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RESEARCH ARTICLE

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Synthesis and properties of polystyrene/polydimethylsiloxane graft copolymers

Abstract Polystyrene-graft-polydimethylsiloxane (PS-*g*-PDMS) copolymers with different PDMS content were synthesized by the radical bulk copolymerization of PDMS macromonomer and styrene. The copolymers were characterized by Fourier transform infrared (FT-IR), ^{1}H-nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), transmission electron microscopy (TEM) and the mechanical properties of the copolymers were also carried out. It was indicated that the notched impact strength and elongation at break of the polymers increased with the increase of PDMS content. The thermal stability of PS-*g*-PDMS is better than that of PS.

Keywords polystyrene, polydimethylsiloxane, graft copolymer, mechanical properties, thermal stability

1 Introduction

The control on polymer architecture or topology may be called an art in polymer science because of its great potential to form the polymer materials with special properties or high performance even from inexpensive monomers. In this field, topologizing the copolymers with the macromonomer that possesses the functional groups at one or both ends of the oligomer is a useful method. Recently advanced polymer chemistry has led to the several synthesis techniques for the macromonomer, such as anionic, cationic, group transfer and atom transfer polymerization. These developments stimulated tremendous efforts to study the structure-properties relationships, which introduced macromonomer has much influence on the properties of the formed polymers. Since the polystyrene (PS)-based macromonomers were developed by Milkovich et al. [1–2], more and more graft copolymers have been synthesized by the macromonomer systems with other polymers, such as poly(vinylpridine) [3], poly(methyl methacrylate) [4], poly(vinyl ether) [5], poly(ethylene oxide) [6] etc. Some graft copolymers have been found industrial applications, for example, rubber, elastomers, hydrogels, gas permeation membranes [7–11] etc.

As is well known, polydimethylsiloxane (PDMS) has very low glass temperature, good biocompatibility, low surface energy, high oxygen permeability and resistance to degradation of atomic oxygen and oxygen plasmas [10, 13]. On the other hand, PS possesses good electrical and mechanical properties [11]. Topologizing them by special technique may obtain outstanding results; for example, the microphase-separated PDMS domains in the PS matrix allow the system to exhibit many desirable properties. However, there is no compatibility between the two components.

Therefore, in this paper, the graft copolymers, consisting of microphase-separated PDMS domains embedding in a PS matrix were synthesized. PDMS macromonomers with a narrow molar mass distribution were synthesized by anionic living ring-opening polymerization of hexamethylcyclotrisiloxane (D3) and terminated with vinyl-dimethyl- chlorosiloxane in order to afford a double bond to PDMS macromonomer, which could subsequently copolymerize with styrene into graft PS-*g*-PDMS copolymers. The copolymers then were characterized by FT-IR, ^{1}H-NMR, DMA, TEM and their mechanical properties and thermal stability were studied also.

2 Experiments

2.1 Materials

Cyclohexane (commercial products) was refluxed with

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sodium and distilled just before use. Tetrahydrofunan (THF) (commercial products) was distilled with sodium under argon. D3 (commercial products) was distilled with calcium hydride and dried with 4 Å molecular sieves. Styrene (commercial products) was washed with dilute sodium hydroxide to remove the inhibitors, dried with calcium hydride and distilled under reduced pressure just before use. *n*-BuLi solution in cyclohexane was made according to Xie et al. [12].

2.2 Characterization

Fourier transform infrared (FTIR) spectra of refined samples were obtained from a Nicolet Avatar360 FTIR spectrophotometer. ^{1}H-NMR spectra of refined samples were recorded on a 500 MHz Avance500 spectrometer, $CDCl_3$ as the solvent and TMS as calibration. Gel permeation chromatograph (GPC) was operated at 20℃ using THF as eluent, at a flow rate of 1 mL/minute with four columns in series, packed with polystyrene gel of 2×10^3, 3×10^4, 2×10^5, 8×10^5, porosities, respectively. The instrument was calibrated by standard PS samples. TEM photographs were taken by Hitachi H-600 in order to look in the formation of microphase separation. The films of the graft copolymer were cast by 10% toluene solutions. Special staining techniques were not needed here because of the difference in electron absorption and scattering between the carbon atoms in PS and the silicon atoms in PDMS. DSC analyses were performed with Netzsch DSC200PC instrument from –150 to 250℃ at 10 ℃/minute heating rate. Dynamitic mechanical analysis (DMA) was carried out with Universal DMA242 instruments dynamic viscoelastometer from –150℃ to 200℃, at 3℃/minute heating rate and 1 Hz operating frequency. The sample size was $59.88 \times 12.88 \times 3.12$ mm^3. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer TGA 7 instrument. Samples were heated at 10℃/minute in a flowing air environment. The percentage weight loss was measured as a function of temperature.

2.3 Macromonomer synthesis

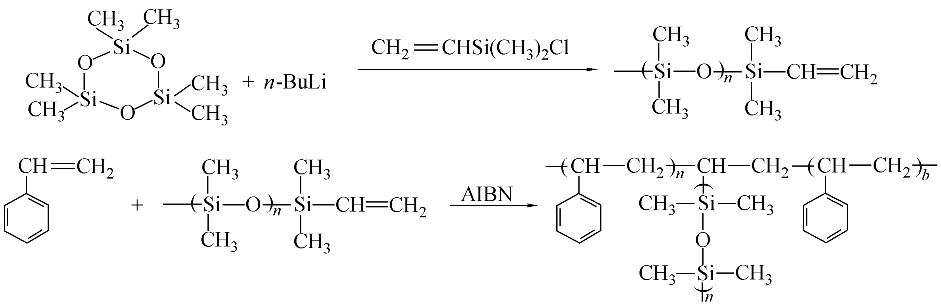
Anionic polymerizations were carried out in rigorously cleaned and dried one-neck round-bottom flasks equipped with a magnetic stirrer and rubber septum under a prepurified argon atmosphere. The D3 in cyclohexane solution was syringed into the reaction flask, and a calculated amount of *n*-butyllithium was added to initiate the ring-opening polymerization. The initial reaction was allowed to proceed for 0.5 hours, followed by adding 10% N,N-dimethylformamide (DMF) by volume to promote propagation of the living siloxanolate species. The polymerization was terminated with vinylchlorosiloxane, then precipitated in methanol and dried under reduced pressure at 60℃. The PDMS macromonomers were characterized by FT-IR, ^{1}H-NMR and GPC to analyze not only their molecular mass but also their functionality at end. The number-average molar masses of PDMS macromonomers varied from 6000–15000. Since the living polymerization was terminated by vinylchlorosiloxane, the PDMS macromonomer at the end possessed the double bond, which could subsequently copolymerize with styrene.

2.4 Radical copolymerization

The radical bulk-copolymerization of the PDMS macromonomer with styrene was carried out at 60℃ for 12 hours with 0.1 wt% azobisisobutyronitrile in an argon atmosphere, shown as Scheme 1. The graft copolymers were dried under reduced pressure, followed by washing with hexane to remove any unreacted PDMS macromonomer and styrene. The PDMS content in the copolymers varied from 5–20% (w/w). Under appropriate conditions, the conversion of macromonomer in the copolymerization was about 90%.

3 Results and discussion

The preparation of double-bond ended PDMS macromonomers illustrated in Scheme 1 was an important first step in the preparation of the fine-topologized graft copolymers. Putting *n*-butyl lithium into D3/cyclohexane solution resulted in the initiation of the ring-opening reaction; however, without any further propagation of polymerization. When the polarity of the solution was changed by adding DMF, the propagation reaction occurs at once in a living manner, in which DMF plays an important role to loosen the ion pairs.



Scheme 1 Schematic representation of the synthesis of PDMS macromonomer and PS-*g*-PDMS copolymer

3.1 PDMS macromonomer characterization

Table 1 summarizes the molecular mass and its distribution of PDMS macromonomers characterized by GPC. One can see that the calculated value (cal) for the number-average molar mass of the PDMS macromonomers is relatively close to the determined value by GPC. On the other hand, the molecular mass distribution (D) is rather narrow, especially while the molecular mass is relatively lower. The end-group analysis was measured by means of FT-IR, shown by Fig. 1. The characteristic absorption at 1620 cm^{-1} confirms the presence of double band at PDMS macromonomer, although the absorption peak is not strong due to only one double bond existed on per PDMS chain.

3.2 Characterization of PS-*g*-PDMS copolymer

The characterization of molar mass for PDMS macromonomers and PS-*g*-PDMS copolymers was illustrated in Table 2. The table summarizes the determined results for PDMS macromonomers with a molar mass from 6000 to 15000 calculation values and PS-*g*-PDMS copolymers containing grafted PDMS from 5 wt% to 15 wt%. It can be seen that the number-average molecular masses of PS-*g*-PDMS copolymers are between 80000 and 90000 and their distributions look rather broad due to their radical polymerization mechanism.

In fact, the average graft number on a PS-*g*-PDMS molecular chain can be calculated when the PDMS chain length and its content in a PS-*g*-PDMS molecule are ascertained, as shown in Table 3. It can be seen from the tables that the structural variability in the graft copolymers prepared by radical copolymerization with the macromonomer method is greater than that in the block copolymers prepared by anion polymerization shown before [14] and it would inevitably play an important role in the relationship between structure and property. Naturally, the branched number on PS-*g*-PDMS molecule chain increases with the decrease in molecular mass of PDMS while holding the same content of PDMS.

Figure 2 shows the infrared spectra of PS-*g*-PDMS copolymer. Typical absorption bands at 3083, 3060 and 3027 cm^{-1} due to aromatic C—H stretching vibration and at 2920

Table 1 Molecular mass and distribution of PDMS macromonomers

Sample	Macromonomer $\overline{M}_n$l(cal)	$\overline{M}_n$ (GPC)	$\overline{M}_w$ (GPC)	*D*
PDMS-1	6000	6900	7400	1.07
PDMS-2	9000	9300	9800	1.05
PDMS-3	15000	15400	18600	1.21

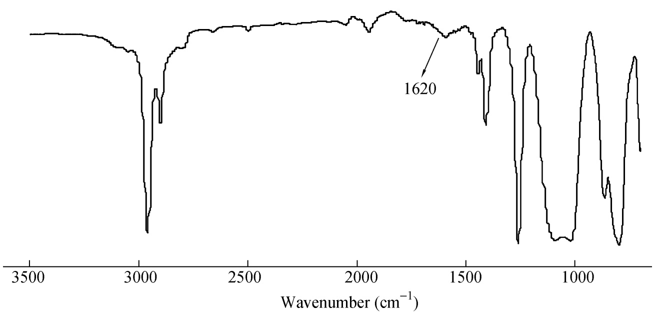


Fig. 1 FT-IR spectra of PDMS macromonomer

Table 2 Characterization of PS-*g*-PDMS copolymer

Sample	PDMS ($\overline{M}_n$ l)(Cal.)	Content of PDMS (wt%)	$\overline{M}_n$ (PS-*g*-PDMS) $\times 10^{-3}$(GPC)	$\overline{M}_\eta \times 10^{-3}$	$\overline{M}_w$ (GPC) $\times 10^{-3}$	*D*
1	15000	5	87.9	171.0	353.4	4.02
2	15000	10	78.8	168.0	323.3	4.10
3	15000	15	86.1	182.0	481.2	5.58
4	15000	20	90.8	170.0	364.1	4.01
5	15000	30	90.3	172.0	361.2	4.00
6	9000	15	89.7	173.5	367.8	4.10
7	6000	15	88.5	163.4	354.0	4.00

Table 3 Calculated branched number per PS-*g*-PDMS copolymer molecule

Sample	PDMS segments $\overline{M}_w$ (GPC)	PDMS content	PDMS content in copolymer (wt%)	Branched number in copolymer (mol%)
1#	18600	5	7.0	0.4
2#		10	13.8	0.7
3#		15	20.3	1.2
4#		20	26.6	1.6
5#		30	38.3	2.3
6#	9800	15	20.3	2.0
7#	6000	15	20.3	3.0

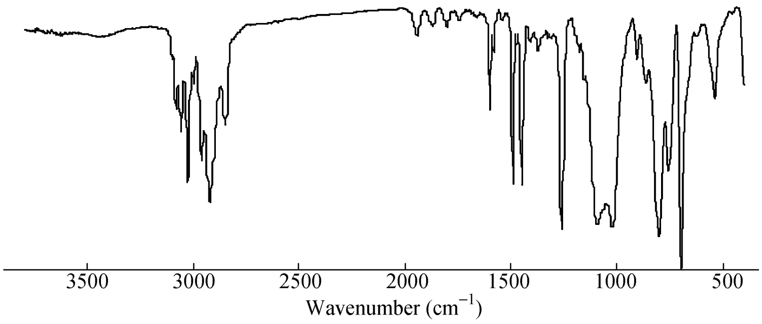


Fig. 2 FT-IR Spectra of PS-*g*-PDMS copolymer

and 2850 cm^{-1} due to aliphatic C—H stretching vibration are observed. Absorption bands at 1602, 1496 and 1455 cm^{-1} due to backbone vibration of the benzene ring and at 760 cm^{-1} for out-of-plane bending deformation of the hydrogen at the benzene ring are also observed. All of these confirm the presence of PS in the copolymer. Furthermore, the peak at 1265 cm^{-1} belongs to the bending vibration absorption of —CH_3 in PDMS, the split peaks at 1100 and 1020 cm^{-1} will be ascribed to the absorptions of dissymmetric and symmetric stretching vibration of the group of Si—O—Si, respectively and the peak at 800 cm^{-1} to the helical confirmation vibration absorption of Si—O groups in PDMS. Therefore, all of these confirm the presence of PDMS macromonomer in the copolymer.

3.3 ¹H-NMR spectra

Figure 3 shows ¹H-NMR spectrum of PS-*g*-PDMS graft copolymer, whose characteristic absorption peaks exhibit the presence of PS and PDMS segments. For example, the peak at δ 6.65 belongs to ortho-protons at the benzene ring and the peak at δ 7.15 to meta- and para-protons at the benzene ring. Well-resolved signals for the —CH_2— protons and —CH proton appear at δ 1.9 and 1.5, respectively. All of these indicate the presence of PS in the copolymer. On the other hand, the peak at δ 0.08 belongs to the protons of CH_3—Si and the peaks at δ 0.9 and 1.3 belong to the —CH_2—protons and —CH proton, respectively, in the —CH—CH—Si— structure, indicating the presence of branched PDMS segments in the copolymer. Furthermore, in light of the ¹H-NMR spectrum, the amount of PDMS grafted onto the copolymers can be calculated easily.

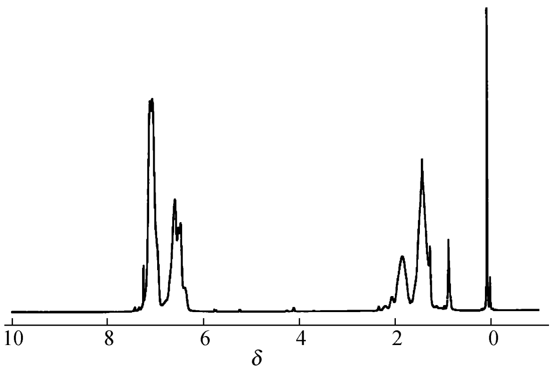


Fig. 3 ¹H-NMR spectra of PS-*g*-PDMS copolymer

3.4 DSC measurement

Figure 4 presents DSC curves of PDMS and PS-*g*-PDMS copolymer. From the PDMS curves, one can see the peaks at –93.4℃ and –39.2℃ corresponding to T_c and T_m of PDMS. However, from PS-*g*-PDMS copolymer curve, one can see not only the peaks at –92.1℃ and –39.2℃, but also a new transformation at 91.1℃. It should be contributed to T_g of PS.

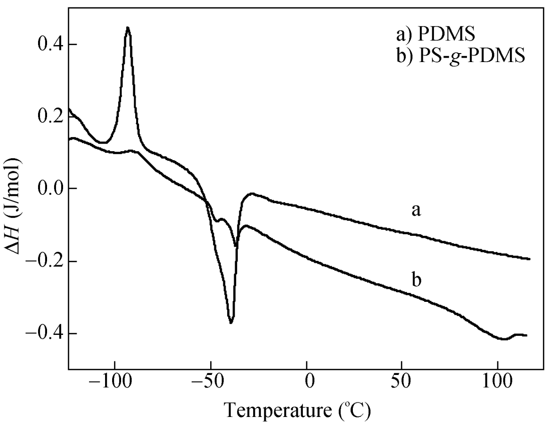


Fig. 4 The DSC curves of PDMS and PS-*g*-PDMS copolymers

3.5 DMA measurement

The DMA measurements of PS-*g*-PDMS copolymers were carried out and the results of tan δ value were shown in Fig. 5. The temperature, at which the tan δ rises to the maximum, is taken as the glass transition temperature, and the values are listed in Table 4. From the table, the T_g of PDMS is −123.0℃, which is close to that of pure PDMS, although the PDMS molar mass in PS-*g*-PDMS copolymer only is about 15000 g/mol. On the other hand, T_g of the PS phase is 114.08℃, which is a little higher than that of PS obtained by DSC measurement. The other two peaks at −81.37℃ and −36.35℃ correspond to T_c and T_m of PDMS.

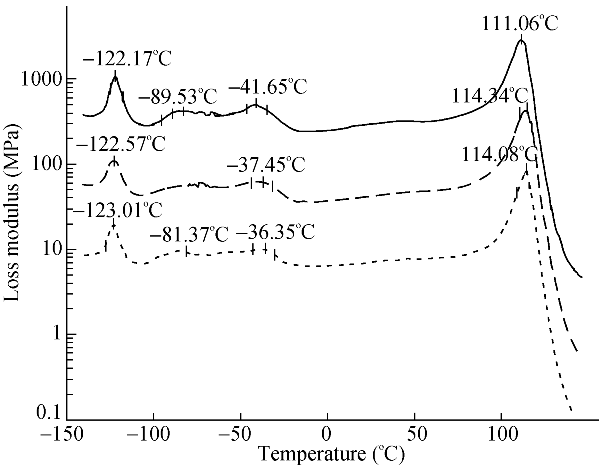


Fig. 5 DMA cures of PS-*g*-PDMS copolymers

Because of the much different solubility parameter between PS and PDMS phases, the immiscibility of the two phases in the graft copolymer must be extremely severe, coinciding with two obviously separate T_gs in Fig. 5 and Table 4 for the PS and PDMS segments, respectively. According to the traditional theory, the greater the difference between the T_gs, the more severe the phase separation becomes between the two phases. With this theory, one can find from Table 4 that the immiscibility between PS segment and PDMS segment in the graft copolymer becomes more and more severe following the increase of molar masses of PDMS grafted on the copolymer from 6000 to 15000, as revealed by the difference between two T_gs (T_{g2}–T_{g1}).

3.6 TEM measurement

The textile structure of PS-*g*-PDMS copolymer was examined by TEM. Figure 6 shows the TEM photograph of PS-*g*-PDMS copolymer films cast by toluene solution. One can directly observe the distinct microphase separation. The dark regions represent the PDMS phase and the white regions the PS phase because of the higher scatter ability of the Si than the C atom without any need for special straining [13]. The black spheres are found only about 10–20 nm in diameter, so it can be called as microphase separation. The reason for the phase separation of PS-*g*-PDMS copolymer is due to different solubility parameter of PDMS segments and PS segments (δ_{PS} = 9.1 cal$^{1/2}$, δ_{PDMS} = 7.35 cal$^{1/2}$)[15]. At same periods, the cause of the microphase separation formation is the graft between the two phases.

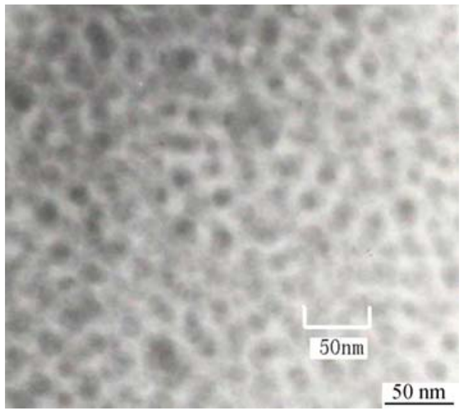


Fig. 6 Transmission electron micrograph of PS-*g*-PDMS copolymer (sample: 3#)

3.7 The mechanical properties of PS-*g*-PDMS copolymers

The mechanical properties of PS-*g*-PDMS copolymers are shown by the toughness curves in Fig. 7. It can be seen that the notched impact strength and the elongation at break of graft copolymers both increasefollowing the increase of PDMS content. It implies that the tenacity of PS as the backbone chain of PS-*g*-PDMS copolymers can be efficiently toughened by PDMS grafted on the copolymer branch chain.

Table 4 DMA data of PS-*g*-PDMS copolymers

Sample	M_n of PDMS(cal.)	$T_{g1(PDMS)}$ (℃)	T_c (℃)	T_m (℃)	$T_{g2(PS)}$ (℃)	(T_{g2} −T_{g1})(℃)
3	15000	−123.01	−81.37	−36.35	114.08	237.09
6	9000	−122.57	–	−37.45	114.34	236.91
7	6000	−122.17	−89.53	−41.65	111.06	233.23

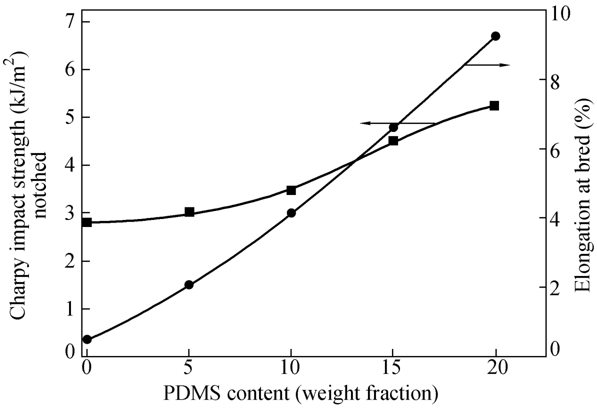


Fig. 7 The notched impact strength and elongation at break of PS-*g*-PDMS copolymers

3.8 Thermal stability

The TGA curves of PS homopolymer and PS-*g*-PDMS copolymers are presented in Fig. 8. It is made clear that the weight loss curves of the graft copolymers were dissimilar in shape from that of pure PS. The threshold temperature for weight loss is observed about 407.7℃ for PS and 423.6℃ for the copolymer, respectively. The maximal loss weight appears at 426.7℃ for PS and 430.7℃ for the copolymer, respectively. Furthermore, there also exists a second maximal loss weight at 520.9℃ in the curves of PS-*g*-PDMS copolymer, which should belong to the Si—O—Si bonds with higher band energy. Therefore, one can sum that PDMS grafted on PS-*g*-PDMS copolymers has enough ability to enhance thermal stability of PS in the copolymers.

4 Conclusions

(1) PDMS macromonomers with controlled molar mass, narrow molar mass distributions and double bond at their ends can be synthesized by the living anionic ring-opening polymerization of D3. Then, PS-*g*-PDMS copolymers can further be bulk radical-copolymerized by styrene and PDMS macromonomer mentioned above.

(2) It can be confirmed by FT-IR and ^{1}H-NMR that PS-*g*-PDMS copolymers take PS as backbone chain and PDMS as branch chain. The textile structure of the copolymers appears in microphase separation with the PS backbone chain as continue phase and PDMS branch chain as scatter phase as illustrated by DMA, TEM.

(3) PDMS grafted on PS-*g*-PDMS copolymers has enough ability to enhance the thermal stability of the PS in the copolymers.

(4) The tenacity of the PS as backbone chain of PS-*g*-PDMS copolymers can be efficiently toughened by the PDMS grafted on the copolymers branch chain.

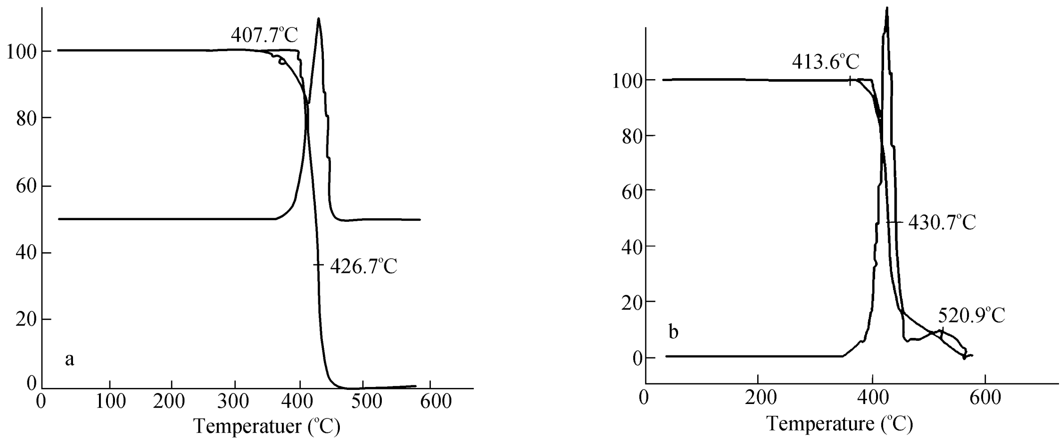


Fig. 8 TGA curves of PS homopolymer and PDMS-*g*-PS copolymer (a) PS; (b) 3#

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