

Effect of Structure and Additives on Thermal Stability of Silicone Fluids

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ABSTRACT: A series of polydimethylsiloxane (PDMS) polymers and poly(dimethyl-diphenyl siloxane) (PDMS-PMPS) copolymers were synthesized by the anionic ring-opening polymerization method and then blended with titanium isooctate as thermal additives. Their thermal stabilities have been investigated by TGA in an inert gas atmosphere. The temperature for 10% conversion, 50% conversion, and the temperature for the maximum rate of decomposition (MRDT) initiated from TGA curves recorded at a heating rate of 5, 10, 15, and 20°C min⁻¹ and the apparent activation energy E_a using the FWO method as a function of conversion α indicated that the thermal stabilities of the polysiloxanes could be enhanced either by modifying the structure of the polymer or by introducing a certain amount of a thermal additive. PDMS-PMPS copolymers with a MePhSiO segment content of 10.2 mol % and terminated by diphenylmethylsiloxyl groups exhib-

ited optimal heat resistance. The thermal stabilities of the polysiloxanes could be further improved by introducing homogenous titanium additives and with the addition of 1550 ppm content of titanium additives, the temperature for 10% conversion, the temperature for 50% conversion, and MRDT have been found to be increased by 20.11, 71.28, and 98.67 K, respectively, relative to the unmodified PDMS-PMPS copolymer. Fourier transform infrared (FTIR) analysis has proven the formation of a Si—O—Ti bond in the titanium-modified PDMS-PMPS copolymer, which may be responsible for the efficient enhancement of its thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2530–2537, 2010

Key words: polydimethylsiloxane; polydimethylsiloxane-polydimethylphenylsiloxane copolymer; thermal stability; titanium additives; thermogravimetric analysis

INTRODUCTION

Polysiloxanes are known to possess a number of remarkable properties relative to other synthetic polymers and they can exhibit different appearances, ranging from free-flowing fluids to stiff viscous gels, depending on their molecular weight. Polydimethylsiloxane (PDMS) is by far the most commonly used member of the family. PDMS with higher molecular weight can be further treated with other components to produce silicone rubber, which offers a unique

combination of chemical and mechanical properties that organic elastomers cannot match.

Generally, linear polysiloxanes with lower molecular weight are free-flowing fluids, namely, silicone oil, an environmental-friendly heat-transfer oil and can retain good flow characteristics between -50°C and 200°C under normal pressure.¹ Once the operational temperature exceeds the maximum allowable temperature of application, the viscosity of silicone fluid increases sharply with a consequent reduction in its flow properties. It has long been recognized that the decrease in the thermal stability of organic polymers stems mainly from the degradation of the molecular structure, and two mechanisms have been proposed to rationalize this. One is so-called thermal depolymerization, degradation, or reversion of the main chain Si—O—Si, which will generate some low molecular weight, volatile cyclosiloxanes comprising a continuous mixture of cyclic oligomers, namely trimers, tetramers, pentamers, and so on. The other is thermo-oxidative degradation or oxidative scission at the side groups of the main chain Si—O—Si,^{1,2} such as Si—CH₃, Si—C₂H₅, Si—C₆H₅, etc. Although such organic groups are inevitably to be thermoxidized at elevated temperature, there still have some difference in thermal resistance, which may provide

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an efficient strategy for enhancing thermal stability of such polymers.

To meet the huge demand for higher temperature applications, the thermal stability of polysiloxanes need to be enhanced. Compared with other kinds of heat-transfer fluids, the thermal properties of silicone oils may be more easily regulated either by the introduction of blocked Si—O—Si copolymers like poly(dimethyl-methyl phenyl siloxane) (PDMS-PMPS) or poly(dimethyl-diphenyl siloxane) (PDMS-PDPS)²⁻⁵ or by the substitution of other capping end-groups³ or the addition of various additives,^{6,7} such as heat stabilizers, antioxidants, or free radical absorbents. These methods had long been widely used in silicone rubber fields while little reports had been disclosed in literature for silicone fluids. In this work, the influences of various factors, such as the nature of the terminal groups, the MePhSiO segment content in PDMS-PMPS copolymers, the preparative methods, and the amounts of thermal stabilizers added, have been investigated in detail.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4) was purchased from Dow Corning; titanium isooctate (purity 97%) and decamethyltetrasiloxane (MD₂M) were obtained from Alfa Aesar and the Panshi City Datian Chemical Auxiliaries Research Institute, respectively. Dimethylphenylchlorosilane (Me_2PhSiCl) was also obtained from Alfa Aesar and it was subsequently hydrolyzed to form 1,1,3,3-tetramethyldiphenyldisiloxane, one of the end-blocking agents used in the following polymerization reactions. The other end-blocking agent, 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane, was obtained from the hydrolysis of methyl-diphenylethoxysilane.⁸ The methylphenyl cyclic oligomers (D_n^{MePh} , $n = 3, 4, 5$), a mixture of cyclic trimer (trimethyltriphenylcyclotrisiloxane), tetramer (tetramethyltetraphenylcyclotetrasiloxane), and pentamer (pentamethylpentaphenylcyclopentasiloxane), were prepared in our laboratory.

Preparation of PDMS polymers and PDMS-PMPS copolymers terminated by different organic groups

A series of PDMS polymers and PDMS-PMPS copolymers with different MePhSiO segment con-

tents were synthesized by anionic ring-opening polymerization method using tetramethylammonium hydroxide (Me_4NOH) as the catalyst and the products were end-capped with different terminal groups. To eliminate the influence of molecular weight on thermal stability, efforts were made to carefully regulate the molecular weights of all samples at the same level by adjusting the ratio between capping agent and monomers. For example, D_4 (103.9 g), D_n^{MePh} ($n = 3, 4, 5$) (10.0 g), and end-capping agent 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane (6.1 g) were placed in a three-necked flask and then heated to 45°C under reduced pressure. After the addition of Me_4NOH , the reactor was heated to 90°C and maintained under reduced pressure (−0.08 MPa) for about 2–3 h to facilitate the polymerization reaction. When the polymerization was complete, the temperature was further increased to 160°C and held at this level for about 4 h so that the remaining catalyst was completely decomposed. The residue was subsequently subjected to vacuum distillation at 200°C for 2 h to remove unreacted or depolymerized monomers during balance polymerization process, and upon cooling 112.1 g of product was obtained. The results are collected in Tables I and II.

Preparation of PDMS-PMPS copolymer fluids modified with thermal stabilizer

PDMS-PMPS copolymer fluids with $M_n = 9.2 \times 10^3$, %MePhSiO = 15.2, and terminated by MePh_2SiO group (Entry 11) was prepared according to the method described in "Preparation of PDMS Polymers and PDMS-PMPS Copolymers Terminated by Different Organic Groups" section. Fifty grams of such PDMS-PMPS copolymer and titanium isooctate (0.657 g) were placed in a three-necked flask equipped with a magnetic stirrer, a thermometer, and a distillation head. Under nitrogen atmosphere and with vigorous agitation, the mixture was heated to 300°C and maintained at this temperature for 12 h. After cooling to room temperature, 43.2 g of titanium isooctate-modified PDMS-PMPS copolymer fluid was collected (Entry 14), with a titanium content of 1550 ppm, which served as a thermal stabilizer.

Titanium isooctate-modified PDMS-PMPS fluids with different titanium contents were produced by adding appropriate amounts of thermal stabilizer to

TABLE I
Inert Atmosphere TGA-Derived Parameters of PDMS Terminated by Different Capping Groups

Entry	End-capping group	$M_n(10^3)$	M_w/M_n	MePhSiO content (mol %)	$D_{0.1}$ (K)	$D_{1/2}$ (K)	MRDT (K)
1	Me_3SiO	8.9	1.7	0	692.11	764.72	760.83
2	Me_2PhSiO	8.1	1.7	0	693.17	782.23	783.73
3	MePh_2SiO	9.2	1.8	0	730.47	805.98	811.57

TABLE II
Inert Atmosphere TGA-Derived Parameters of PDMS-PMPS Copolymers Terminated by Different Capping Groups

Entry	End-capping group	$M_n(10^3)$	M_w/M_n	MePhSiO content (mol %)	$D_{0.1}$ (K)	$D_{1/2}$ (K)	MRDT (K)
4	Me ₃ SiO	8.4	1.9	3.8	695.00	787.71	789.86
5	Me ₂ PhSiO	8.3	1.8	5.3	709.73	802.06	804.00
6	MePh ₂ SiO	8.8	1.7	5.6	729.63	823.26	834.13

PDMS-PMPS copolymers with the same molecular weight. For example, sample 12, with a titanium level of 100 ppm, was prepared by adding 3.46 g of previously produced thermal stabilizer to 50.0 g of PDMS-PMPS copolymer and agitating vigorously at room temperature. Sample 13, with a titanium level of 500 ppm, was prepared by adding 23.82 g of thermal stabilizer to 50.0 g of PDMS-PMPS copolymer and treating the mixture in the same way.

Measurements

The structures and molecular weights of the synthesized PDMS polymers and PDMS-PMPS copolymers were characterized by ²⁹Si-NMR, ¹H-NMR, Fourier transform infrared (FTIR), and gel-permeation chromatography (GPC). The heat resistance of the polysiloxanes was characterized by thermogravimetric analysis (TGA). The molar content of phenyl groups in the PDMS-PMPS copolymers was calculated from the ¹H-NMR (or ²⁹Si-NMR) spectra.⁹

¹H-NMR and ²⁹Si-NMR spectra of the PDMS polymers and PDMS-PMPS copolymers were obtained with an AVANCE AV400 MHz spectrometer (Bruker, Germany). Molecular weights were determined by GPC (Waters 1525, Germany) with toluene as the eluant and polystyrene samples as standards. TGA was carried out by using a TG209C apparatus (Germany), in which samples were heated from ambient temperature to 600°C or higher temperatures at a rate of 5, 10, 15, and 20°C/min in a dynamic nitrogen atmosphere with a flow rate of 20 mL/min.

Nonisothermal decomposition kinetics

There are many semi-empirical methods of determining the apparent activation energy of thermal degradation,^{10–12} E_a , from nonisothermal thermogravimetric (TG) curves of PDMS polymer or PDMS-PMPS copolymers. Among them, the Flynn-Wall-Ozawa (FWO) method is often used to determine the E_a of polymers and it can be described by eq. (1).

$$\lg \beta = \lg \left[\frac{AE_a}{G(\alpha)R} \right] - 2.315 - \frac{0.4567E_a}{RT} \quad (1)$$

where α is a conversion and is defined as

$$\alpha = \frac{w_i - w_T}{w_i - w_f} \quad (2)$$

In eq. (2), where w_i , w_T , and w_f stand for the initial, actual, and final sample weights, respectively. T is absolute temperature, R is gas constant, E_a is apparent activation energy, β is linear heating rate, A is pre-exponential factor, and $G(\alpha)$ is integration mechanism function.

The apparent activation energy E_a could be determined by linear regression of TG curves in the usual way. The E_a value of the polymers at a certain amount of conversion is proportional to the slope, $d\beta/d(1/T)$, of the linear dependence of the reciprocal absolute temperature at which a certain conversion reaches, $1/T$, on the logarithm of the applied heating rate β ¹². For example, the TG and DTG (differentiate thermo gravimetric) curves for Entry 3 at different heating rates were drawn in Figures 1 and 2, respectively. When the apparent activation energy E_a was calculated from the curves presented in Figure 1 using FWO method as a function of conversion, the results shown in Figure 3 could be obtained. To illustrate the various influence on thermal stability of silicone oils, the apparent activation energy E_a for other samples were also calculated in the same manner and the results were listed in Figures 4–6, respectively.

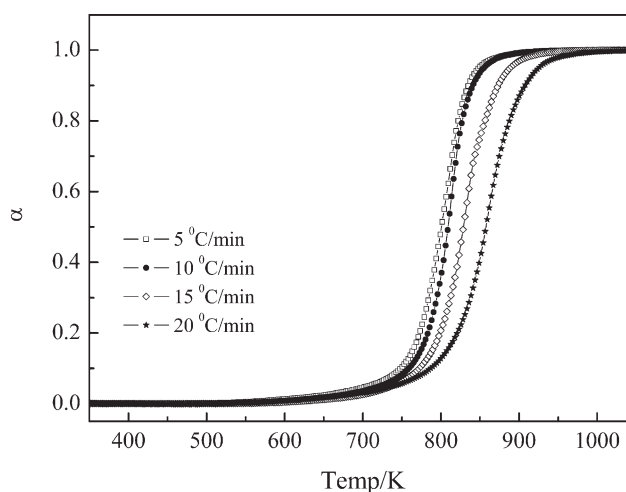


Figure 1 TG curves for Entry 3 at different heating rates.

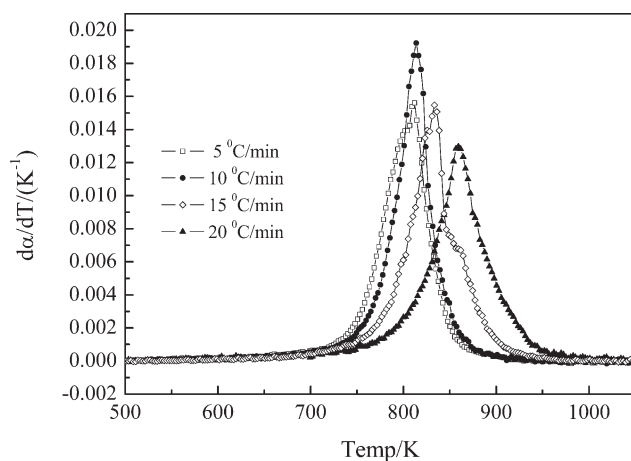


Figure 2 DTG curves for Entry 3 at different heating rates.

RESULTS AND DISCUSSION

PDMS polymers terminated by different capping agents

Inert atmosphere TG and DTG curves of all PDMS polymers terminated by different capping groups at different heating rates could be drawn in the same way like Figures 1 and 2. For the sake of clarity, only characteristic degradation temperatures and corresponding associated parameters obtained from TG curves recorded at a heating rate of 10°C/min were provided and summarized in Table I, where $D_{0.1}$ denotes the temperature at which the 10% of decomposition occurs, $D_{1/2}$ indicates the temperature at which half of decomposition occurs and MRDT is the maximum rate of decomposition (MRD) temperature.

Thus the thermal stabilities of the PDMS polymers were evaluated by comparing their $D_{0.1}$, $D_{1/2}$, or MRDT temperatures. As shown in Table I, diphenyl-

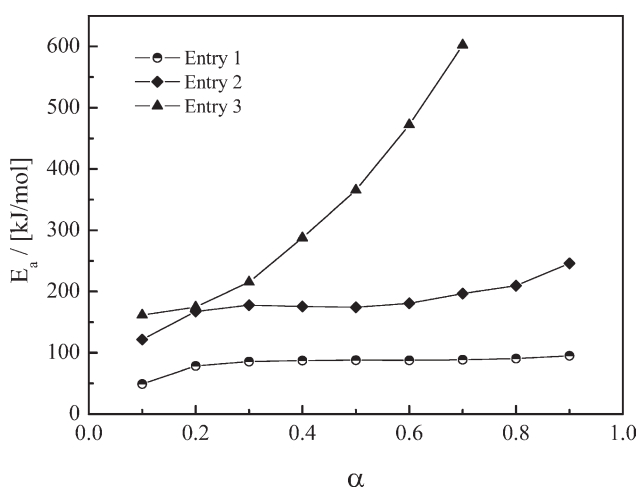


Figure 3 Apparent activation energy (E_a) vs. conversion (α) for Entries 1 to 3.

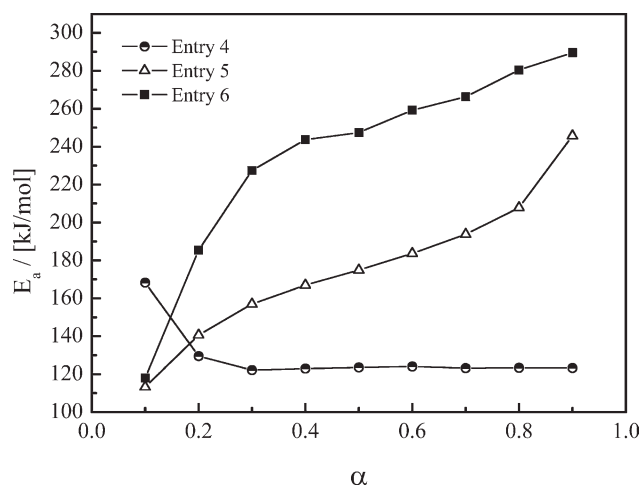


Figure 4 Apparent activation energy (E_a) vs. conversion (α) for Entries 4 to 6.

methylsiloxyl-terminated PDMS shows much better thermal stability than PDMS terminated with either a dimethylphenylsiloxyl group or a trimethylsiloxyl group as its $D_{0.1}$ value in inert atmosphere is found to be 730.47 K while for the other two polymers, their $D_{0.1}$ values are 693.17 K (in Entry 2) and 692.11 K (in Entry 1), respectively. Temperature for half of decomposition $D_{1/2}$ and temperature for MRDT are found to be of the same trend. The $D_{1/2}$ value for diphenylmethylsiloxyl terminated PDMS reaches up to 805.98 K while for dimethylphenylsiloxyl terminated PDMS and trimethylsiloxyl terminated PDMS, their $D_{1/2}$ values are 782.23 and 764.72 K, respectively. The MRDT values for diphenylmethylsiloxyl terminated PDMS, dimethylphenylsiloxyl terminated PDMS and trimethylsiloxyl terminated PDMS are 811.57, 783.73, and 760.83 K, respectively.

Except for characteristic degradation temperatures and corresponding associated parameters, the apparent activation energies E_a initiated from four

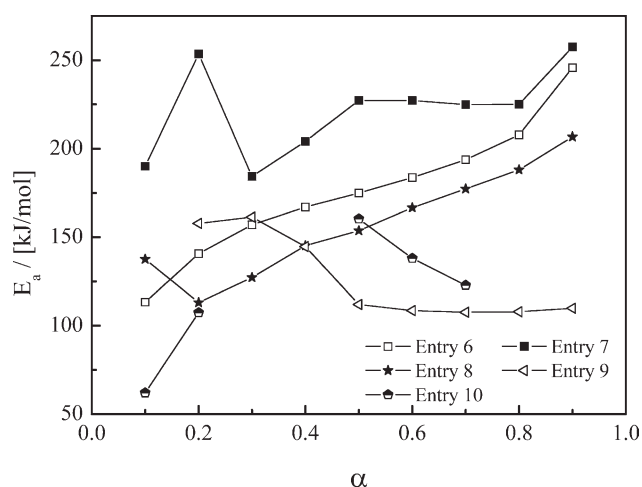


Figure 5 Apparent activation energy (E_a) vs. conversion (α) for Entries 6 to 10.

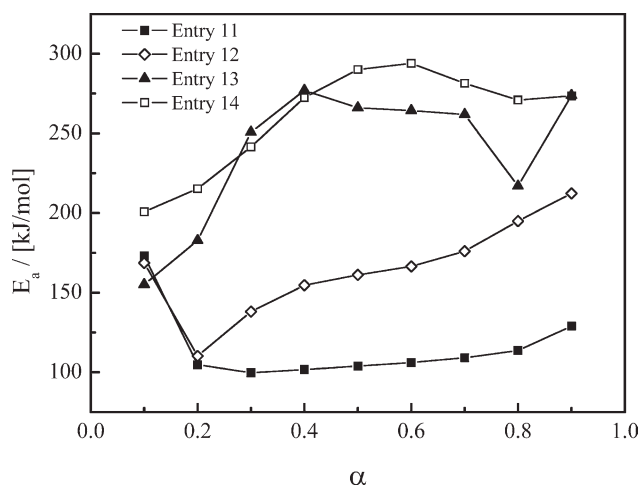


Figure 6 Apparent activation energy (E_a) vs. conversion (α) for Entries 11 to 14.

different heating rates of TG curves are also plotted as a function of conversion α in Figure 3, where E_a values are calculated according to the FWO method described before and the values of E_a may vary with conversion.¹² It can be seen from Figure 3 that the E_a values for trimethylsiloxy terminated PDMS (Entry 1) almost hold constant despite of increasing conversion. While for dimethylphenylsiloxy terminated PDMS, its E_a values almost hold constant when the conversion is lower than 0.6. After then, its E_a values increases gradually. At each conversion, the E_a values of diphenylmethylsiloxy terminated PDMS are the highest in these three PDMS polymers and they increase steadily with the increase of conversion. The values of E_a are directly related to the easiness and the extent of degradation reaction, the higher the E_a value, the more stability the PDMS polymer. Therefore, diphenylmethylsiloxy-terminated PDMS exhibits better thermal stability than the other two kinds of polysiloxanes and it seems that trimethylsiloxy terminated PDMS exhibits the worst thermal stability.

PDMS-PMPS copolymers terminated by different capping agents

To investigate the influence of different kinds of capping agents on thermal stabilities of PDMS-PMPS copolymers, similar analysis had also been conducted and the data obtained from TG curves recorded at four heating rates like before were treated in the same way and the results were listed in Table II. It can be seen that the influence of capping agents on PDMS-PMPS copolymers exhibit the same trend as seen for PDMS polymers. For PDMS-PMPS copolymers with almost the same molecular weights and similar MePhSiO segment contents (Entries 4, 5, and 6), the copolymer terminated by a

diphenylmethylsiloxy group exhibits much better thermal stability (729.63 K for $D_{0.1}$, 823.26 K for $D_{1/2}$ and 834.13 K for MRDT in Entry 6, respectively) than those terminated by either a dimethylphenylsiloxy group (709.73 K for $D_{0.1}$, 802.06 K for $D_{1/2}$ and 804.00 K for MRDT in Entry 5, respectively) or a trimethylsiloxy group (695.00 K for $D_{0.1}$, 787.71 K for $D_{1/2}$ and 789.86 K for MRDT in Entry 4, respectively). The apparent activation energy E_a as a function of conversion α drawn in Figure 4 manifest the same result. For PDMS-PMPS copolymers with similar molecular weight and the same level of MePhSiO segment content while terminated by different capping agents, diphenylmethylsiloxy terminated copolymer exhibit the highest E_a at each conversion and its E_a value increase steadily with increasing conversion. Dimethylphenylsiloxy terminated PDMS-PMPS copolymers exhibits the same trend as the former, although its E_a values are somewhat lower than the former's at each conversion. Trimethylsiloxy terminated PDMS-PMPS copolymer exhibits the worst stability as its E_a values are the smallest in these three polymers and they almost hold constant in whole range of conversion, which is much similar to the case observed in trimethylsiloxy terminated PDMS polymer (Entry 1).

A comparison between E_a values listed in Figures 1 and 2 for PDMS polymers and PDMS-PMPS copolymers terminated with the same capping end-group may help us to understand the influence of MePhSiO segment on thermal stability of PDMS. It can be seen that the E_a values of PDMS-PMPS copolymers terminated either with trimethylsiloxy or with dimethylphenylsiloxy group are almost increased by 20 kJ/mol relative to the E_a values of pure PDMS polymers, which indicates that the introduction of MePhSiO segment is beneficial to enhance thermal stability of PDMS polymers. Similar conclusions can also be obtained when comparisons of the respective $D_{0.1}$, $D_{1/2}$, and MRDT temperatures between Tables I and II are conducted. While for diphenylmethylsiloxy terminated PDMS and PDMS-PMPS copolymer, both of their E_a values increase steadily as a function of conversion and it seems that the introduction of MePhSiO has little influence on its thermal stability. This result can also be confirmed by the comparison of $D_{0.1}$ values between Entry 3 and Entry 6, as there is almost no significant difference.

When further comparing degradation temperatures listed in Tables I and II, it can be clearly seen that diphenylmethylsiloxy group exhibits the best stability in these three end-capping agents. Nevertheless, it is still difficult to conclude that the higher the number of phenyl groups contained in a capping agent, the better the thermal stability of the respective polymer. For example, Skorokhodov et al.¹³

TABLE III
Inert Atmosphere TGA-Derived Parameters of Methylphenylsiloxy-Terminated PDMS-PMPS Copolymers with Different Content of MePhSiO Segment

Entry	$M_n(10^3)$	M_w/M_n	MePhSiO content (mol %)	$D_{0.1}$ (K)	$D_{1/2}$ (K)	MRDT(K)
3	9.2	1.8	0	730.47	805.98	811.57
6	8.8	1.7	5.6	729.63	823.26	834.13
7	10.3	1.9	10.2	739.42	831.09	846.87
8	9.8	1.9	14.9	730.32	819.38	826.75
9	9.8	2.1	25.3	735.04	807.50	814.03
10	9.8	2.5	64.8	679.62	774.62	786.77

have demonstrated that a terminal Ph_3SiO group is particularly effective in lowering thermal stability, even though it contains three phenyl groups. The reason may be related to the steric hindrance effect resulted from three phenyl groups attached to a silicon atom. Therefore, it is not straightforward to choose a suitable terminal group for polysiloxanes or for these copolymers; rather, the appropriate terminating group must be experimentally screened in advance.

Diphenylmethylsiloxy terminated PDMS-PMPS copolymers with different MePhSiO segment contents

As is well known, the thermal stability of phenyl containing silicone rubber is not only influenced by their terminal groups but also by their MePhSiO content. To investigate the effect of different MePhSiO segment contents on thermal stability of silicone oils, a series of diphenylmethylsiloxy-terminated PDMS-PMPS copolymers with similar molecular weights and similar polydispersity indices was prepared. TGA tests were conducted in inert gas atmosphere, and the results initiated from four different heating rates according to the method described before were presented in Table III. The apparent activation energies E_a as a function of conversion α were calculated and plotted in Figure 5.

It can be seen that not only the 10% conversion temperatures $D_{0.1}$ but also the half conversion temperatures $D_{1/2}$, and the MRDT values in Entries 3, 6, and 7 increase with increasing MePhSiO segment content and the optimal enhancement of thermal stability was obtained when the MePhSiO segment content reached 10.2 mol %. This result is in quite good agreement with the findings of Chyuan and Mei-Hui,¹⁴ who observed that the thermal stability of diblocked PDPS-PMPS copolymers was improved with increasing PDPS content and that the optimal stabilization was obtained when the PDPS content reached 14 mol %.

When the MePhSiO segment content is further increased (for example, Entries 8, 9 and 10), the temperature for $D_{0.1}$, $D_{1/2}$, and MRDT from the respec-

tive samples decrease steadily and the worst result is obtained (679.62 K for $D_{0.1}$, 744.62 K for $D_{1/2}$, or 786.77 K for MRDT in Entry 10) when the MePhSiO segment content reaches 64.8 mol %. This result is even inferior to that of the control sample (Entry 3; PDMS terminated by diphenylmethylsiloxy groups without a MePhSiO segment).

The apparent activation energies E_a for Entries 6 to 10 as a function of conversion α were presented in Figure 5. It can be seen that the E_a value of Entry 7 at each conversion is almost the biggest in these five samples, which is quite well with the result listed in Table III where diphenylmethylsiloxy terminated PDMS-PMPS copolymer with 10.2 mol % content of MePhSiO segment exhibits the best thermal stability. It also can be seen that when the MePhSiO segment contents is low (i.e., in Entries 6 to 8), their E_a values increase steadily with increasing conversion. In case of higher MePhSiO segment contents (Entries 9 and 10), the E_a values change with increase of conversion in opposite trends, which implies that the influence of the level of MePhSiO segment contents on thermal stability of PDMS-PMPS copolymers is quite complex.

The results in Table III and Figure 5 indicate that the thermal stability of PDMS-PMPS copolymers is significantly influenced by the MePhSiO segment content. An appropriate amount of MePhSiO segments is beneficial and improves the heat resistance of PDMS-PMPS copolymers, but higher MePhSiO segment contents are deleterious to thermal stability. Although a phenyl group exerts a much more significant steric hindrance effect than a methyl group, its thermal stability is also superior to that of a methyl group. Therefore, if a small amount of methylphenylsiloxy segments is incorporated into copolymer molecules, the phenyl group content will be low and the few side-chain phenyl groups will be relatively unperturbed by neighboring methyl groups or other adjacent phenyl groups. Under such circumstances, a side-chain phenyl group could still easily rotate along the Si—C axis, heat energy would be transferred normally in each direction by means of molecular motion, and no heat would be accumulated within the molecule. Hence, the thermal stability of the

TABLE IV
Inert Atmosphere TGA-Derived Parameters of PDMS-PMPS Copolymers Modified with Different Content of Titanium Additives

Entry	Titanium content/ppm	$D_{0.1}$ (K)	$D_{1/2}$ (K)	MRDT (K)
11	0	707.79	789.08	797.89
12	100	712.83	832.99	881.20
13	500	722.42	853.49	870.79
14	1550	727.90	860.36	896.56

PDMS-PMPS copolymer will be increased by the incorporation of MePhSiO segments.

If dimethylsiloxyl segments are gradually substituted by more and more methylphenylsiloxyl segments, the volume of the copolymer will increase and some phenyl groups within the molecule will be significantly affected by other adjacent phenyl groups. Consequently, the rotation of these groups along their Si–C axes will be hindered, thereby inhibiting the transfer of heat energy. Once heat accumulation within a molecule exceeds a certain level, Si–C bond fracture will occur, resulting in decreased thermal stability.

Effect of titanium isooctate on the thermal stability of PDMS-PMPS copolymers

As is well known, the heat resistance of silicon rubber may be greatly enhanced by incorporating a certain amount of heterogeneous thermal stabilizers, such as nanosized AlN, CeO₂, TiO₂, etc., into the polymer matrix. For silicone fluids, however, such additives are inadequate because macro-phase separation is inevitable and hence the inorganic additives will eventually precipitate from the polymer matrix, even though, smaller size particles are used. Therefore, titanium isooctate-modified PDMS-PMPS copolymers containing different amounts of homogeneous titanium additives were prepared, their heat resistances were investigated, and the results are presented in Table IV. The apparent activation energies E_a as a function of conversion for each sample are also calculated in the same way introduced before and the results are plotted in Figure 6.

It can be clearly seen from Table IV that the addition of titanium additives is effective in improving the thermal stability of PDMS-PMPS copolymers and its influence on thermal stability is almost proportional to the amount mixed into the polymer. For example, compared with the control sample (Entry 11), the temperature for 10% conversion for PDMS-PMPS copolymer modified with 100 ppm titanium (Entry 12) is increased by 5.04 K, whereas for PDMS-PMPS copolymer modified with 500 ppm titanium (Entry 13), the 10% conversion temperature is increased by almost 10 K. When the amount of titanium additive is further increased, the thermal sta-

bility of the copolymer increases and the temperature for 10% conversion from PDMS-PMPS copolymer modified with 1550 ppm titanium (Entry 14) is 5.48 K higher than that in Entry 13. Meanwhile, the temperature for half conversion and MRDT are also greatly improved with increase of titanium additives.

The influence of titanium content on apparent activation energies E_a at each conversion is presented in Figure 6. It can be clearly seen from Figure 6 that almost in whole range of conversion, the E_a values are directly related to titanium contents the sample contains. The E_a values for PDMS-PMPS modified with 1550 ppm content of titanium additives are the highest in these four Entries and it exhibits the best thermal stability, which is quite well with what observed in Table IV.

With a view to elucidating why titanium additives are effective in enhancing the thermal stability of PDMS-PMPS copolymers, FTIR spectra of PDMS-PMPS copolymer (Entry 11) and titanium-modified PDMS-PMPS copolymer (Entry 14) were recorded to investigate the formation of chemical species or bonding between the copolymers and the thermal additives. The IR spectra of the samples are shown in Figure 7. Peaks at 1080, 800, and 480 cm⁻¹ observed for both samples may be assigned to asymmetric stretching, symmetric stretching, and bending vibrations of Si–O–Si linkages, as described by

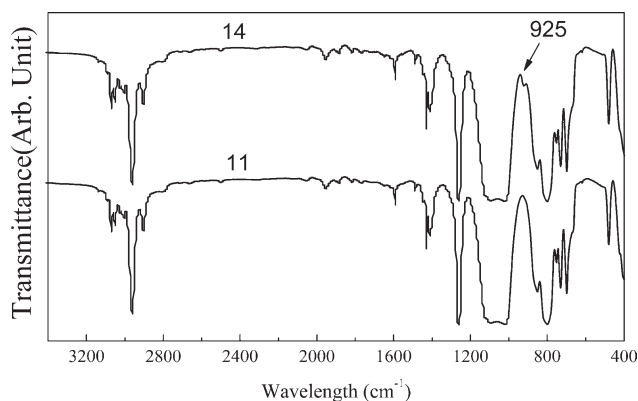


Figure 7 FTIR spectra of unmodified PDMS-PMPS copolymer (Entry 11) and Titanium modified PDMS-PMPS copolymer (Entry 14).

Ehrman and Friedlander.¹⁵ Asymmetric C—Si—O stretching for linear PDMS-PMPS copolymer containing Me₂SiO segment, is seen in both samples at 1263 cm⁻¹.¹⁶ Peaks at 2900 and 2964 cm⁻¹ observed for both samples may be assigned to symmetrical and asymmetrical stretching vibration of methyl groups. Meanwhile, Si—Ph stretching vibration is observed at 1429 cm⁻¹.¹⁷ A characteristic absorption band near 925 cm⁻¹ is observed in the IR spectrum of the titanium-modified PDMS-PMPS copolymer (Entry 14), as also reported by Sayilkan¹⁸ and by Li,¹⁹ which is absent from the IR spectrum of the unmodified PDMS-PMPS copolymer (Entry 11). This band is due to an asymmetric Si—O—Ti stretching mode, thus indicating that a Si—O—Ti bond had been formed in the titanium-modified PDMS-PMPS copolymer, which we assume to be responsible for the efficient enhancement of its thermal stability.

CONCLUSIONS

This study has revealed the influences of structure, end-capping groups, and thermal additives on the thermal stability of PDMS polymers and PDMS-PMPS copolymers. For PDMS terminated with MePh₂SiO groups, the temperature for 10% conversion, the temperature for 50% conversion, and the temperature for the MRD have been found to be increased by 38.36, 41.26, and 50.74 K, respectively, compared to PDMS terminated with Me₃SiO groups. The thermal stability of PMPS-modified PDMS polymer has been found to be greatly influenced by the MePhSiO segment content incorporated into the main chain of the copolymer. The optimal stabilization was obtained with a MePhSiO content of 10.2 mol %, as a result of which the temperature for 10% conversion, the temperature for 50% conversion and the temperature for the MRD increased to 739.42, 831.09, and 846.87 K, respectively. Titanium additives have also proved to be effective in enhancing the thermal stability of PDMS-PMPS copolymers and with the addition of 1550 ppm content of titanium

additives, the temperature for 10% conversion, the temperature for 50% conversion and the temperature for the MRD have been found to be increased by 20.11, 71.28, and 98.67 K, respectively, relative to the unmodified PDMS-PMPS copolymer. This would seem to be due to the formation of Si—O—Ti linkages, as evidenced by IR spectral analysis, and the effects of different contents of titanium additives on the thermal stabilities of PDMS-PMPS copolymers is directly related to the content of titanium additives.

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