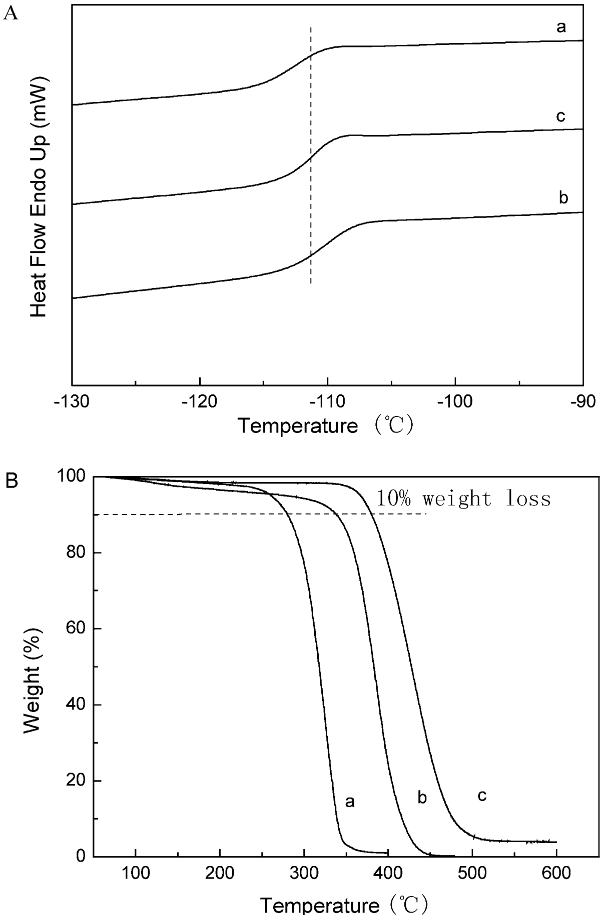


Fig. 7. The DSC thermograms (A) and the TG curves (B) of the cross-linked polysiloxanes; a, the cross-linked polysiloxane synthesized with KOH siloxanolate, its swelling ratio: 460%; b, the cross-linked polysiloxane synthesized with Me_4NOH siloxanolate, its swelling ratio: 620%; c, the extracted cross-linked polysiloxane synthesized with Me_4NOH siloxanolate, its swelling ratio: 620%.

Additionally, anionic ring-opening polymerization of cyclosiloxane with most strong bases is an equilibrium reaction, so the bases are not only its catalyst also its decomposer. Trace amount of KOH can dramatically accelerate polysiloxanes decomposing, which seriously affects the thermal stability of polysiloxanes. Compared *b* and *c*, it can be concluded that the extracted cross-linked polysiloxane has much better thermal stability than that without extraction due to the thorough removal of the uncross-linked polysiloxanes and the unreacted monomers, which can decompose easily under lower temperature. The easy decomposition of uncross-linked polysiloxanes and unreacted monomers also contributes to the higher weight loss of *b* under lower temperature.

4. Conclusions

The cross-linked polysiloxanes were directly synthesized by a novel anionic ring-opening copolymerization with D_4 and Ph_8D_4 via adding multifunctional monomer Ph_{12}-POSS under KOH or Me_4NOH siloxanolate. A series of cross-linked polysiloxanes with different swelling ratio have been successfully obtained by adjusting the content of Ph_{12}-POSS monomer. Gelation time decreases obviously via adding the polar additive DMAc in the bulk polymerization. The cross-linked polysiloxanes are not highly crystalline and most of Ph_{12}-POSS monomers had reacted. The cross-linked polysiloxanes have distinct glass transition temperatures (T_g) and excellent thermal stability. The cross-linked polysiloxane synthesized with Me_4NOH siloxanolate has more preferable thermal stability than that with KOH siloxanolate because Me_4NOH siloxanolate catalyst decompounds thoroughly and loses easily its catalyst reactivity under high temperature at above 130 °C.

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